Polymerizable and polymeric zwitterionic surfactants: 1. Synthesis and bulk properties

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The synthesis of a series of permanently zwitterionic surfactant monomers based on sulphobetaines and the preparation of their polymers is described. Solubilities, thermal properties and bulk structures of the zwitterionic polymers are studied with respect to their molecular architecture, and compared with cationic analogues. The various solubilities of the polymers can be correlated with their molecular geometry, enabling differentiation into distinct classes. This behaviour is paralleled by the observed bulk structures of the polymers where distinct classes of superstructures are present. However, independently of the molecular geometry, no thermal transition could be detected for any of the zwitterionic polymers studied.

(Keywords: polymerizable surfactants; polyzwitterions; solubility; d.s.c.; X-ray diffraction)

INTRODUCTION

Many amphiphilic, water-soluble polymers are characterized by very low viscosities of their aqueous solutions and the ability to solubilize hydrophobic, water-insoluble compounds. Therefore, such polymers are referred to as 'micellar polymers' or as 'polysoaps', because they behave analogously to micelles or low molecular weight surfactants[1,2].

Polysoaps can be prepared by three methods: by polymerization of reactive surfactants[3–8]; by copolymerization of hydrophilic and hydrophobic monomers[2,9,10]; or by appropriate modification of preformed polymers, such as grafting hydrophobic chains onto hydrophilic polymers[1,11–13]. The first method produces polymers with the best defined molecular structures.

According to the nature of their hydrophilic moieties, polysoaps can be distinguished as ionic and non-ionic types. Both exhibit inherent advantages and disadvantages. Ionic polysoaps in water are characterized by high hydrophilicity and the absence of lower critical solution temperatures. But they are subject to polyelectrolyte effects upon dilution, and tend to gelatinize upon concentration. Ionic polysoaps also exhibit a high sensitivity to added salt. In contrast, non-ionic polysoaps in water are rather insensitive to added salt and lack polyelectrolyte effects. But they generally show reduced hydrophilicity and hence exhibit lower critical solution temperatures[6].

To overcome these problems and to combine ionic and non-ionic polysoap behaviour advantageously, the use of fully zwitterionic polysoaps can be considered. Such polymers bear an equivalent number of cationic and anionic groups, and thus have an overall neutral charge. The ionic groups will render the polymer very hydrophilic, avoiding the problems of a lower critical solution temperature. Additionally, the option to modify aqueous solutions by adding salt is preserved.

Synthesis strategy

Based on the considerations above, we have prepared a series of reactive, zwitterionic surfactants, and therefrom the zwitterionic polysoaps. Trialkylammoniopropanesulphonate was chosen as hydrophilic group (head group), because of its zwitterionic character over a wide pH range (at least pH 2–12)[14]. Major emphasis was placed on the variation of the polymer skeleton, since the importance of the position of the polymer backbone in polysoaps (*Figure 1*) has been discussed in the past[15,16]. Therefore, keeping the length of the hydrophobic tail constant, the nature and the position of the polymerizable moiety were varied systematically to study their influence on solubility and self-organization behaviour[17].

The monomers were generally prepared in three stages. First, the basic tertiary amine structure was prepared; in the second stage, the polymerizable moiety was attached and finally, the zwitterionic surfactant was obtained by quaternization of the polymerizable tertiary amine with propanesultone[18]. This synthesis scheme guarantees the preparation of sulphobetaines free of salt contaminants. *Table 1* lists the sulphobetaine surfactants and polysoaps synthesized, some cationic analogues and the model compounds used for comparative studies.

EXPERIMENTAL

Materials

Solvents. All solvents used were analytical grade. Acetonitrile and triethylamine were dried over molecular sieves of 3 Å. Tetrahydrofuran (THF) was distilled over potassium metal. All other solvents were dried by neutral Al_2O_3 (Merck, activity 1). Water used for the ionic and zwitterionic compounds was purified by a Milli Q water purification system. Flash chromatography was performed on Silicagel (Baker, 230 mesh).

*11-*N,N*-Dimethylaminoundecanol.* 11-Bromoundecanol (Fluka), 99.2 g (0.4 mol), 120 ml (0.94 mol) of

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7.9 M aqueous dimethylamine and 17.4 g (0.435 mol) of NaOH in 400 ml ethanol are stirred for 6 days under nitrogen at 75°C. The solvent is removed, and the residue is dissolved in acetone, filtered from the insoluble parts, and evaporated. Distillation *in vacuo* yields 80.3 g (94% yield) crude product, b.p. 104–106°C (0.15 mbar), ($n_D^{25} = 1.4510$). According to ^{1}H n.m.r. data, the crude product is contaminated by ~5–10 mol% 11-ethoxyundecanol, but can be used for the following synthesis without further purification. Using isopropanol/Na_2CO_3 instead of ethanol/NaOH, pure 11-*N*,*N*-dimethylaminoundecanol is obtained, but in much lower yields (25%). Colourless liquid $n_D^{25} = 1.4550$, solidifies on standing, m.p. 26°C.

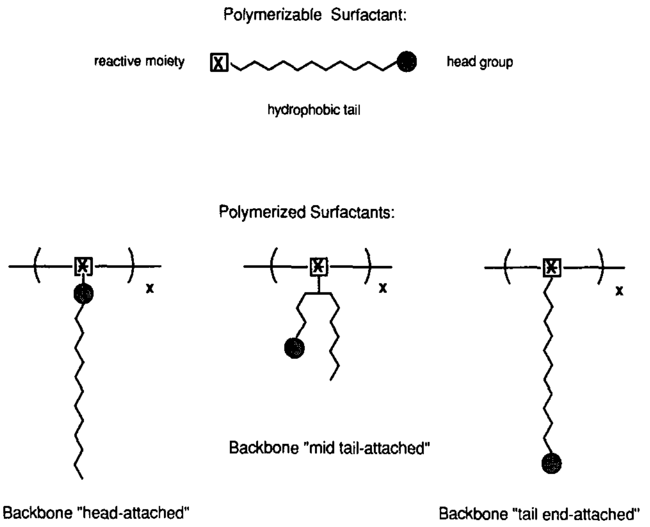


Figure 1 Scheme of the molecular architecture of polysoaps

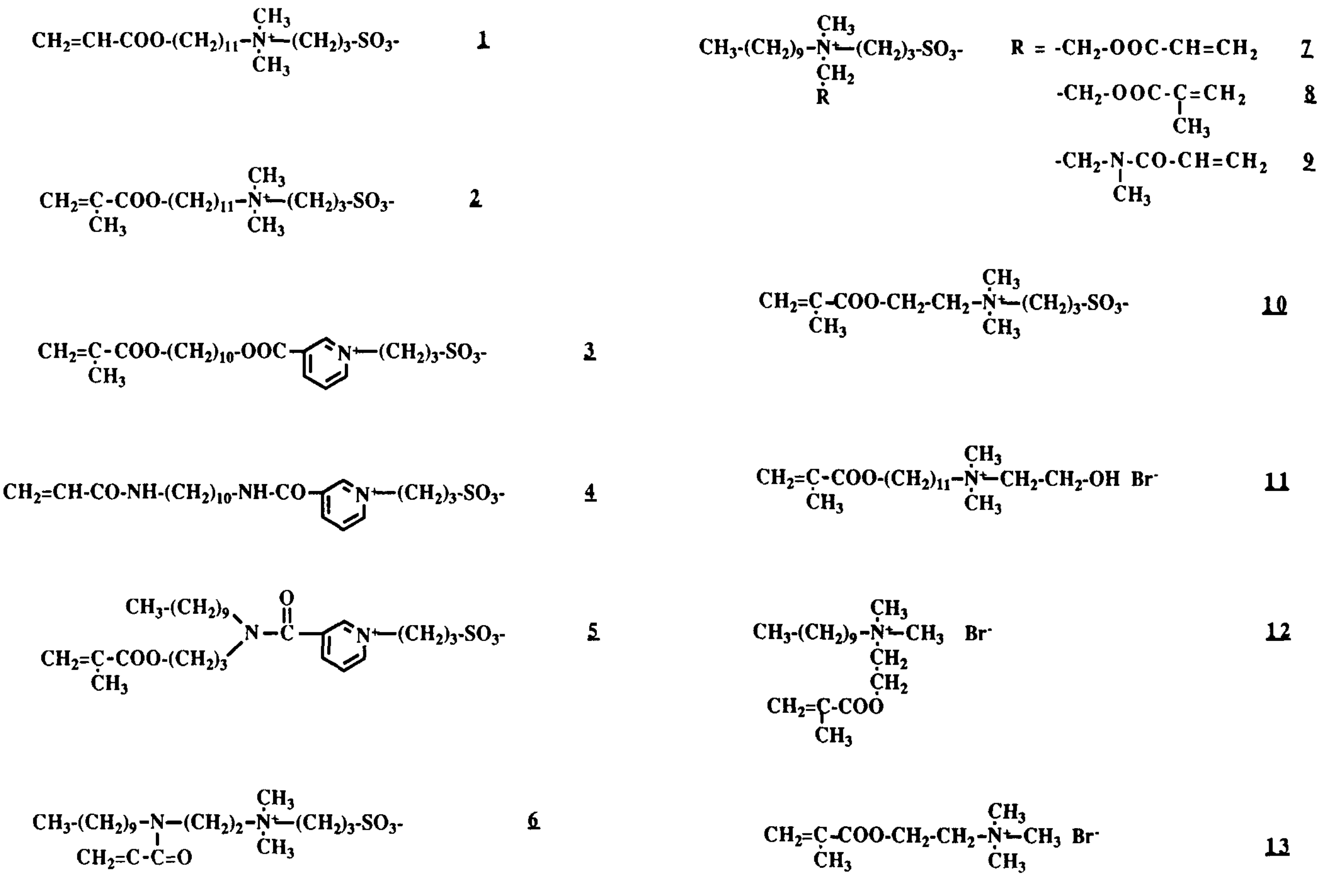
^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 1.11m$ (14H, $-(CH_2)_7-$), 1.28*m* (2H, CH_2-C-N-), 1.37*m* (2H, $-CH_2-C-O-$), 2.0–2.1*m* (8H, $-CH_2-N(CH_3)_2$), 3.38*t* (2H, $-CH_2-O$).

11-N,N-*Dimethylaminoundecylacrylate*. 11-*N*,*N*-Dimethylaminoundecanol, 9.4 g (44 mmol), 7.0 g (77 mmol) of acryloylchloride (Fluka, stabilized with CuCl) and 5.3 g (50 mmol) of powdered anhydrous Na_2CO_3 in 130 ml dichloromethane are stirred at room temperature for 2 days, and are refluxed for another 7 h. The precipitate is removed by filtration, the filtrate washed three times with half-saturated aqueous Na_2CO_3, dried over $MgSO_4$ and evaporated after addition of two drops of nitrobenzene. Yield: 7.5 g (63%) colourless oil, $n_D^{24} = 1.4509$.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 1.4*m* (18 H, $-(CH_2)_9-$), 1.9–2.25*m* (8H, $-CH_2-N-(CH_3)_2$), 4.12*t* (2H, $-CH_2-OOC-$), 5.2–6.4*m* (3H, $-OOC-CH{=}CH_2$).

3-(N-(*11-Acryloyloxyundecyl*)-N,N-*dimethyl*)*ammonio propane sulphonate 1*. 11-*N*,*N*-Dimethylaminoundecylacrylate, 7.5 g (28 mmol), 5.4 g (44 mmol) of propanesultone (Aldrich), 110 ml dry acetonitrile and 2 ml nitrobenzene are refluxed for 3 days under nitrogen. On cooling, the crude product crystallizes from the reaction mixture and is recrystallized repeatedly from acetonitrile. Yield: 8.3 g (76%) hygroscopic colourless powder, m.p. 133/156°C (two crystal modifications). Field desorption (FD) mass spectrum: peak at 391 (M^+).

Table 1 Polymerizable zwitterionic surfactants synthesized, cationic analogues and reference compounds



$CH_2{=}CH{-}COO{-}(CH_2)_{11}{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$ 1

$CH_2{=}\underset{CH_3}{C}{-}COO{-}(CH_2)_{11}{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$ 2

3

4

5

$CH_3{-}(CH_2)_9{-}\underset{CH_2{=}C{-}C{=}O}{N}{-}(CH_2)_2{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$ 6

$CH_3{-}(CH_2)_9{-}\overset{CH_3}{\underset{\underset{R}{CH_2}}{N^+}}{-}(CH_2)_3{-}SO_3^-$ R = $-CH_2{-}OOC{-}CH{=}CH_2$ 7

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

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

$CH_2{=}\underset{CH_3}{C}{-}COO{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}(CH_2)_3{-}SO_3^-$ 10

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

$CH_3{-}(CH_2)_9{-}\overset{CH_3}{\underset{\underset{\underset{CH_2{=}\underset{CH_3}{C}{-}COO}{CH_2}}{CH_2}}{N^+}}{-}CH_3\ Br^-$ 12

$CH_2{=}\underset{CH_3}{C}{-}COO{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{N^+}}{-}CH_3\ Br^-$ 13

Elemental analysis ($C_{19}H_{37}NO_5S$). Calculated: C = 58.27%, H = 9.52%, N = 3.58%, S = 8.19%; found: C = 58.01%, H = 9.51%, N = 3.60%, S = 8.37%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (14H, $-(CH_2)_7-$), 1.6–1.75 (4H, $-CH_2-C-O-$, $-CH_2-C-N^+-$), 2.20*m* (2H, $-N^+-C-CH_2-C-SO_3$), 2.86*t* (2H, $-CH_2-SO_3$), 3.16*s* (6H, $-N^+(CH_3)_2$), 3.25*m* (2H, $-CH_2-N^+$), 3.70*m* (2H, $-N^+-CH_2-C-C-SO_3$), 4.11*t* (2H, $-CH_2-OOC-$), 5.79*m* (1H, CH=C–COO *trans*), 6.08*m* (1H, =CH–COO), 6.36*m* (1H, CH=C–COO *cis*).

*3-(*N*-(11-Methacryloyloxyundecyl)-*N,N*-dimethyl) ammonio propane sulphonate* **2**. Monomer **2** is prepared from 11-*N*,*N*-dimethylaminoundecanol via 11-*N*,*N*-dimethylaminoundecylmethacrylate in analogy to the acrylate **1**, with comparable yields. Hygroscopic colourless powder, m.p. 132°C. FD-mass spectrum: peak at 405 (M^+).

Elemental analysis ($C_{20}H_{39}NO_5S$). Calculated: C = 59.22%, H = 9.69%, N = 3.46%, S = 7.90%; found: C = 58.99%, H = 9.48%, N = 3.66%, S = 7.94%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (14H, $-(CH_2)_7-$), 1.6–1.75 (4H, $-CH_2-C-O-$, $-CH_2-C-N^+-$), 1.91*s* (3H, $=C-CH_3$), 2.22*m* (2H, $N^+-C-CH_2-C-SO_3$), 2.87*t* (2H, $-CH_2-SO_3$), 3.17*s* (6 H, $-N^+(CH_3)_2$), 3.25*m* (2H, $-CH_2-N^+$), 3.71*m* (2H, $-N^+-CH_2-C-C-SO_3$), 4.11*t* (2H, $-CH_2-OOC-$), 5.53*m* (1H, CH=C–COO *trans*), 6.07*m* (1H, CH=C–COO *cis*).

Nicotinic acid-10-(methacryloyloxy)-decylester. Nicotinic acid methylester (Fluka), 31 g (0.23 mol), 39.4 g (0.23 mol) of 1,10-decanediol (Fluka) and a small piece of sodium metal are reacted at 90°C for 3 days under nitrogen. The reaction mixture is suspended in 100 ml chloroform, filtered, and the filtrate evaporated. The residue is purified by flash chromatography (Silicagel, eluent $CHCl_3$) to yield 45.2 g (71%) colourless nicotinic acid-10-hydroxy-decylester of m.p. 36°C. Eleven grams (39 mmol) of this ester, 4.5 g (43 mmol) methacryloylchloride (stabilized with di-*t*-butyl-*p*-cresol, DBPC) and 3.9 g dry triethylamine in 100 ml dry ether are stirred at 20°C for 3 days. The precipitate formed is removed by filtration, the filtrate washed three times with saturated aqueous Na_2CO_3, dried over $MgSO_4$ and evaporated after addition of two drops of nitrobenzene. Yield: 11 g (80%) colourless oil.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (12H, $-(CH_2)_6-$, 1.55–1.85 (4H, $-CH_2-C-OOC-$), 1.92*s* (3H, $=C-CH_3$), 4.10*t* (2H, –CH_2–OOC–C=C), 4.32*t* (2H, $-CH_2-OOC-Ar$), 5.52*m* (1H, CH=C–COO *trans*), 6.07*m* (1H, CH=C–COO *cis*), 7.40*m*/8.30*m*/8.75*m*/9.21*m* (1H each, C_6H_4N).

3-(3′-(10″-Methacryloyloxydecyl)oxycarbonyl)-pyridinio propane sulphonate 3. Nicotinic acid-10-(methacryloyloxy)-decylester, 11 g (32 mmol), 3.6 g (29 mmol) of propanesultone and 1 ml of nitrobenzene in 100 ml dry acetonitrile are refluxed for 3 days under nitrogen. On cooling, the crude product crystallizes from the reaction mixture, and is recrystallized from acetonitrile. Yield: 10.3 g (71%) hygroscopic colourless powder, m.p. 81°C (monohydrate). FD-mass spectrum: peak at 470/471 (M^+, $(M+1)^+$).

Elemental analysis ($C_{23}H_{35}NO_7S \cdot H_2O$). Calculated: C = 56.65%, H = 7.65%, N = 2.87%, S = 6.58%; found: C = 56.40%, H = 7.53%, N = 2.69%, S = 6.88%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (12H, $-(CH_2)_6-$), 1.63*m* (2H, –CH_2–C–OOC–C=C), 1.75*m* (2H, $-CH_2-C-OOC-Ar$), 1.90*s* (3H, $=C-CH_3$), 2.48*m* (2H, $-N^+-C-CH_2-C-SO_3$), 2.85*t* (2H, $-CH_2-SO_3$), 4.09*t* (2H, –CH_2–OOC–C=C), 4.34*t* (2H, $-CH_2-OOC-Ar$), 5.09*t* (2H, $-CH_2-N^+$), 5.51*m* (1H, CH=C–COO *trans*), 6.05*m* (1H, CH=C–COO *cis*), 8.34*m*/8.83*d*/9.41*s*/9.61*d* (1H each, $C_6H_4N^+$).

Nicotinic acid-10-(acrylamido) decylamide. Nicotinic acid methylester, 19.9 g (0.15 mol), 25.0 g (0.15 mol) 1,10-diaminodecane (Fluka) and 0.5 g ammonium chloride are sintered at 100°C for 15 h under nitrogen. The reaction mixture is dissolved in 300 ml hot methanol and cooled to 25°C. The resulting precipitate of the decane-1,10-nicotindiamide (12.6 g) is removed and the filtrate evaporated. The residue is purified by flash chromatography (Silicagel, eluent $CHCl_3/CH_3OH$ 4v/1v) to yield 15.1 g (30%) colourless nicotinic acid-10-aminodecylamide of m.p. 122°C. Fifteen grams (54 mmol) of this amide, 5.7 g (54 mmol) of acryloylchloride and 0.1 g of DBPC in 600 ml dry chloroform are refluxed for 1 h. The mixture is washed with 200 ml 0.05 N aqueous NaOH, dried over $MgSO_4$ and evaporated after addition of one drop of nitrobenzene. The black residue is purified by flash chromatography (Silicagel, eluent acetone), and recrystallized from acetone. Yield: 4.2 g (23%) colourless crystals, m.p. 118°C.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (12H, $-(CH_2)_6-$), 1.45–1.75 (4H, $CH_2-C-NH-CO-$), 3.31*m* (2H, –CH_2–NH–CO–C=C), 3.45*m* (2H, $-CH_2-NH-CO-Ar$), 5.55–5.70*m* (2H, CH=C–CON– *trans* and –CONH–), 6.0–6.3*m* (2H, CH=C–CON *cis*, =CH–CON–), 7.37*m*/8.12*m*/8.70*m*/8.95*m* (1H each, C_6H_4N).

3-(3′-(10′-Acrylamido-decyl)azacarbonyl)pyridinio propane sulphonate 4. Nicotinic acid-10-(acrylamido)-decylamide, 2.7 g (0.1 mmol), 0.95 g (7.8 mmol) of propanesultone and 1 ml nitrobenzene in 50 ml dry acetonitrile are refluxed under nitrogen for 20 h. On cooling, the crude product precipitates, is collected and recrystallized from acetonitrile and ethanol. Yield: 3.1 g (89%) hygroscopic colourless powder, m.p. 176°C. FD-mass spectrum: peak at 454 (M^+).

Elemental analysis ($C_{22}H_{35}N_3O_5S$). Calculated: C = 58.25%, H = 7.78%, N = 9.26%, S = 7.07%; found: C = 57.89%, H = 7.89%, N = 9.36%, S = 6.97%.

^{1}H n.m.r. (400 MHz, CD_3OD): δ (in ppm) = 1.3–1.5*m* (12H, $-(CH_2)_6-$), 1.57*m* (2H, –CH_2–C–CO–N–C=C), 1.70*m* (2H, $-CH_2-C-N-CO-Ar$), 2.53*m* (2H, $N^+-C-CH_2-C-SO_3$), 2.93*t* (2H, $-CH_2-SO_3$), 3.27*t* (2H, –CH_2–N–CO–C=C), 3.48*t* (2H, $-CH_2-N-CO-Ar$), 4.93*t* (overlap with HDO signal, $-CH_2-N^+$), 5.65*m* (1H, CH=C–CON *trans*), 6.24*m* (2H, CH=C–CON *cis*, =CH–CON–), 8.24*m*/8.95*m*/9.18*m*/9.47*s* (1H each, $C_6H_4N^+$).

N-(3-Hydroxypropyl)-1-aminodecane. 3-Aminopropan-1-ol (Merck), 137.4 g (1.8 mol), and 314.0 g (1.8 mol) of decanoic acid (Fluka) are refluxed in 250 ml toluene in a Dean–Stark water trap for 3 days, until water separation has ceased. Crude decanoic acid-(3-hydroxypropyl)amide crystallizes quantitatively on cooling, m.p. 62°C. It is dried *in vacuo* and used without further purification. THF, 800 ml, containing 130 g

(0.57 mol) of the amide are added dropwise to a cooled suspension of 25 g (0.66 mol) of $LiAlH_4$ in 200 ml dry THF. When the addition is completed, the mixture is stirred for 1 h at 20°C, and then refluxed for 1 h. Then 15 g ethyl acetate is added. The mixture is decomposed with 49 ml water while cooling and stirring, and allowed to settle overnight. The precipitate is removed by filtration, extracted twice with 300 ml boiling dry THF, and filtered again. The combined filtrates are concentrated by evaporation. The product crystallizes from THF, and is recrystallized from petrolether. Yield: 62.0 g (51%) colourless powder, m.p. 43°C.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.43*m* (2H, $-CH_2-C-N-$), 1.67*m* (2H, $-N-C-CH_2-C-O-$), 2.56*t* (2H, $-CH_2-N$), 2.84*t* (2H, $-N-CH_2-C-C-O$), 3.78*t* (2H, $-CH_2-O-$).

N-*Decyl*,N-(*3-hydroxypropyl*)*nicotinamide*. Nicotinic acid methylester, 8.9 g (65 mmol), 14 g (58 mmol) of 4-aza-tetradecan-1-ol and 0.1 g of NH_4Cl are stirred under nitrogen for 3 days at 80°C. The resulting brownish oil is purified by flash chromatography (Silicagel, eluent petrolether/acetone 2v/1v). Yield: 12.4 g (66%) colourless, waxy solid, m.p. 24°C.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.54*m* (2H, $CH_2-C-NCO-$), 1.83*m* (2H, $-CON-C-CH_2-C-O-$), 3.18*t* (2H, $-CH_2-NCO$), 3.45–3.75*m* (4H, $-CON-CH_2-C-C-O$, $-CH_2-O-$), 7.35*m*/7.68*m*/8.54*m* (1H/1H/2H, C_6H_4N).

N-*Decyl*,N-(*3-methacryloyloxypropyl*)*nicotinamide*. *N*-Decyl,*N*-(3-hydroxypropyl)nicotinamide,6.8 g (21 mmol), 2.3 g (22 mmol) of methacryloylchloride, a few milligrams DBPC, 1.4 g powdered anhydrous Na_2CO_3 and 50 ml anhydrous dichloromethane are stirred at 20°C for 16 h. The resulting slurry is washed with 2 N aqueous NaOH, the organic phase separated, dried over $MgSO_4$ and evaporated. Purification by flash chromatography (Silicagel, eluent: petrolether/acetone 2v/1v). Yield: 6.0 g (73%) slightly yellow oil, $n_D^{24} = 1.4974$.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.85*t* (3H, $-CH_3$), 1.2–1.3*m* (14H, $-(CH_2)_7-$), 1.4–1.7*m* (2H, $CH_2-C-NCO-$), 1.75*s*/1.91*s* (3H, $=C-CH_3$), 2.0–2.2*m* (2H, $-CON-C-CH_2-C-OOC-$), 3.17*t*/3.31*t* (2H, CH_2-NCO), 3.4–3.6*m* (2H, $-CON-CH_2-C-C-OOC$), 3.88*t*/4.21*t* (2H, CH_2-O-), 5.4–5.6*m* (1H, $CH=C-COO$ *trans*), 5.8–6.2*m* (1H, $CH=C-COO$ *cis*), 7.30*m*/7.65*m*/8.60*m* (1H/1H/2H, C_6H_4N).

The complexity of the spectrum is due to the overlay of the amide *cis–trans* conformers.

3-(N-*Decyl*,N-(*3-methacryloyloxypropyl*)*aza-carbonyl*)*pyridinio propane sulphonate* **5**. *N*-decyl,*N*-(3-methacryloyloxypropyl)nicotinamide, 11 g (28.3 mmol), 3.4 g (27.9 mmol) of propanesultone and 1 ml nitrobenzene in 100 ml anhydrous acetonitrile are refluxed for 40 h under nitrogen. Upon cooling, the crude product precipitates and is recrystallized several times from acetonitrile. Yield: 7.2 g (50%) colourless, hygroscopic powder, m.p. 155°C. FD-mass spectrum: peaks at 511, 512 (M^+, $(M+1)^+$).

Elemental analysis ($C_{26}H_{42}N_2O_6S \cdot H_2O$). Calculated: C = 59.07%, H = 8.39%, N = 5.29%, S = 6.07%; found: C = 58.99%, H = 8.24%, N = 5.08%, S = 6.04%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.1–1.35*m* (14H, $-(CH_2)_7-$), 1.50/1.63*m* (2H, $-CH_2-C-NCO-$), 1.84*s*/1.92*m* (3H, $=C-CH_3$), 1.92*m*/2.06*m* (2H, $-N-C-CH_2-C-OOC-$), 2.47*m* (2H, $-N^+-C-CH_2-C-SO_3$), 2.86*t* (2H, $-CH_2-SO_3$), 3.27*t*/3.43*m*/3.57*t* (4H, $-CH_2-N(CH_2-)CO-$), 4.06*t*/4.22*t* (2H, $-CH_2-O-$), 5.04*m* (2H, $-CH_2-N^+$), 5.52/5.57*m* (1H, $CH=C-COO$ *trans*), 5.95/6.09*m* (1H, $CH=C-COO$ *cis*), 8.18*m*/8.30*m*/8.97*s*/9.19*s*/9.35–9.45*m* (1H/1H/0.43H/0.57H/1H, $C_6H_4N^+$).

The complexity of the spectrum is due to the overlay of the amide *cis–trans* conformers (approx. 43% *cis*, 57% *trans*). The signals were assigned by double resonance and NOE experiments.

Decanoic acid-2-(*dimethylamino*)*ethylamide*. Decanoic acid (Fluka), 164 g (0.95 mol), and 82.5 g (0.94 mol) of dimethylaminoethylamine (Fluka) are refluxed in 250 ml benzene for 2 days in a Dean–Stark water trap. After evaporation of the benzene, the crude product is purified by distillation *in vacuo*, b.p. 111–114°C (0.2 mbar). Yield: 216 g (95%) colourless oil, $n_D^{23} = 1.4580$, solidifies on standing, m.p. 30°C.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.2–1.4*m* (12H, $(CH_2)_6-$), 1.57*m* (2H, $CH_2-C-CON-$), 2.13*t* (2H, $-CH_2-CON-$), 2.21*s* (6H, $-N(CH_3)_2$), 2.37*t* (2H, $-CH_2-N$), 3.38*m* (2H, $-CON-CH_2-$).

1-N,N-*Dimethylamino-3-aza-tridecane*. $LiAlH_4$, 25 g (0.66 mol), is suspended in 200 ml dry THF. While cooling, 189 g (0.78 mol) of decanoic acid-2-(dimethylamino)ethylamide in 800 ml THF are added dropwise. When the addition is completed, the mixture is stirred for 1 h at 20°C. Then, 15 g ethyl acetate is added. The mixture is decomposed with 49 ml water while cooling and stirring, and allowed to settle overnight. The precipitate is removed by filtration, extracted twice with 300 ml boiling dry THF, and filtered again. The combined filtrates are evaporated, and the residue distilled *in vacuo* over a 30 cm Vigreux column. Sixty-five grams of starting material are recovered, b.p. 111–114°C (0.2 mbar), in addition to the product. Yield: 77.5 g (44%) colourless oil, $n_D^{23} = 1.4446$.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.45*m* (2H, $CH_2-C-CN-$), 2.18*s* (6H, $-N(CH_3)$), 2.37*t* (2H, $-CH_2-N$), 2.5–2.7*m* (4H, $-N-CH_2-CH_2-N$).

N-*Decyl*,N-(*2-dimethylaminoethyl*)*acrylamide*. 1-*N*,*N*-Dimethylamino-3-aza-tridecane, 23 g (0.10 mol), are added to a solution of 6 g (0.15 mol) NaOH in 200 ml of water. Into this suspension, 10.7 ml acryloylchloride are dropped slowly, resulting in a clear, foaming reaction mixture. After addition of 4 g NaOH in 20 ml of water, the resulting suspension is extracted with chloroform. The organic phase is washed with 2 N aqueous NaOH, dried over $MgSO_4$, filtered over a short column of basic Al_2O_3, and the solvent evaporated after addition of a few milligrams of DBPC. The residue is purified by flash chromatography (Silicagel, eluent isopropanol/ concentrated ammonia 99.5v/0.5v). Yield: 5.7 g (31%) colourless oil, $n_D^{28} = 1.4686$.

^{1}H n.m.r. (400 MHz, $CDCl_3$): 0.85*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.55*m* (2H, $CH_2-C-CON-$), 2.23*s* (6H, $-N(CH_3)_2$), 2.46*t* (2H, $-CH_2-N-$), 3.25–3.55*m* (4H, $-CH_2-NCO-CH_2-$), 5.65*m* (1H, CH=C–CON– *trans*), 6.33*m* (1H, CH=C–CON– *cis*), 6.4–6.6*m* (1H, =CH–CON–).

*3-(*N,N-*Dimethyl*-N-*3'-(*N'-*acryloyl)aza-tridecyl)-ammonio propane sulphonate* **6**. *N*-Decyl,*N*-(2-dimethyl-amino)ethylacrylamide, 5.6 g (29 mmol), 2.4 g (20 mmol) of propanesultone and 1 ml nitrobenzene in 50 ml dry acetonitrile are refluxed for 3 days under nitrogen. Upon cooling, the crude product precipitates, is recrystallized several times from acetonitrile. Yield: 5.6 g (70%) colourless, hygroscopic powder, m.p. 159°C. FD-mass spectrum: peak at 405 (M^+).

Elemental analysis ($C_{20}H_4ON_2O_4S \cdot H_2O$). Calculated: C = 56.84%, H = 10.02%, N = 6.63%, S = 7.59%; found: C = 57.76%, H = 10.47%, N = 6.53%, S = 7.75%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 0.86*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.56*m* (2H, $CH_2-C-CON-$), 2.25*m* (2H, $-N^+-C-CH_2-C-SO_3$), 2.88*t* (2H, $-CH_2-SO_3$), 3.24*s* (6H, $-N^+(CH_3)_2-$), 3.44*t* (2H, $-CH_2-NCO$), 3.56*m* (2H, $-CO-N-CH_2-C-N^+$), 3.7–3.9*m* (4H, $-CH_2-N^+-CH_2-$), 5.72*m* (1H, CH=C–CON– *trans*), 6.30*m* (1H, CH=C–CON *cis*), 6.4–6.6*m* (1H, =CH–CON–).

N-*Decyl*,N-*methyl-2-aminoethanol*. *N*-Methylaminoethanol (Fluka), 70 g (0.93 mol), and 82 g (0.37 mol) of 1-bromo-decane (Fluka) are stirred at 100°C under nitrogen for 20 h. After cooling, the viscous mixture is mixed with 150 ml 10% aqueous NaOH, the organic phase separated, diluted with 300 ml ether and washed several times with 2 N NaOH. The organic phase is dried over $MgSO_4$, evaporated and fractionated *in vacuo*. Yield: 56.8 g (71%) colourless liquid, $n_D^{23} = 1.4501$.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.84*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.41*m* (2H, CH_2-C-N-), 2.20*s* (3H, $-N-CH_3$), 2.35*t* (2H, $-CH_2-N$), 2.47*t* (2H, $N-CH_2-C-O$), 3.54*t* (2H, CH_2-O-).

N-*Decyl*,N-*methyl-2-aminoethylacrylate and* N-*decyl*,N-*methyl-2-aminoethylmethacrylate*. The acrylate and methacrylate are prepared from the acid chlorides and *N*-decyl,*N*-methyl-2-aminoethanol in analogy to the preparation of 11-*N*,*N*-dimethylaminoundecylacrylate above in 90% yields. Both are colourless liquids, $n_D^{25} = 1.4501$ (acrylate) and $n_D^{20} = 1.4527$ (methacrylate).

*3-(*N-*decyl*,N-*(2-acryloyloxyethyl)*,N-*methyl)-ammonio propane sulphonate* **7**. **7** is prepared from *N*-decyl,*N*-methyl-2-aminoethylacrylate and propanesultone in analogy to the acrylate **1**, as described above, in 50% yield. Colourless, hygroscopic powder, m.p. 71/150°C (two crystal modifications). Fast atom bombardment mass spectrum: peak at 391 (M^+).

Elemental analysis ($C_{19}H_{37}NO_5S$). Calculated: C = 58.27%, H = 9.52%, N = 3.58%, S = 8.19%; found: C = 58.36%, H = 9.53%, N = 3.46%, S = 8.51%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 0.83*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.69*m* (2H, CH_2-C-N^+-), 2.21*m* (2H, $-N^+-C-CH_2-C-SO_3$), 2.84*t* (2H, $-CH_2-SO_3$), 3.20*s* (3H, $-N^+-CH_3$), 3.28*m* (2H, $-CH_2-N^+$), 3.65–3.95*m* (4H, $O-C-CH_2-N^+-CH_2-C-C-SO_3$), 4.65*t* (2H, $-CH_2-OOC-$), 5.88*m* (1H, CH=C–COO *trans*), 6.08*m* (1H, =CH–COO), 6.39*m* (1H, CH=C–COO *cis*).

*3-(*N-*Decyl*,N-*(2-methacryloyloxyethyl)*,N-*methyl)-ammonio propane sulphonate* **8**. **8** is prepared from *N*-decyl,*N*-methyl-2-aminoethylmethacrylate and propanesultone in analogy to the acrylate **1**, as described above, in 62% yield. Colourless, hygroscopic powder, m.p. 137°C.

Elemental analysis ($C_{20}H_{39}NO_5S$). Calculated: C = 56.71%, H = 9.76%, N = 3.31%, S = 7.57%; found: C = 57.40%, H = 9.61%, N = 3.27%, S = 7.83%.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.83*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $-(CH_2)_7-$), 1.68*m* (2H, CH_2-C-N^+-), 1.86*s* (3H, $=C-CH_3$), 2.20*m* (2H, $N^+-C-CH_2-C-SO_3$), 2.82*t* (2H, $-CH_2-SO_3$), 3.19*s* (3H, $-N^+-CH_3$), 3.36*m* (2H, $-CH_2-N^+$), 3.65–3.90*m* (4H, $O-C-CH_2-N^+-CH_2-C-C-SO_3$), 4.60*t* (2H, $-CH_2-OOC-$), 5.58*m* (1H, CH=C–COO *trans*), 6.03*m* (1H, CH=C–COO *cis*).

N-*(2-Methylamino)ethyl*,N-*methyldecylamine*. 1-Bromodecane (Fluka), 24.3 g (0.11 mol), and 22.3 g (0.25 mol) *N*,*N'*-dimethylethylenediamine (Fluka) are stirred for 36 h at 100°C under nitrogen. To the cooled two-phase mixture, 109 ml 2 N aqueous NaOH are added, and the resulting mixture is extracted three times with diethylether. The combined ether phases are washed twice with 2 N NaOH, dried over $MgSO_4$, evaporated and fractionated *in vacuo*. Yield: 13.6 g (55%) clear liquid, $n_D^{25} = 1.4444$.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 0.85*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $(CH_2)_7-$), 1.42*m* (2H, CH_2-C-N-), 2.17*s* (3H, $C-N(CH_3)-C-$), 2.28*t* (2H, $-CH_2-N$), 2.35–2.5*m* (5H, $C-N-CH_2-C-N, -N-CH_3$), 2.63*t* (2H, $-C-N-C-CH_2-N-$).

N-*(*N-*Methyl-2-aminoethyl)*,N-*methyldecyl acrylamide*. *N*-(2-Methylamino)ethyl,*N*-methyldecylamine, 12.7 g (55.6 mmol), is dissolved in 80 ml diethylether, and placed above 8 g NaOH in 50 ml water. Acryloylchloride, 9.2 g (0.11 mol) (Merck, stabilized with 0.1% CuCl) in 25 ml anhydrous ether are added slowly, while stirring and cooling, and the mixture is stirred for 12 h at 20°C. The organic phase is separated, washed with 2 N NaOH, dried over $MgSO_4$, and evaporated. Purification is by flash chromatography (Silicagel, eluent: chloroform/methanol 20v/1v). Yield: 11.2 g (76%) colourless oil, $n_D^{24} = 1.4691$.

^{1}H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 0.85*t* (3H, $-CH_3$), 1.2–1.3*m* (14H, $-(CH_2)_7-$), 1.40*m* (2H, CH_2-C-N-), 2.22*m* (3H, $C-N(CH_3)-C$), 2.31*m* (2H, $-CH_2-N$), 2.5*m* (2H, $C-N-CH_2-C-N$, $-N-CH_3$), 2.98/3.08*s* (3H, $N(CH_3)-CO-$), 2.63*t* (2H, $-C-N-C-CH_2-N-$), 3.35–3.6*m* (2H, $-CH_2-NCO$), 5.6–5.7*m* (1H, CH=C–CON– *trans*), 6.2–6.4*m* (1H, CH=C–CON– *cis*), 6.45–6.65*m* (1H, =CH–CON–).

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

*3-(*N-*Decyl*,N-*methyl*,N-*(2-(*N-*methyl)acrylamido-ethyl)ammonio propane sulphonate* **9**. Monomer **9** is prepared from *N*-(*N*-methyl-2-aminoethyl),*N*-methyl-decyl acrylamide and propanesultone in analogy to the acrylate **1**, in 71% yield. Colourless hygroscopic crystals, m.p. 138°C.

Elemental analysis ($C_{20}H_{40}N_2O_4S$). Calculated: C = 59.37%, H = 9.96%, N = 6.92%, S = 7.92%; found: C = 59.29%, H = 9.87%, N = 7.04%, S = 8.13%.

^{1}H n.m.r. (400 MHz, $CDCl_3$): δ (in ppm) = 0.85*t* (3H, $-CH_3$), 1.2–1.35*m* (14H, $(CH_2)_7-$), 1.73*m* (2H, CH_2-C-N^+-), 2.22*m* (2H, $N^+-C-CH_2-C-SO_3$), 2.88*t* (2H,

$-CH_2-SO_3$), 3.15*s* (3H, $-N^+-CH_3$), 3.2–3.3*m* (5H, $-CH_2N^+$, $-N(CH_3)-CO$), 3.5–3.8*m* (4H, $-CON-CH_2)-C-N^+-C-C-SO_3$), 3.87*m* (2H, $-CON-C-CH_2-N^+-$), 5.72*m* (1H, CH=C–CON *trans*), 6.28*m* (1H, CH=C–CON– *cis*), 6.55*m* (1H, =CH–CON–).

3-(N-(*2-Methacryloylethyl*)-N,N-*dimethyl*)*ammonio propane sulphonate **10***. A gift from Raschig, this was repeatedly recrystallized from ethanol prior to use.

11-Bromoundecylmethacrylate. Methacryloylchloride, 23 g (0.22 mol), is dropped into a cooled mixture of 50.2 g (0.2 mol) of 11-bromoundecanol and 20 g of (0.2 mol) dry triethylamine in 400 ml ether. The mixture is stirred for 12 h at room temperature, the precipitate is separated by filtration, and the filtrate passed over neutral Al_2O_3, until thin layer chromatography (t.l.c.) shows the complete removal of unreacted alcohol. The solvent is removed *in vacuo*. Yield: 28.6 g (45%) colourless liquid, $n_D^{21} = 1.4736$.

^1H n.m.r. (200 MHz, $CDCl_3$): δ (in ppm) = 1.2–1.4*m* (14H, $-(CH_2)_7-$), 1.6–1.8 (4H, $-CH_2-C-O-$, $-CH_2-C-Br-$), 1.95*s* (3H, $=C-CH_3$), 3.45*t* (2H, $-CH_2-Br$), 5.55*s* (1H, CH=C–COO *trans*), 6.10*s* (1H, CH=C–COO *cis*).

N-(*2-Hydroxyethyl*),N-(*11-methacryloylundecyl*),N,N-*dimethyl ammonium bromide **11***. 11-Bromoundecylmethacrylate, 28.0 g (88 mmol), 7.8 g (88 mmol) and 60 mg di-*t*-butyl-*p*-cresol are refluxed in 70 ml dry acetone under nitrogen for 3 days. On cooling, the crude product precipitates. Recrystallization is from acetone. Yield: 27.0 g (75%) colourless crystals, m.p. 123°C.

Elemental analysis ($C_{19}H_{38}NO_3Br$). Calculated: C = 55.88%, H = 9.38%, N = 3.43%, Br = 19.56%; found: C = 56.34%, H = 9.55%, N = 3.39%, Br = 18.44%.

^1H n.m.r. (400 MHz, D_2O): δ (in ppm) = 1.2–1.4*m* (14H, $-(CH_2)_7-$), 1.6–1.75 (4H, $-CH_2-C-O-$, $-CH_2-C-N^+-$), 1.90*s* (3H, $=C-CH_3$), 3.15*s* (6H, $-N^+(CH_3)_2-$), 3.35*m* (2H, $-CH_2-N^+$), 3.50*m* (2H, N^+-CH_2-C-O-), 4.00*m* (2H, $-CH_2-O-$), 4.15*t* (2H, $-CH_2-OOC-$), 5.65*m* (1H, CH=C–COO *trans*), 6.10*m* (1H, CH=C–COO *cis*).

N-*Decyl*,N-(*2-methacryloyloxyethyl*),N,N-*dimethyl ammonium bromide **12***. This was prepared according to the literature[7,8].

N-(*2-Methacryloyloxyethyl*)*trimethyl ammonium bromide **13***. This was a gift[18].

Polymerization of monomers

Polymers were obtained from monomers by free radical polymerization. Polymerizations were performed in ethanolic solution as well as in aqueous, micellar solution. Monomer solutions of ~2–5% by weight in ethanol or of ~0.5–2% in water respectively were purged with nitrogen for 30 min, sealed and reacted for 12–18 h at 60°C, using 1–2 mol% azobis(isobutyronitrile) (AIBN) as initiator.

Polymer purification

The polymers produced were worked up depending on their solubilities.

In aqueous reaction mixtures, the mixture was cooled until the polymer precipitated and could be collected. Water-soluble polymers were repeatedly redissolved in hot water and precipitated by cooling and subsequently lyophilized. Water-insoluble samples were extracted and washed several times with hot water and lyophilized. The dry polymers were dissolved in ethanol if possible, otherwise they were dissolved in formamide and precipitated into acetone. The precipitates were extracted and washed thoroughly with water and lyophilized again.

In ethanolic reaction mixtures, ethanol-soluble polymers were precipitated into acetone after removal of most of the solvent. The precipitates were extracted and washed thoroughly with water and lyophilized. Ethanol-insoluble but water-soluble samples were repeatedly extracted with ethanol, dissolved in hot water and precipitated into acetone. After repeated dissolution in hot water and precipitation by cooling, the purified polymers were lyophilized. In the case of polymers insoluble in both ethanol and water, the samples were extracted several times with hot water, then dissolved in formamide and precipitated into acetone. The precipitates were extracted and washed thoroughly with water and lyophilized.

The purified polymers were free of residual monomer according to *FT*i.r., ^1H n.m.r. and t.l.c. This result was confirmed by aqueous gel permeation chromatography (g.p.c.) for poly(**1**), poly(**2**), poly(**10**), poly(**11**) and poly(**13**). The absolute values of molecular weight obtained by g.p.c. have to be taken with great care, as the g.p.c. calibration by poly(sodium methacrylate) is not necessarily valid for the polymers studied. The calculated average molecular weights of the polymers range from 10^4 to 5×10^6 depending on the polymerization conditions.

Methods

N.m.r. spectra were recorded with an Aspect 3000 400 MHz spectrometer (Bruker). Thermogravimetry was performed on a thermogravimetric analyser type TGS-2 (Perkin Elmer). The samples were heated under nitrogen, with a heating rate of 10°C min^{-1}. Differential scanning calorimetry (d.s.c.) was performed with a Perkin Elmer DSC2. Heating rates of 5°C min^{-1} to 40°C min^{-1} were applied. X-ray scattering experiments were done with a diffractometer Kristalloflex (Siemens), using the Ni-filtered Cu–Kα-line ($\lambda = 0.1541$ nm).

RESULTS AND DISCUSSION

Solubility of monomers

The monomers are easily soluble in warm water, formamide, methanol, ethanol and isopropanol, and moderately soluble in chloroform, dimethyl formamide (DMF) and acetonitrile. Aqueous solutions exhibit micellar properties[19]. Comparing 400 MHz ^1H n.m.r. spectra of the monomers in CD_3OD and in $CDCl_3$, the proton signals in the polar region of the surfactants, but not in the non-polar regions, are notably broadened in $CDCl_3$, suggesting the formation of aggregates, such as reverse micelles.

Solubility of polymers

The solubilities of the polymers in some standard solvents are shown in *Table 2*. They do not depend on the preparation method, i.e. solubilities are the same for polymers prepared in isotropic solution and in micellar solution. Although the solubilities show distinct differences depending on the molecular structure, there are some noteworthy common features. Whereas the

Table 2 Solubility of the polymers in selected solvents. + = Soluble; − = not soluble

	Solvent						
Polymer	$CHCl_3$	C_2H_5OH	CH_3OH	$HCONH_2$	H_2O (20°C)	H_2O (40°C)	H_2O 2% NaCl
Poly(**1**)	−	−	−	+	−	+	+
Poly(**2**)	−	−	−	+	−	+	+
Poly(**3**)	−	−	−	+	−	−	−
Poly(**4**)	−	−	−	+	−	−	−
Poly(**5**)	−	−	−	+	−	−	−
Poly(**6**)	−	+	+	+	−	−	−
Poly(**7**)	−	+	−	−	−	−	−
Poly(**8**)	−	+	−	−	−	−	−
Poly(**9**)	−	+	−	−	−	−	−
Poly(**10**)	−	−	−	+	−	−	+
Poly(**11**)	−	+	+	+	+	+	+
Poly(**12**)	+	+	+	−	−	−	−
Poly(**13**)	−	+	+	+	+	+	+

monomers and the polycations are soluble in polar, aprotic solvents such as chloroform or DMF, all the zwitterionic polymers require protic solvents independent of their molecular structure and the solvent polarity needed for a given sample. Furthermore, the zwitterionic polymers show limited solubility compared to their cationic analogues. The zwitterionic poly(**2**), poly(**8**) and poly(**10**) are soluble in a smaller choice of solvents than the cationic poly(**11**), poly(**12**) and poly(**13**). In particular, the zwitterionic poly(**2**) and poly(**10**) require elevated temperatures for dissolution in water, in contrast to their cationic analogues poly(**11**) and poly(**13**). Characteristically, the solubility of the zwitterionic polymers in water is improved by adding salt. These observations are in agreement with reports on simple polybetaines[17,20,21]. This is not surprising as the repulsion of the cationic groups should favour dissolution of the polymers, compared to the attractive forces between the zwitterionic groups which have to be overcome by strong solvent–polymer interactions.

Studying the solubility in more detail, three major groups of polymerized zwitterionic surfactants are distinguished. The first group, represented by poly(**1**) and poly(**2**), is soluble in formamide and aqueous systems. The second one, represented by poly(**3**)–(**5**) dissolves only in formamide. The third group, consisting of poly(**7**)–(**9**) is soluble in chloroform/methanol mixtures and ethanol.

The solubility groups found can be correlated with the molecular structures shown in *Figure 1*. Polymers with the ammonio propane sulphonate moiety close to the polymer backbone, i.e. the head attached type dissolve in chloroform/methanol mixtures with high chloroform content and ethanol, whereas polymers with the ammonio propane sulphonate moiety away from the polymer backbone, i.e. the tail end attached type, dissolve in formamide and aqueous systems only. The polycations studied fit well into these classes: the head attached poly(**12**) requires less polar solvents than the tail end attached analogue poly(**11**) which is water-soluble. The fact that in vinyl polymers only polymers of the tail end attached type are water-soluble, agrees well with previous reports on non-ionic and ionic polymeric surfactants[4–8,15]. Obviously, the solubility characteristic is mainly controlled by the 'skin' of the polymers exposed to the solvent. Thus ionic/zwitterionic skins require polar solvents, and hydrocarbon skins require less polar solvents. In agreement with this classification poly(**5**), which represents the mid-tail attached type, exhibits an intermediate solubility behaviour. This polymer is soluble in polar chloroform/methanol mixtures, ethanol, methanol and formamide, but insoluble in water and rather non-polar chloroform/methanol mixtures such as 20v/1v.

The 'skin controlled' solubility can be visualized in the ^1H n.m.r. spectra as well. Whereas all proton signals of the monomers are well resolved (*Figures 2a* and *3a*), the proton signals of the polymer spectra are markedly broadened, such that the closer the protons are located to the polymer backbone, the broader are the signals. Only the protons located at the skin of the polymers exhibit structured signals and yield correct signal intensity by integration (*Figures 2b* and *3b*). This effect is most pronounced in the spectra of poly(**2**).

This simple geometrical model will be helpful in the prediction of solubility of new surfactant polymers despite its obvious limitations, e.g. strict skin control of the solubility fails to explain the need of protic cosolvents for the head attached polymers.

The group of polymers which are only soluble in formamide consists of the polymerized pyridinio propane sulphonates of the head attached type and of the mid-tail attached type. The restricted solubility compared to the ammonio propane sulphonate analogues may be attributed to additional strong interactions of the aromatic rings, as concluded for the surfactant monomers from their high Krafft temperatures[19].

Comparing the solubility data of the polymerized surfactants in *Table 2*, an explanation is required for the fact that poly(**2**) is more readily water-soluble than the model polymer poly(**10**). Both are polymethacrylates and have the same structure except for the longer hydrocarbon chain of poly(**2**). Hence the more hydrophobic polymer is more water-soluble. This behaviour is apparently contradictory to the general perception of water solubility. Most likely, the unexpected solubility behaviour is caused by the different bulk polymer structures. In contrast to the non-crystalline superstructure found for poly(**2**), X-ray

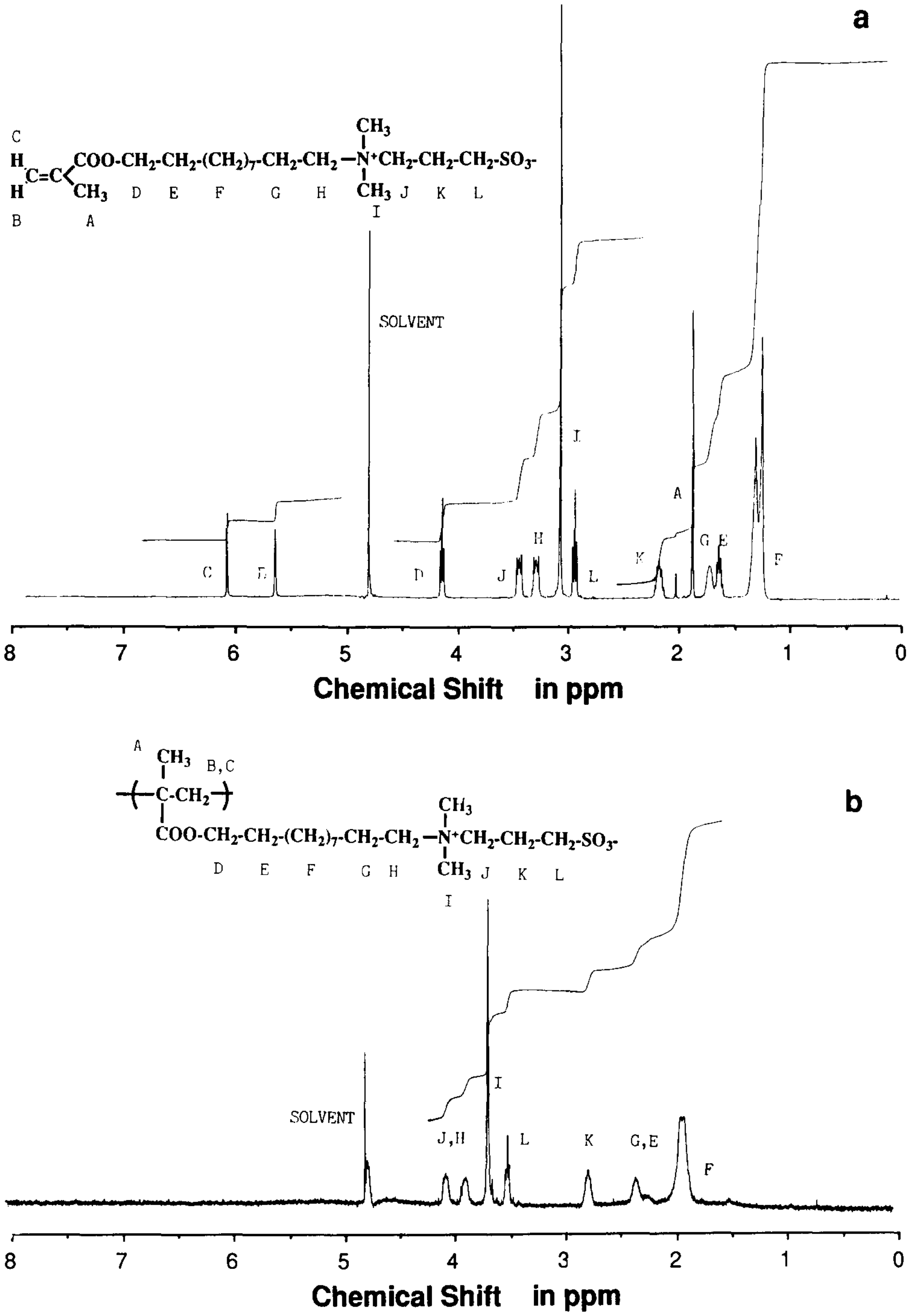


Figure 2 ^1H N.m.r. spectra of tail and attached surfactant polymers in D_2O, chemical shift calibrated as water signal at $\delta = 4.80$ ppm. (a) Monomer **2** at room temperature, above critical micelle concentration, 4 g l^{-1}; (b) poly(**2**) at 75°C

scattering reveals the high crystallinity of poly(**10**) (see *Figure 4A* and *B*), easily accounting for the reduced solubility.

Thermal properties

The polymers prepared are colourless, hygroscopic solids. When stored in air, the polymers take up approximately 5% by weight water, which is equivalent to one molecule of water per repeat unit. The bound water is reversibly removed by prolonged exposure to vacuum, or heating to 100–120°C.

Thermogravimetry under nitrogen shows that thermal decomposition of the polymers starts at 180–200°C. There is no indication for premature decomposition of the polymers due to the quaternary ammonium groups. No difference is observed between polymers prepared in isotropic and in micellar media. The thermal stability of the polyzwitterions hence corresponds to that of standard polyacrylates and polymethacrylates.

In the temperature range between –70°C to 180°C, no thermal transition could be detected by d.s.c. for dry polymers, in agreement with previous studies on polyzwitterions[22]. Obviously, the ionic groups of the polymers either shift the glass transition above the decomposition temperature or they give rise to such a substantial broadening of the transition that it cannot

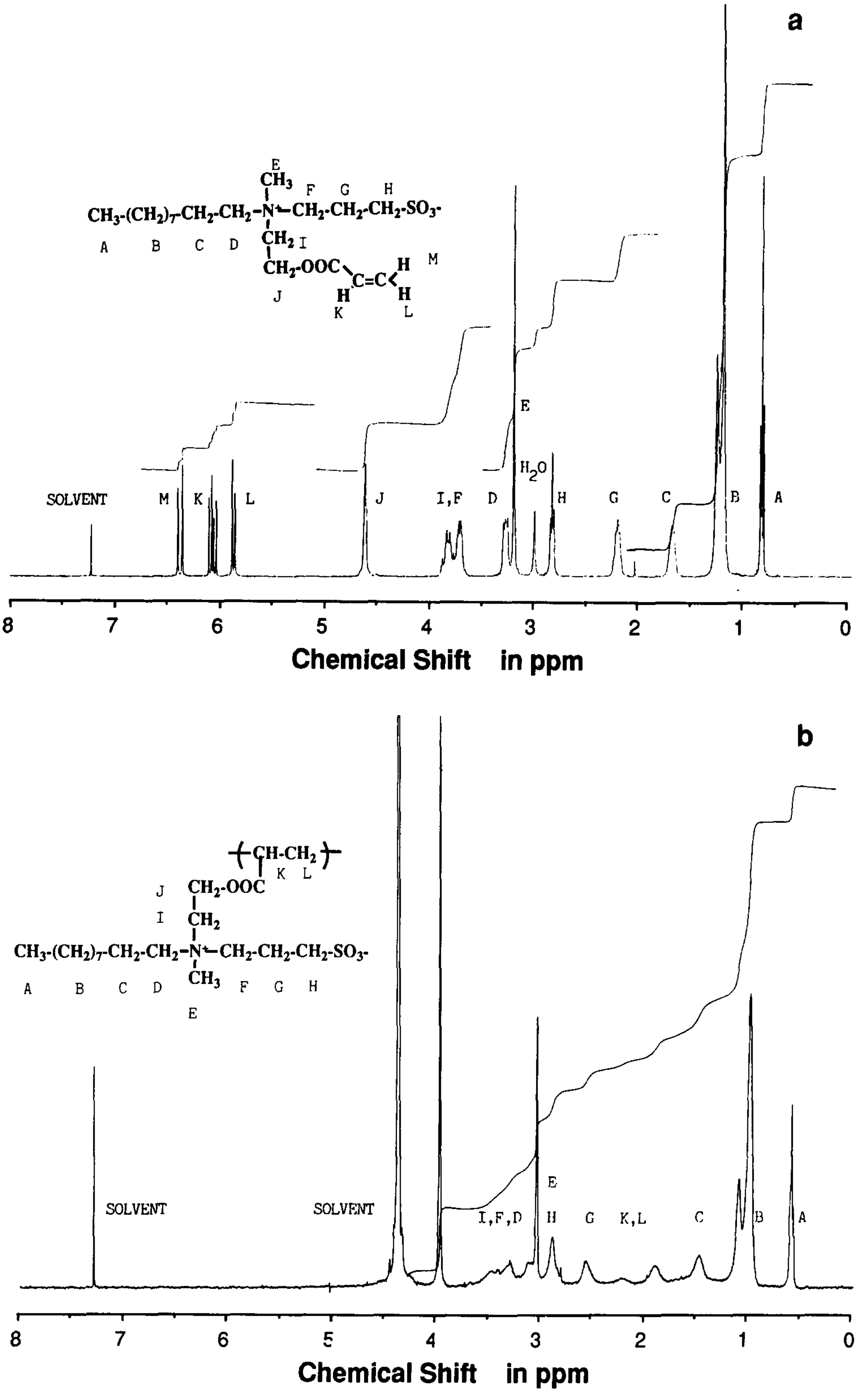


Figure 3 ^{1}H N.m.r. spectra of head attached polymers, chemical shift calibrated as $CHCl_3$ signal at $\delta = 7.26$ ppm. (a) Monomer 7 in $CDCl_3$ at room temperature; (b) poly(7) in $CD_3OH/CDCl_3$ (1v:1v) at room temperature

be detected. Samples stored at ambient atmosphere show an endothermic peak in the d.s.c. trace between 80°C and 120°C, but exclusively in the first heating run. This peak is observed for all polymers independent of their molecular structure. In subsequent runs, the d.s.c. traces correspond to that of extensively dried samples. As the observation of the peak is accompanied by a weight loss of ~5%, this peak is attributed to the loss of bound water. In support of this theory, the peak reappears after extended storage of the d.s.c. samples (several days to weeks in the original sample pans) in ambient atmosphere, when they regain the original weight, but not after storage in dry air.

X-ray scattering investigations

The polymers were characterized by X-ray powder

Table 3 X-ray powder diffraction data of the polymers

		Bragg peak		Halo	
Polymer	Pattern type	Angle, 2θ	Distance (Å)	Angle, 2θ	Distance (Å)
Poly(**1**)	1	2.7/5.3	33/17	19.6	4.5
Poly(**2**)	1	2.7/5.5	33/16	19.6	4.5
Poly(**3**)	2	2.4/4.8/(7.1)	37/18/(12)	19.2	4.6
Poly(**4**)	2	2.2/4.4/(6.5)	40/20/(14)	20.0	4.4
Poly(**5**)	3	3.2	27	19.5	4.5
Poly(**6**)	3	3.0	29	19.8	4.5
Poly(**7**)	3	3.3	27	19.7	4.5
Poly(**8**)	3	3.4	26	19.4	4.5
Poly(**9**)	3	3.4	26	19.5	4.5
Poly(**11**)	1	2.9/5.5	30/16	19.5	4.5
Poly(**12**)	3	3.3	27	19.8	4.5

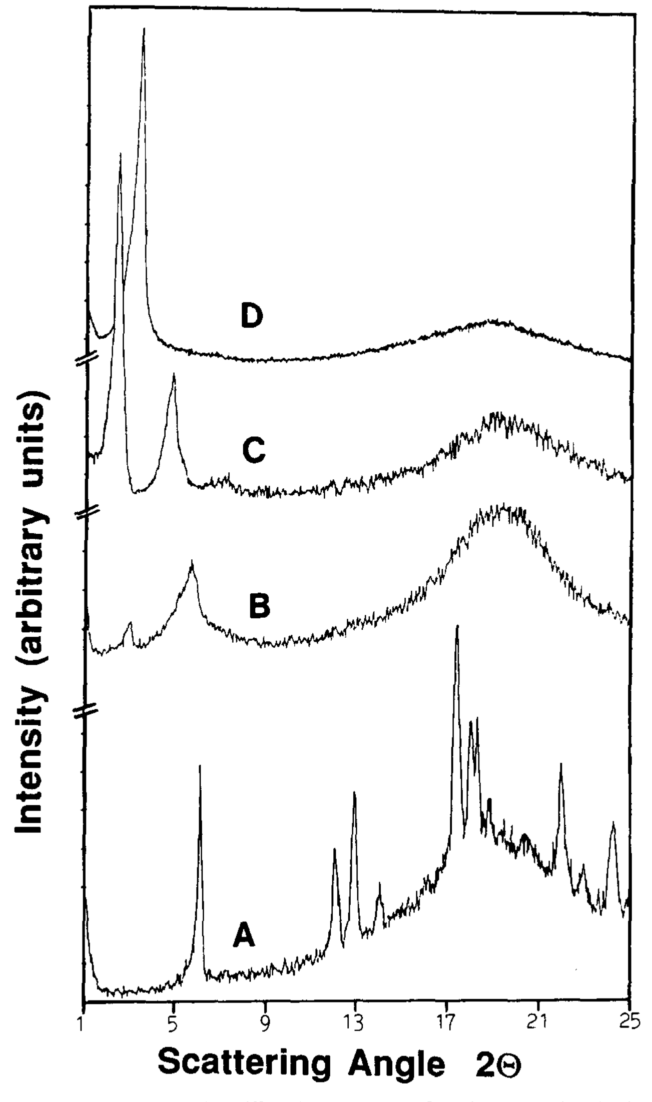


Figure 4 X-ray powder diffraction patterns of analogous zwitterionic polymethacrylates at 300 K. A, Poly(**10**); B, poly(**2**); C, poly(**3**); D, poly(**8**)

diffractograms at 300 K (*Table 3*). Characteristic diffraction patterns are displayed in *Figure 4*. Whereas the model polymer poly(**10**) is crystalline according to its diffractogram (*Figure 4A*), the zwitterionic polysoaps are amorphous exhibiting a broad halo between 17–22°C where the maximum corresponds to a distance of 0.45 nm. Additionally, all polysoaps show small angle reflections indicative of a superstructure (*Figure 4B–D*). The small angle reflections correspond to distances of 2.5–4 nm (*Table 3*). As noted for other properties, the X-ray diffraction patterns observed are characteristic for a given polymer species but do not depend on the polymerization method chosen.

Three types of diffraction patterns are observed. Pattern 1 (*Figure 4B*) is characterized by two diffraction peaks at small angles with low intensity compared to the halo. The peak at the smaller angle is much narrower but less intense than the second one, thus preventing definitive assignments as first order and second order reflections, despite the apparent linear correlation of the distances. Pattern 2 (*Figure 4C*) is characterized by several diffraction peaks at small angles with high intensity compared to the halo. The peaks show analogous shape and decreasing intensity with increasing scattering angle. The distances calculated from the scattering angles are correlated by the factor $1/n$ with $n = 1, 2, 3$. Thus, they are assigned as first order and second order reflections etc. of a lamellar structure. Pattern 3 (*Figure 4D*) is characterized by only one diffraction peak at small angle, but with high intensity compared to the halo. The single reflection found does not allow an assignment of the morphology of the superstructure.

Type 1 patterns are observed for poly(**1**), poly(**2**) and poly(**11**), i.e. the polymers where the surfactant side chain is attached to the backbone via the tail end (*Figure 1*). Type 2, the diffraction pattern of the most ordered superstructures, are observed for the pyridinio propane sulphonates poly(**3**) and poly(**4**), where the surfactant side chain is attached to the backbone via the tail end as well. This result accords well with their strongly reduced solubility (*Table 2*) and the assumption of strong interaction between the aromatic head groups[19]. Patterns of type 3 are observed for poly(**5**)–poly(**9**) and poly(**12**). In these polymers, the surfactant side chain is attached to the backbone via the head group or via the middle of the hydrophobic tail, i.e. the ionic groups are close to the backbone (*Figure 1*). Characteristically, the small angle reflections for these polymers are found at nearly the same scattering angles, which are substantially larger than the ones found for the tail end attached isomers, i.e. the repeat distances are smaller.

Clearly the X-ray patterns observed depend on the polymer architecture (*Figure 1*, *Table 3*). The characteristic differences between the diffraction patterns of tail end attached polysoaps and head attached polysoaps are evident. It is noteworthy that the patterns are independent of the detailed nature of the ionic head groups: cationic and zwitterionic analogues behave in the same way. The distances of 2.5–4 nm calculated from the small angle reflections are approximately twice the length of the hydrophobic chains, thus pointing to a bilayer superstructure. Such structures with microphase separated ionic and hydrophobic regions can easily be imagined and could resemble the well known smectic phases of classical soaps[23].

CONCLUSIONS

A series of zwitterionic surfactant vinyl monomers were synthesized and polymerized under isotropic and micellar conditions. Characteristically, many of the resulting polymers are water-insoluble. As demonstrated most instructively by the comparison of isomers, the solubility of the polymers is controlled by their molecular geometry, such that the groups at the 'skin' of the macromolecules determine the solvent required. Thus only polymers where the surfactant structure is attached via the hydrophobic tail are water-soluble, in agreement with previous studies. Not only the balance of hydrophilic and hydrophobic units but in particular the geometry decides whether polymers represent polyions or rather ionomers, with high ion contents.In bulk, no thermal transition could be observed for the polymers below their decomposition temperatures of ~190°C, independent of the preparation method. X-ray studies show that all surfactant polymers are amorphous but form superstructures. The superstructures obtained are correlated to the molecular geometry too and occurred independently of the polymerization conditions chosen. Typically, the more ordered the superstructure, the less soluble are the polymers.

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