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ORIGINAL CONTRIBUTION

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Amphiphilic hyperbranched polyelectrolytes: a new type of polysoap

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Abstract Hyperbranched hydrophobized polyelectrolytes of the ionene type are prepared. They are investigated as a new type of polysoap, with respect to viscosifying behaviour, surface activity and solubilization power. Compared to linear analogues, the viscosifying effect is reduced. Compared to classical polysoap architectures, such as analogous "tail-end-type" and "head-type" polysoaps, the hyperbranched polysoaps behave rather similarly to the "head-type" ones: they exhibit notable surface activity, whereas the solubilization capacity is moderate only.

Key words Hyperbranched polymer – Polyelectrolyte – Polysoap – Micellar polymer – Ionene

Introduction

Water-soluble amphiphilic polymers ("micellar polymers") find a considerable practical interest, for example, for potential uses such as protective colloids, emulsifiers, surfactants, wetting agents, or viscosity modifiers. A particular subclass are the so-called "polysoaps" which can be regarded as individual low-molar-mass surfactant fragments, tied together by a polymer backbone [1–3]. The structural similarity of the individual polymer fragments with low-molar-mass surfactants is paralleled by the similarity of two important properties of polysoaps and of surfactants: (1) marked solubilization capacity for hydrophobic molecules implying a "molten character" of the aggregated hydrophobic parts, and (2) low viscosities of aqueous solution due to the hydrophobic aggregation which reduces the hydrodynamic radius dramatically. In fact, polysoaps are characterized by their primary intramolecular aggregation, for which a critical micelle concentration (cmc) is usually not detectable [3].

There are several possibilities to link the surfactant fragments of polysoaps together (Fig. 1). Mostly, the surfactants are attached to a polymer backbone via the end of the hydrophobic chain ("tail-end type") or via the hydrophilic head group ("head type") [3, 4]. So the amphiphilicity results from the functional side-chains. Mainly such polysoaps have been studied in the past. The alternative anchoring of all surfactants to one central point leads to star polymers. For steric reasons, only oligomeric soaps can be realized in this way. Very few examples of polysoap stars have been reported so far [3, 5–8]. In a different approach, the surfactants are linked via both the end of the hydrophobic chain and the hydrophilic head group. In this way, the surfactants are incorporated in the polymer main chain. This approach has been applied occasionally [3, 9–13], but little is known about their soap-like properties.

Here we report on a new class of polysoaps with hyperbranched [14] architecture. This architecture combines features of side-chain and main-chain polysoaps, as surfactant fragments are found in the main chain as well as in the side-chain. Additionally, as for other hyperbranched polymers and dendrimers of higher generations, a particularly compact form is expected for hyperbranched polysoaps. A synthetic approach to such polysoaps is described here, as well as studies on key properties such as viscosifying effects in water, surface activity, and solubilization of sparingly water-soluble dyes. These properties are compared to those of low-molar-mass analogues, and to those of analogous linear polysoaps, of both the main-chain type and the

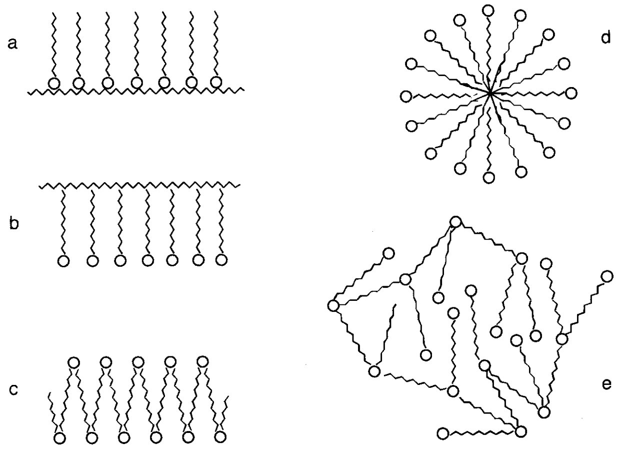


Fig. 1 Diverse molecular architectures of polysoaps (from *left* to *right* and *top* to *bottom*): head type, tail-end type, main-chain type, star type, hyperbranched type

side-chain type. The compounds investigated are listed in Table 1.

The hitherto known amphiphilic dendrimers and hyperbranched polymers do not consist of individual surfactant fragments, but are made of a more or less large hydrophobic core coated with a hydrophilic shell. The amphiphilic character is thus based on the overall macromolecular architecture [14–20]. In the case of the hyperbranched polysoaps studied here, however, hydrophilic and hydrophobic moieties, as well as the resulting surfactant fragments are present throughout the full volume of the polymer.

Experimental

Methods

NMR spectra were taken with a Gemini 200 spectrometer (Varian). Infrared spectra were recorded with a 1710 infrared fourier transform spectrometer (Perkin-Elmer). UV/vis spectra were recorded in quartz cuvettes of 1 mm thickness with an Aminco model DW-2000. Viscosimetric studies were performed with an automatic Ubbelohde viscometer at 25 °C (Schott AVS 350). Surface tensions were measured with a manual tensiometer (Krüss 8501, De Noüy) at 22 °C. For solubilization studies, 1 ml of an aqueous solution of the amphiphile with a concentration of 20 mg/ml was mixed with 4 mg powdered solubilizate, and the suspension was shaken for 3 weeks (2.5 Hz, 30 cm amplitude). Then the solutions were centrifuged for 10 min at 13000 rpm, the undissolved material was filtered off, and the UV/vis spectra of the solutions were taken. The values given are averages of three samples, the deviations found for individual samples being ± 1 nm for the wavelength of the absorbance maximum λ_{max}, and below 20% for the amount of solubilized material.

Materials

11-bromoundecanoic acid, 3,3′-iminobis-(*N*,*N*-dimethylpropylamine) [or *N*′-(3′-dimethylaminopropyl)-*N*,*N*-dimethyl-1, 3-propanediamine], *N*,*N*-dimethylpropanediamine, 2-dimethylamino-ethanol and 1,3-bis(dimethylamino)propan-2-ol, were purchased from Aldrich and used as received. Synthesis of reference compounds **11**–**13** was described previously [21–23]. Flash chromatography was performed on silica gel (Merck). All solvents were distilled before use. Water was deionized and purified by an Elgastat Maxima (Elga, resistance 18.2 MΩ).

Synthesis of *N*′-(11-bromoundecanoyl)-*N*′-(3′-dimethylaminopropyl)-*N*,*N*-dimethyl-1,3-propanediamine **1**: 3.6 g (56 mmol) $SOCl_2$ is added to 4.0 g (15 mmol) 11-bromoundecanoic acid while stirring, and the mixture is refluxed (110 °C) for 4 h. Then the excess of $SOCl_2$ is removed under reduced pressure. The resulting 11-bromoundecanoylchloride was pure according to ^{1}H NMR, and was used without further purification.

At about 0 °C, 4.0 g (14 mmol) 11-bromoundecanoylchloride is added dropwise to a mixture of 4.0 g (21 mmol) 3,3′-iminobis-(*N*′,*N*′-dimethylpropylamine) in 15 ml diethylether with 15 ml 2 M aqueous Na_2CO_3, while stirring. The emulsion is stirred for 8 h. Then the mixture is washed 5 times with aqueous 2 M NaOH and twice with half-saturated aqueous NaCl. The organic phase is separated and dried using $MgSO_4$. The solvent is removed in vacuo at ambient temperature in order to avoid premature polycondensation. Yield: 2.6 g (42%) of **1** (yellowish, viscous liquid).

^{1}H NMR ($CDCl_3$, δ in ppm): 3.4–3.2 (m, 6H, $-CH_2-Br$, $-CONCH_2-$); 2.3–2.1 (m, 18H, $-CH_2-NCH_3$, $-CH_2CON<$); 1.9–1.5 (m, 8H, $Br-C-CH_2-$, $-CH_2-C-CON<$, $-CON-C-CH_2-C-N$); 1.45–1.15 (m, 12H, $-(CH_2)_6-$).

IR (film, selected bands) : 2972, 2929, 2855, 2815 and 2765 cm^{-1} (C-H$_{alkyl}$ valence); 1645 cm^{-1} (C=O amide).

Synthesis of hyperbranched polyamide **2**: 1.0 g (2.3 mmol) trifunctional monomer **1** is dissolved in 10 ml anhydrous dimethyl formamide. Oxygen is removed by 3 freeze-thawing cycles, and is replaced by argon. The solution is heated at 60 °C for 3 days. The polymer is precipitated into ethyl acetate, separated by centrifugation, dissolved in water and lyophilized. Yield: 42% of yellowish, hygroscopic solid.

^{1}H NMR (D_2O, δ in ppm): 3.4–3.0 (8H, $-CH_2-N^+-CH_2-$, $-CON-CH_2-$); 2.9 (6H, N^+-CH_3); 2.35–2.13 (4H, $-CH_2-N-$, $-CH_2-CON<$); 2.11–2 05 (6H, $N-CH_3$); 1.85 (2H, $-N-C-CH_2-C-N^+-$); 1.7–1.3 (6H, $-N^+-C-CH_2-$, $-CH_2-C-CON-C-CH_2-$); 1.15 (12H, $-(CH_2)_6-$).

^{13}C NMR (CD_3OD, δ in ppm): 176.3 (-CON-); 66.3, 63.6 ($-CH_2-N^+-CH_2-$); 57.9 ($-CH_2-N<$); 51.8 ($-N^+-CH_3$); 45.6 ($-N-CH_3$); 44.2 ($-CONCH_2$); 34.4 ($-CH_2-CON<$); 30.7, 30.6, 27.9, 27.8, 27.0, 26.2, 24.1 ($-CON-C-CH_2-$, $-(CH_2)_7-$); 23.2 ($-N^+-C-CH_2-$).

IR (film, selected bands): 2928, 2856 cm^{-1} (C-H$_{alkyl}$ valence); 1647 cm^{-1} (C=O, amide).

Synthesis of *N*-(3′-dimethylaminopropyl)-11-bromoundecanoamide **5**: The monomer is prepared from 4.0 g (14 mmol) 11-bromoundecanoylchloride and 2.2 g (21 mmol) 3-dimethylaminopropylamine, as described for **1**. Yield: 2.7 g (54%) of yellow-brownish viscous liquid.

^{1}H NMR ($CDCl_3$, δ in ppm) 6.90 (s, 1H, -NH-); 3.5–3.3 (m, 4H, $-CH_2-Br$, $-CON-CH_2-$); 2.35 (t, 2H, $-CH_2-N<$); 2.25 (s, 6H, $-NCH_3$); 2.15 (t, 2H, $-CH_2-CON-$); 1.82 (m, 2H, $-CON-C-CH_2-C-N<$); 1.7–1.5 (m, 4H, $Br-C-CH_2-$, $-CH_2-C-CON-$); 1.45–1.2 (m, 12H, $-(CH_2)_6-$).

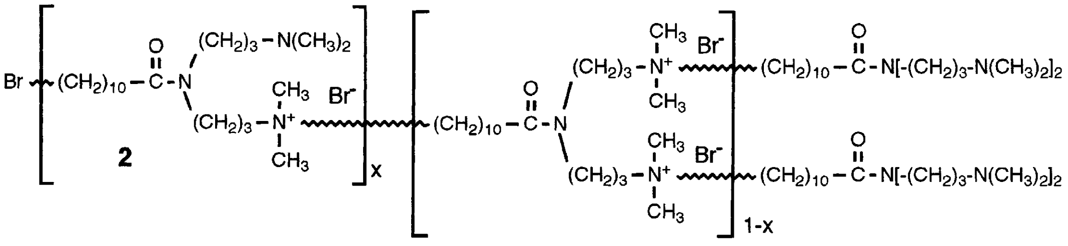
IR (film, selected bands) : 2917, 2850, 2813 and 2763 cm^{-1} (C-H$_{alkyl}$ valence); 1634 cm^{-1} (amide I); 1548 cm^{-1} (amide II).

The linear polyamide **6** is prepared from 1.0 g (2.9 mmol) monomer **5** in analogy to the synthesis of polyamide **2**. Yield: 79% of yellowish hygroscopic solid.

^{1}H NMR (D_2O, δ in ppm) 3.3–3.1 (6H, $-CH_2-N^+-CH_2-$, $-CON-CH_2-$); 2.97 (6H, $CH_3-N^+-CH_3$); 2.15 (2H, $-CH_2-$); 1.85 (2H, $-CON-C-CH_2-C-N^+-$); 1.7–1.4 (4H, $-N^+-C-CH_2-$, $-CH_2-C-CON-$); 1.35–1.1 (12H, $-(CH_2)_6-$).

^{13}C NMR (CD_3OD, δ in ppm) 176.7 (-CONH-); 65.6, 63.2 ($-CH_2-N^+-CH_2-$); 51.4 ($-N^+CH_3$); 37.15 ($-CH_2-CONH$); 30.5, 30.4, 30.2, 27.4, 26.9, 24.0, 23.6, 21.8 ($-(CH_2)_7-$, $-N^+-C-CH_2-$, $-CON-C-CH_2-C-N^+$); signals of $-CONCH_2$-group covered by solvent.

Table 1 Monomeric and polymeric amphiphiles studied (the structure of the hyperbranched polymers **2** and **4** is simplified)



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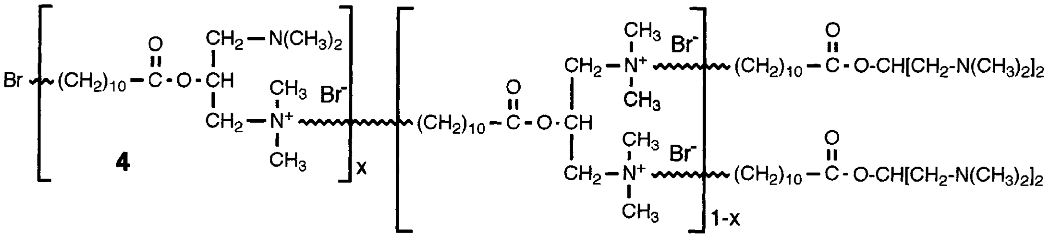

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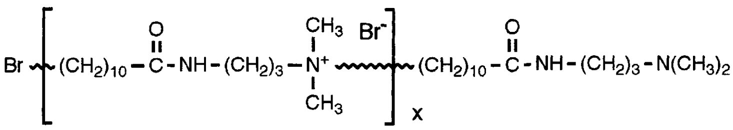
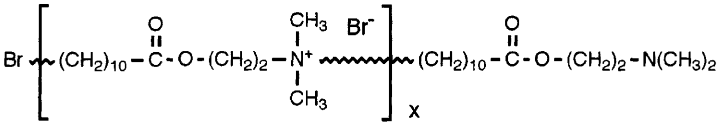


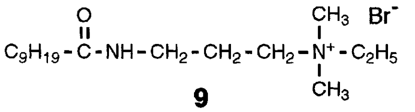
6

$Br\left[(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}\right]_x(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_3-N(CH_3)_2$



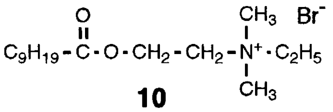
8

$Br\left[(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}\right]_x(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-N(CH_3)_2$



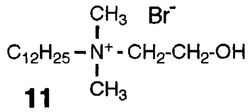
9

$C_9H_{19}-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}-C_2H_5$



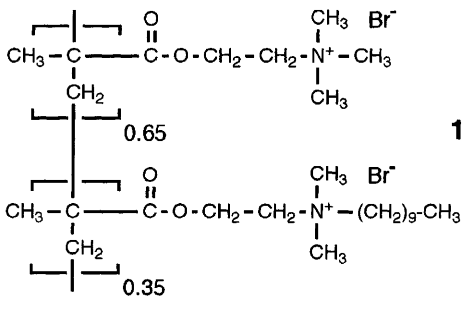
10

$C_9H_{19}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}-C_2H_5$

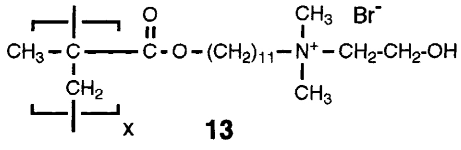


11

$C_{12}H_{25}-\underset{CH_3}{\overset{CH_3\ Br^-}{N^+}}-CH_2-CH_2-OH$



12



13

IR (KBr pellet, selected bands): 2928 and 2855 cm^{-1} (C-H$_{alkyl}$ valence); 1648 cm^{-1} (amide I); 1560 cm^{-1} (amide II).

Synthesis of [1,3-bis(dimethylamino)prop-2-yl]-11-bromoundecanoate **3**: A mixture of 4.0 g (15 mmol) 11-bromoundecanoic acid, 2.0 g (14 mmol) 1,3-bis(dimethylamino)-2-propanol and 0.15 g (1.22 mmol) 4-dimethylaminopyridine (DMAP) in 15 ml CH_2Cl_2 is cooled to 0 °C. 1.36 g (7.0 mmole) dicyclohexylcarbodiimide (DCC) was added dropwise while stirring. The mixture is then stirred for 10 h at ambient temperature. The solution is filtered to remove the precipitated urea. The solvent is removed in vacuo at room temperature to avoid a premature polycondensation. The crude product is purified by two successive flash chromatographies [eluents: $CHCl_3/CH_3OH$ (10v/1v) and ethyl acetate]. Yield: 2.7 g (46%) of yellowish liquid.

^{1}H NMR ($CDCl_3$, δ in ppm): 5.1 (m, 1H, -COO-CH<); 3.48 (t, 2H, Br-CH$_2$-); 2.4 (m, 4H, -COO-C-CH$_2$-); 2.35–2.1 (m, 14H, -CH$_2$-COO-, -NCH$_3$); 1.8 (m, 2H, Br-C-CH$_2$-); 1.6 (m, 2H, -CH$_2$-C-COO-); 1.45–1.15 (m, 12H, -(CH$_2$)$_6$-).

IR (film, selected bands): 2927, 2854, 2821 and 2769 cm^{-1} (C-H$_{alkyl}$ valence); 1734 cm^{-1} (C=O valence).

The hyperbranched polyester **4** is made from monomer **3** in analogy to the synthesis of polymer **2**. Yield: 56% of yellowish hygroscopic acid.

^{1}H NMR (D_2O, δ in ppm) 4.57 (1H, -COO-CH<); 3.4–3.2 (4H, -COO-C-CH$_2$-N$^+$-CH$_2$-); 3.19–3.0 (8H, -CH$_2$-N< protonated, -COO-C-C-N$^+$CH$_3$); 2.85 (6H, -NCH$_3$ protonated); 2.17 (2H, -CH$_2$-COO-); 1.8–1.4 (4H, N$^+$-C-CH$_2$-, -CH$_2$-C-COO-); 1.35–1.0 (12H, -(CH$_2$)$_6$-).

^{13}C NMR (CD_3OD, δ in ppm) : 180.6 (-*C*OO-); 67.2 (-COO-*C*H<); 62.7, 62.3 (-CH$_2$-N$^+$-CH$_2$-); 52.8 (-CH$_2$-N<); 52.5 (-N$^+$CH$_3$); 44.9 (-N-CH$_3$); 36.7 (-*C*H$_2$-COO-); 34.8, 30.5, 30.2, 29.9, 27.2, 26.7 (-(CH$_2$)$_6$-); 26.0 (-*C*H$_2$-C-COO-), 23.5 (-N$^+$-C-*C*H$_2$-).

IR (KBr pellet, selected bands): 2927, 2855 cm^{-1} (C-H$_{alkyl}$ valence); 1735 cm^{-1} (C=O, ester).

Synthesis of 2-dimethylaminoethyl 11-bromoundecanoate **7**: 4.0 g (15 mmol) 11-bromoundecanoic acid, 1.22 g (14 mmol) 2-dimethylaminoethanol, 0.15 g (1.22 mmol) DMAP and 1.36 g (7 mmol) DCC are reacted in analogy to the synthesis of monomer **3**. Yield: 3.1 g (62%) of yellowish liquid.

^{1}H NMR ($CDCl_3$, δ in ppm): 4.15 (t, 2H, -COO-CH$_2$-); 3.4 (t, 2H, Br-CH$_2$-); 2.55 (t, 2H, -CH$_2$-N<); 2.35–2.25 (t, 8H, -CH$_2$-COO-, -NCH$_3$); 1.85 (m, 2H, Br-C-CH$_2$-); 1.6 (m, 2H, -CH$_2$-C-COO-); 1.5–1.2 (m, 12H, -(CH$_2$)$_6$-).

IR (film, selected bands): 2927, 2854, 2851 and 2741 cm^{-1} (C-H$_{alkyl}$ valence); 1737 cm^{-1} (C=O, ester).

The linear polyester **8** was prepared from monomer **7**, in analogy to the making of polymer **2**. Yield: 67% of white hygroscopic solid.

^{1}H NMR (D_2O, δ in ppm): 4.42 (2H, -COO-CH$_2$-); 3.52 (2H, -COO-C-CH$_2$-N$^+$-); 3.3 (2H, -N$^+$-CH$_2$-); 3.05 (6H, -N$^+$CH$_3$); 2.25 (2H, -CH$_2$-COO-); 1.7 (2H, -N$^+$-C-CH$_2$-); 1.5 (2H, -CH$_2$-C-COO-); 1.3–1.1 (12H, -(CH$_2$)$_6$-).

^{13}C NMR (CD_3OD, δ in ppm): 174.2, (-COO-); 66.7, 63.9 (-CH$_2$-N$^+$-CH$_2$-); 59.2 (-COO-*C*H$_2$-); 52.5 (-N$^+$CH$_3$); 35.2 (-*C*H$_2$-COO-); 30.3, 30.0, 28.7 (-(CH$_2$)$_6$-); 25.9 (-*C*H$_2$-C-COO-); 23.9 (-N$^+$-C-*C*H$_2$-).

IR (KBr pellet, selected bands): 2923, 2852 (C-H$_{alkyl}$ valence); 1736 cm^{-1} (C=O, ester).

Synthesis of *N*-(*N*′-ethyl-*N*′,*N*′-dimethyl-3-ammoniopropyl) decanoamide bromide **9**: 10.06 g (39 mmol) dimethylaminopropyl decanoylamide and 17.5 g (161 mmol) ethyl bromide are stirred in 100 ml acetone for 3 days under an argon atmosphere. The crude product is purified by two flash chromatographies [eluents: $CHCl_3/CH_3OH$ (2v/1v) and $CHCl_3/CH_3OH$ (1v/1v)]. Yield: 8.6 g (60%) of slightly brownish, hygroscopic solid.

^{1}H NMR ($CDCl_3$, δ in ppm): 3.4–3.1 (m, 6H, -CON-CH$_2$-, -CH$_2$-N$^+$-CH$_2$-); 2.98 (s, 6H, -N$^+$CH$_3$); 2.15 (t, 2H, -CH$_2$-CON); 1.9 (m, 2H, -CON-C-CH$_2$-C-N$^+$); 1.5 (m, 2H, -CH$_2$-C-CON); 1.3–1.1 (m, 15H, -(CH$_2$)$_6$-, -N$^+$-C-CH$_3$); 0.75 (t,3H, CH$_3$-C-).

IR (KBr pellet, selected bands): 2926, 2856 cm^{-1} (C-H$_{alkyl}$ valence); 1655 cm^{-1} (C=O, amide I); 1561 cm^{-1} (C=O, amide II).

Synthesis of (*N*-ethyl-*N*,*N*-dimethyl-2-ammonioethyl) decanoate bromide **10**: 10.0 g (41 mmol) 2-dimethylaminoethyl decanoate and 17.5 g (161 mmol) ethyl bromide are reacted in 100 ml acetone, as described for **9**. The crude product is repeatedly crystallized from acetone, then dissolved in water and lyophilized. Yield: 65% of white hygroscopic solid.

^{1}H NMR (D_2O, δ in ppm): 4.45 (t, 2H, -COO-CH$_2$-); 3.65 (t, 2H, -COO-C-CH$_2$-N$^+$-); 3.45 (m, 2H, -N$^+$-CH$_2$-); 3.1 (s, 6H, -N$^+$CH$_3$); 2.35 (t, 2H, -CH$_2$-COO-); 1.5 (m, 2H, -CH$_2$-C-COO-); 1.4–1.1 (m, 15H, CH$_3$-C-N$^+$, -(CH$_2$)$_6$-); 0.75 (t, 3H, CH$_3$-).

^{13}C NMR (CD_3OD, δ in ppm): 174.3 (-COO-); 63.2, 62.0 (-CH$_2$-N$^+$-CH$_2$-); 58.6 (-COO-*C*H$_2$-); 51.4 (-N$^+$CH$_3$); 34.7 (-*C*H$_2$-COO-); 33.0, 30.5, 30.4, 30.15, (-(CH$_2$)$_5$-); 25.7 (-*C*H$_2$-C-COO-); 23.7 (CH$_3$-*C*H$_2$-); 14.4 (CH$_3$-); 8.6 (*C*H$_3$-C-N$^+$-).

IR (KBr pellet, selected bands): 2926, 2856 (C-H$_{alkyl}$ valence); 1736 cm^{-1} (C=O, ester).

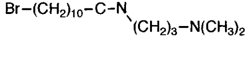
Results and discussion

Synthesis

The most convenient access to hyperbranched polymers is the polycondensation of trifunctional molecules of the AB$_2$ type [24]. In order to obtain amphiphilicity and water solubility, strongly hydrophilic moieties must be incorporated. In the simplest case, these are ionic groups. However, amphiphilic monomers are difficult to purify, and are often quite hygroscopic. This makes it difficult to obtain the high purities and yields needed for an efficient polycondensation reaction. Therefore, we have chosen to create the ionic groups needed by the polyreaction, namely by the alkylation of tertiary amines. The resulting polymers can be classified as ionenes, due to the ammonium groups localized in the polymer backbone [25, 26]. This strategy is rather new even for non-amphiphilic hyperbranched polymers. So far, very few examples of dendrimers or hyperbranched polyelectrolytes are reported in which permanently charged groups (independent of the pH) are incorporated throughout the macromolecules [27–33], and not only in the form of functional end groups at the surface.

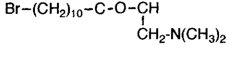
The AB$_2$ type monomers **1** and **3** were designed to contain two tertiary amines and one alkylating group (Table 2), as the residual tertiary amine groups in the polymers are mostly protonated at neutral pH thus

Table 2 Monomers used for the polyreactions to make hyperbranched polysoaps and their linear analogues



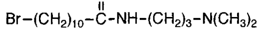
$Br{-}(CH_2)_{10}{-}C({=}O){-}N[(CH_2)_3{-}N(CH_3)_2]_2$

1



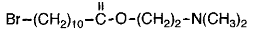
$Br{-}(CH_2)_{10}{-}C({=}O){-}O{-}CH[CH_2{-}N(CH_3)_2]_2$

3



$Br{-}(CH_2)_{10}{-}C({=}O){-}NH{-}(CH_2)_3{-}N(CH_3)_2$

5



$Br{-}(CH_2)_{10}{-}C({=}O){-}O{-}(CH_2)_2{-}N(CH_3)_2$

7

becoming strongly hydrophilic. If instead, one tertiary amine and two alkylating groups are incorporated in the monomers, the residual alkylating groups are hydrophobic and the resulting hydrophilic-hydrophobic balance of the hyperbranched polyion may be not sufficient to enable water solubility [34]. Secondary functionalization of the residual alkylating group with low-molar-mass amines may overcome this problem [34], but the resulting hyperbranched polyelectrolytes are a priori less well defined than in the approach chosen here. In addition to the crucial functional groups for the polyreaction (ω-monobromo-α-α'-diamines), monomers **1** and **3** contain an amide group or an ester group, respectively. Therefore, the hyperbranched polyelectrolytes **2** and **4** obtained can also be classified as polyamides or polyesters.

The synthesis of monomers **1**, **3**, **5**, and **7** needs some precautions. The monomers tend to react notably with each other at room temperature, and so all synthetic procedures and purification steps must be fast. However, the direct reaction of pure 11-bromoundecanoylchloride with *N*,*N*-dimethyl-1,3-propanediamine or with 2-dimethylaminoethanol always resulted in a partial exchange of bromine against chlorine. Long-chain bromoalkanes are moderately strong alkylating agents; the analogous chlorines are not reactive enough to obtain polymers of sufficiently high molar mass. Presumably, the protonated tertiary amines catalyze the exchange of the halogenes. Therefore, a biphasic system was employed to synthesize amides **1** and **5** from the acid chloride in the presence of NaOH. As this procedure is not possible for esters **3** and **7**, the coupling of the free acid with the alcohols by carbodiimide was chosen. This pathway requires rather slow purification by chromatography.

The linear analoguous ionene-type polyester and polyamide, used as references, are obtained by polycondensation of the corresponding ω-bromo-alkyl-α-amines **5** and **7** (Table 2) . The analogous "tail-end-type" and "head-type" standard polysoaps have been described and investigated extensively in the past [21–23, 35–38]. The content of non-hydrophobized ammonium groups in the "head-type" polysoap copolymer **12** is the minimum necessary to achieve water solubility, as discussed in detail previously [3, 22, 39].

Due to the amphiphilic, ionic, associating and hygroscopic character of the polymers, the estimation of the molar masses by conventional methods such as size-exclusion chromatography, light scattering or osmometry is extremely difficult, if not impossible. However, end-group analysis is possible, at least in principle. The ^{1}H NMR spectra of the linear and the hyperbranched polymers are shown in Fig. 2. The -CH$_2$-Br terminal groups cannot be detected as they would be hidden by the signals of the α-methylene protons of the ammonium moieties at about 3.2–3.5 ppm. However, residual tertiary -N(CH$_3$)$_2$ groups should show a resolved singlet signal in the spectra, either as free amines at about 2.1 ppm under basic conditions, or in the protonated form at about 2.8 ppm.

In the case of the linear ionenes, the signal of the tertiary -N(CH$_3$)$_2$ groups indicates directly the content of terminal amine moieties. Assuming one amine group per macromolecule, for example, neglecting the presence of macrocycles, we estimate an average degree of polymerization of 15 for both polyamide **6** and polyester **8** ($M_n \approx 5000$).

In the case of the hyperbranched ionenes, the method becomes increasingly inprecise with increasing degree of polymerization. For a given degree of polymerization n, the ratio of quaternized -N$^+$(CH$_3$)$_2$ groups to not quaternized -N(CH$_3$)$_2$ groups is $(n-1)/(n+1)$. Again neglecting the presence of macrocycles, we estimate an average degree of polymerization of 15 for polyester **4** ($M_n \approx 6000$). For polyamide **2**, the integration of the signals of the quaternized -N$^+$(CH$_3$)$_2$ groups is so close to the one of the not quaternized -N(CH$_3$)$_2$ groups, that no meaningful value can be deduced. This suggests that the degree of polymerization is rather high.

Rheology of dilute solutions

The viscosifying effect of the hyperbranched polymers, and of their linear analogues was studied in water and methanol. Figure 3 illustrates that all polymers behave as polyelectrolytes, exhibiting an increase in the reduced viscosity at low concentrations. In general, the viscosifying effects are somewhat lower in water than in methanol, but the differences are small. The values of the reduced viscosities are small for all polymers, which is on the one hand attributed to the moderate molar masses of the polymers and on the other hand, the low values are attributed to the high content of hydrocarbon chains for which methanol and even more so water are poor solvents. Such behaviour is expected for polysoaps [1, 3] and is indeed found for the reference polymers **12** [38] and **13** [36]. Interestingly, the linear ionenes **6** and **8** are more viscosifying than their hyperbranched analogues **2** and **4**, despite comparable molar masses. This suggests a more compact conformation of the hyperbranched polysoaps. In fact, the viscosifying effect of the hyperbranched polymers **2** and **4** in water is hardly higher than that of their low-molar-mass analogues **9** and **10**.

Surface activity

The surface activity of the hyperbranched polysoaps, as well as of their linear analogues and their low-molar-mass ones is illustrated in Fig. 4. As the series of the amide analogues and of the ester analogues are very

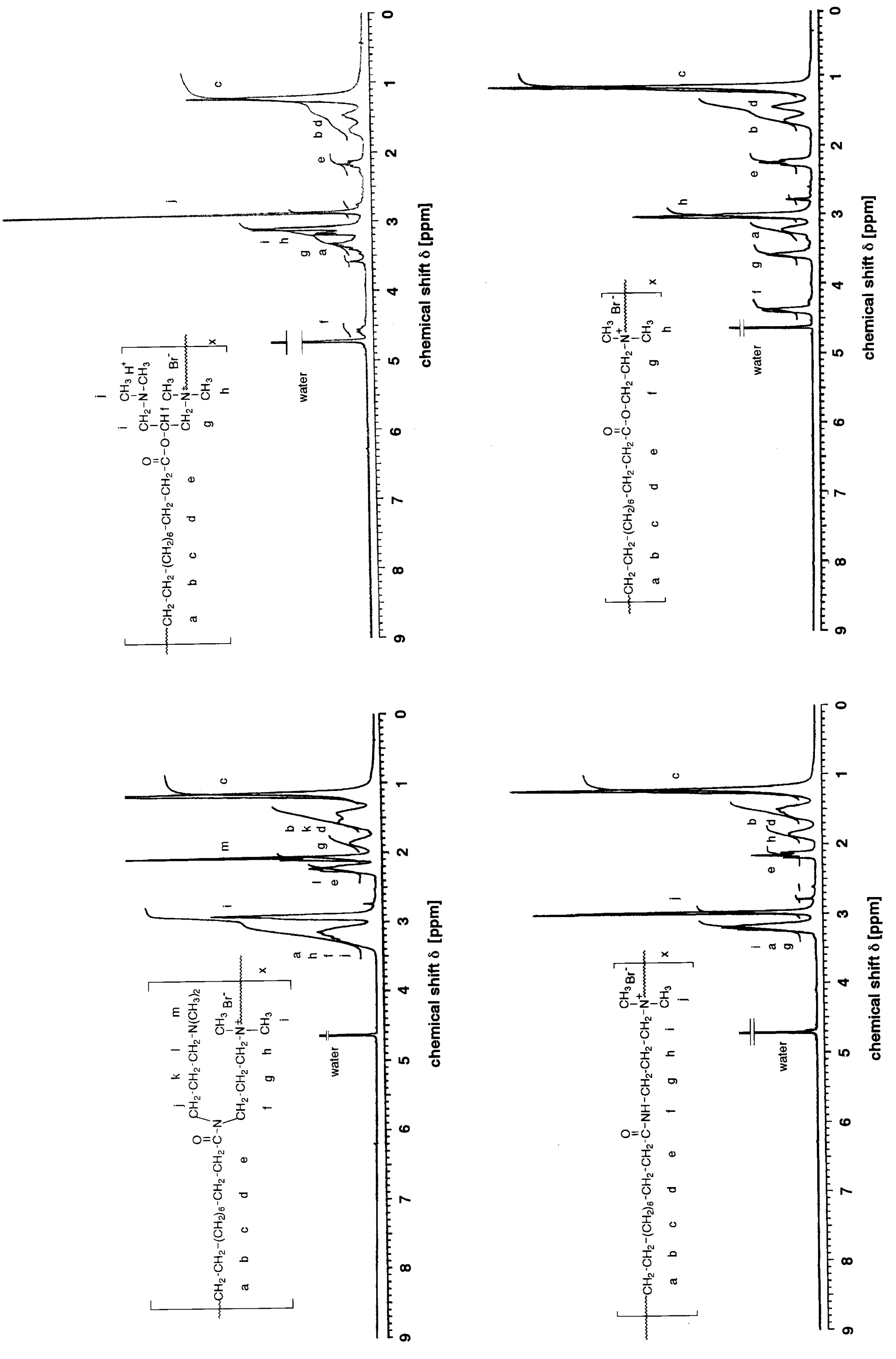


Fig. 2 ^{1}H NMR spectra of hyperbranched polysoaps and their linear analogues in D_2O (spectrum of **2** taken in dilute aqueous NaOD, spectra of **4**, **6** and **8** taken at neutral pH)

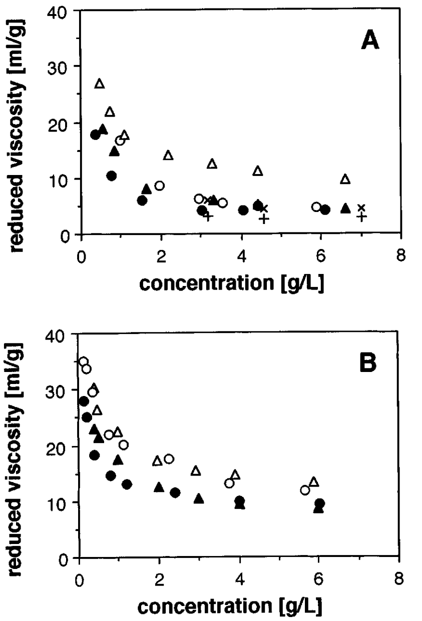


Fig. 3 Viscosifying effects of polysoaps **A** in water and **B** in methanol. Amide series: **2** = (▲), **6** = (△), **9** = (×). Ester series: **4** = (●), **8** = (○), **10** = (+)

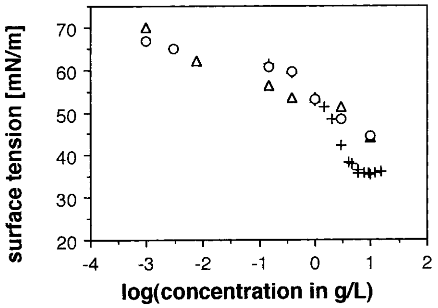


Fig. 4 Surface activity of polysoaps in water (amide series): **2** = (○), **6** = (△), **9** = (+)

similar, only the amide series is shown. The curves of the low-molar-mass surfactants **9** and **10** show a continuous reduction of the surface tension with increasing concentration until a break point indicating the cmc from which point on the surface tension stays nearly constant.

The measured cmc's of 6.5 g/l (i.e. 0.018 mol/l) for both **9** and **10** compare well to the cmc's of 0.015 mol/l of *N*-dodecyl-*N*,*N*,*N*-trimethylammonium bromide [40] and of reference **11** [21]. Also, the surface tensions at the cmc of about 37 mN/m are in the normal range for a C_{10} chain. Therefore, the additional amide or ester groups close to the ammonium head group do not interfere with the normal surfactant behaviour of the model compounds **9** and **10**.

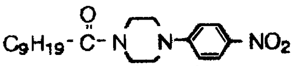
The hyperbranched and the linear polymers behave very similarly. They all show a limited surface activity, the surface tension of solutions of 10 g/l being as low as about 45 mN/m; however, the curve of the decrease of the surface tension with increasing polymer concentration shows no break point indicative of a cmc. This parallels the behaviour of polysoaps of the "head type" such as reference polymer **12** [22, 36]. Its moderate surface activity, and that of many other polysoaps [3, 41, 42] despite their intramolecular hydrophobic aggregation, can be attributed to an incomplete shielding of the hydrophobic chains from water, due to the steric constraints imposed by the fixation of the surfactant fragments to a polymer backbone. In contrast, polysoaps of the "tail-end type" such as **13** are hardly surface active [3, 22, 35, 36]. The particular geometry inherently favours the shielding of the hydrophobic chains from water, and thus the marginal surface activity of such polysoaps is easily understood.

Solubilization of hydrophobic dyes

The solubilization of poorly water soluble compounds is a key property of micelles, as they provide hydrophobic domains in an aqueous environment [43]. To investigate the solubilization capacity of the polysoaps, two different dyes were employed, the nitroaniline 4-(*N*′-n-decanoylpiperazino)nitrobenzene **14** (extinction coefficient in isopropanol at $\lambda_{\max} = 372$ nm: $\varepsilon = 18\,600\ \mathrm{l \cdot mol^{-1}\,cm^{-1}}$), and the azo dye 4-diethylamino-(4′-butylphenylazo)benzene **15** (extinction coefficient in isopropanol at $\lambda_{\max} = 411$ nm: $\varepsilon = 32\,000\ \mathrm{l \cdot mol^{-1}cm^{-1}}$ [36–38]). The latter is a rather compact hydrophobic molecule, whereas **14** presents a weak amphiphile with a long hydrocarbon chain. Both dyes exhibit notable solvatochromism. Dye **14** has $\lambda_{\max} = 372$ nm in isopropanol g and $\lambda_{\max} = 391$ nm in water, whereas dye **15** exhibits its $\lambda_{\max}$ at 411 nm in isopropanol, and at 423 nm in water. The results of the solubilization experiments are listed in Table 3.

As solvatochromic effects are frequently used to characterize the solubilization site of dyes, we tried to analyse the spectral data. Solvatochromic shifts are small-to-moderate, the shifts of the absorbance maximum deviating at maximum 11 nm from the value found in water. Quite generally, the environment of the chromophore of **14** appears to be more polar when solubilized by the polysoaps than when dissolved in water. This at first sight surprising finding may be rationalized by preferential solubilization of the polar nitroaniline group at the "micellar surface", in which the ammonium groups are concentrated. According to the absorbance maxima, "head-type" copolymer **12** and the hyperbranched polyamide **2** seem to encounter the most polar environment within the compounds studied; however, the solvatochromic shift points to a much less polar environment for the linear anologous

Table 3 Solubilization of dyes **14** and **15** in water by monomeric and polymeric amphiphiles (concentration of amphiphiles: 20 g/l)



dye 14

dye 15

Amphiphile	λ_{max} (nm)	Solubilized amount (mg/l)	λ_{max} (nm)	Solubilized amount (mg/l)
None	391	9.5	423	2.3
2	402	11.7	414	13.2
6	387	11.5	410	19.9
9	396	77.0	416	21.2
4	393	17.1	419	25.2
8	393	31.3	424	26.6
10	395	123.0	422	71.8
11	395	278.7	423	175.9
12	399	36.5	420	23.2
13	396	177.6	429	100.7

polyamide **6**. Also for the other soaps, the individual spectral shifts found could not be correlated to a particular molecular pattern, but rather seem to be at random.

Similarly, the spectral shifts for azo dye **15** upon solubilization given in Table 3 are difficult to interprete even qualitatively. The amide surfactant and the polyamide polysoaps apparently provide a less polar environment than the systems containing ester groups which is difficult to rationalize, and there is no obvious tendency within the subclasses. Clearly, the spectral shifts found do not coincide with the ones observed for dye **14**. As seen in previous solubilization studies [36, 37, 44, 45], the results illustrate once more the difficulties to study the local environment of micellar aggregates by using dye probes.

In contrast to the apparent solubilization site deduced from solvatochromism, the solubilization capacity shows some clear trends. The low-molar-mass surfactants **9**–**11** are always more efficient than their polymeric analogues. Their higher solubilization power is particularly marked for nitroaniline **14**. This may be attributed to the long hydrocarbon chains which should be more difficult to accomodate in the polymers for steric reasons [3, 36]. Nevertheless, all the polymers studied are capable of solubilization, and thus behave as true polysoaps. The highest capacities for both dyes are obtained with the simple reference surfactant **11** in the low-molar-mass series, and with the "tail-end-type" polysoap **13** in the polymer series. Reference copolymer **12**, the amphiphiles **4**, **8** and **10** with ester groups in the main chain, and in particular the amphiphiles **2**, **6** and **9** with amide groups are considerably less efficient. The hyperbranched polysoaps and their linear main-chain analogues exhibit comparable solubilization capacities, with a slight advantage for the linear polymers (cf. **2** with **6**, and **4** with **8**). They compare well with the reference "head-type" polysoap **12** which, however, is known not to be a particularly efficient solubilizing agent [36].

Conclusions

Hydrophobized cationic hyperbranched polymers are conveniently accessible. Such polymers behave like polysoaps. Concerning their surface activity and solubilization capacity, they show many similarities to their linear analogues, and to polysoaps of the "head type", i.e. they exhibit moderate surface activity and moderate solubilization power. Characteristically, their viscosifying effect is extremely low, even compared to the low effect of standard polysoaps.

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