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Hydrophobically Modified Zwitterionic Polymers: Synthesis, Bulk Properties, and Miscibility with Inorganic Salts

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ABSTRACT: A series of new poly(sulfobetaines) has been synthesized and characterized in bulk. Appropriate substitution enables the preparation of polymers with high ion contents and still accessible glass transitions. The hydrophobic alkyl chains incorporated induce microphase separation, resulting in superstructures whose detailed forms depend on the polymer geomergy. All polymers are miscible in bulk with selected salts such as NaI in stoichiometric amounts, or even beyond. However, miscibility with inorganic salts in large amounts is not a general feature but depends both on the salt chosen and on the polymer structure. Some rules for successful mixing are established. The organic polymer–inorganic salt blends exhibit modified superstructures and glass transitions.

Introduction

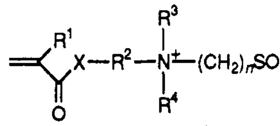
Stable zwitterionic polymers represent highly dipolar materials with a wide spectrum of unique and specific properties.[1] Although known since the late 1950s, such polymers have only recently attracted more attention, particularly due to their "antipolyelectrolyte" behavior in solution.[1-6] Solid-state studies have been rather scarce,[7-14] which is partially due to limited structural variations so far. The majority of the systems are based on the quaternization of vinylpyridine, vinylimidazole, and (meth)-acrylic esters or amides of small amines.[1,2] They are amorphous materials with high glass transition temperatures which are attributed to the high amounts of ionic groups present. One of the most interesting observations was the formation of homogeneous blends of zwitterionic polymers with some inorganic salts in equimolar amounts.[7-10,15-17]

In the search for new micellar polymers, a new type of polyzwitterions has been developed recently in form of hydrophobically modified poly(ammoniopropanesulfonate)s.[18] Besides their specific properties in aqueous solution, these amphiphilic polymers exhibited interesting solid-state properties in initial studies, such as the presence of microphase-separated, supramolecular structures[11,12] and miscibility with some inorganic salts.[16] On the basis of the previous work, we have extended the structural variations of such hydrophobically modified polyzwitterions to elucidate the effect of the molecular structure on basic solid-state properties and on the phenomenon of miscibility with inorganic salts in bulk.

Aliphatic poly(ammonioalkanesulfoante)s were chosen by virtue of the good chemical and thermal stability of the zwitterionic sulfobetaine moieties, of the full dissociation of both ionic groups under ambient conditions, and of their acceptable solubility in some standard solvents.[1,11,19] Furthermore, their synthesis via the ring-opening quaternization by sultones enables the preparation of monomers—and finally of polymers—free of salt impurities which are tenaciously held and which are difficult to remove completely.

The investigated compounds are listed in Tables 1–3. They are mainly derived from esters and amides of acrylic and methacrylic acids, by variations of the spacer group R^2 separating the polymer backbone and ammonium moiety, of the alkyl substituents R^3 and R^4 of the ammonium moiety, and of the number of methylene groups *n* separating the cationic ammonium moiety from the anionic sulfonate group. Polymers of **17–19** address the problems of rigidification and local concentration of the betaine moieties, whereas polymers of **21–26** address the problems of steric crowding of the polymer backbone. Polymers of **25–31** enable studies on the influence of the polymer geometry.

Table 1. Acrylic and Methacrylic Monomers of "Tail-End" Geometry and Monomers without Hydrophobic Substituents Used



monomer	X	R^1	R^2	R^3	R^4	*n*
1	NCH_3	H	$(CH_2)_{11}$	CH_3	CH_3	3
2	NCH_3	H	$(CH_2)_{11}$	C_2H_5	C_2H_5	3
3	NCH_3	CH_3	$(CH_2)_{11}$	CH_3	CH_3	3
4	O	H	$(CH_2)_{11}$	CH_3	CH_3	3
5	O	H	$(CH_2)_{11}$	CH_3	CH_3	4
6	O	H	$(CH_2)_{11}$	CH_3	n-C_4H_9	3
7	O	H	$(CH_2)_{11}$	CH_3	n-C_4H_9	4
8	O	H	$(CH_2)_{11}$	C_2H_5	C_2H_5	3
9	O	CH_3	$(CH_2)_6$	CH_3	CH_3	3
10	O	CH_3	$(CH_2)_{11}$	CH_3	CH_3	3
11	O	CH_3	$(CH_2)_{11}$	CH_3	CH_3	4
12	O	CH_3	$(CH_2)_{11}$	CH_3	n-C_4H_9	3
13	O	CH_3	$(CH_2)_{11}$	CH_3	n-C_4H_9	4
14	O	CH_3	$(CH_2)_{11}$	C_2H_5	C_2H_5	3
15	O	CH_3	$(CH_2)_2$	CH_3	CH_3	3
16	O	CH_3	$(CH_2CH_2O)_3$	CH_3	CH_3	3

Experimental Section

Materials. All solvents used were analytical grade. Acetonitrile and triethylamine were dried over molecular sieves (3 Å). All other solvents were dried by passing them through a short column of neutral Al_2O_3 (Merck; activity 1). Water used for the zwitterionic compounds was purified by a Milli Q water purification system (resistance 18 MΩ). Flash chromatography was performed on silica gel (Baker; 230 mesh). Initiator 2,2′-azobis-[2-methyl-*N*-(2-hydroxyethyl)]propionamide was a gift from Wako Chemicals GmbH (Germany). Monomer **15** was a gift from Raschig (Germany). The synthesis of monomers **1**, **4**, **10**, **20–24**, and **25–31** and of their polymers was described previously.[11,12,20,21] Due to the carcinogenic properties of propanesultone, handling requires certain precautions.[22]

Amides **2** and **3** were prepared by analogy[12] with monomer **1** in comparable yields, replacing dimethylamine by diethylamine

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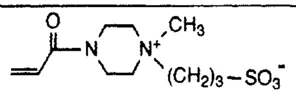
Table 2. Functionalized Monomers and Monomers of "Midtail" Geometry Used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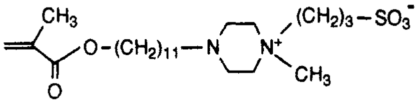
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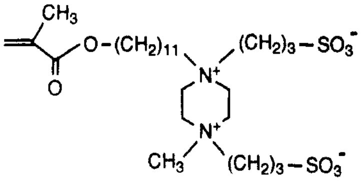
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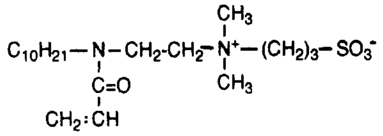
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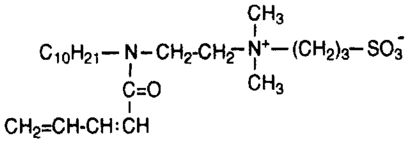
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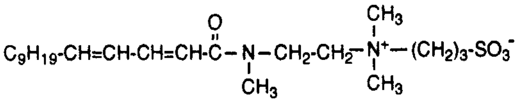
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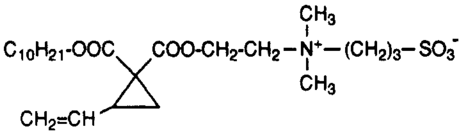
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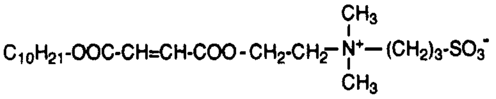
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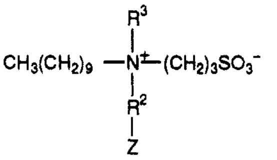
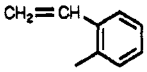
Table 3. Monomers of "Head" Geometry Used



Monomer	R^2	Z	R^3
25	$-CH_2-$		$-CH_3$
26	$-CH_2-$	$-CH=CH_2$	$-CH_2CH=CH_2$
27	$-(CH_2)_2-$	$-OCH=CH_2$	$-CH_3$
28	$-(CH_2)_2-$	$-\underset{CH_3}{N}COCH=CH_2$	$-CH_3$
29	$-(CH_2)_2-$	$-OCOCH=CH_2$	$-CH_3$
30	$-(CH_2)_2-$	$-OCO\underset{CH_3}{C}=CH_2$	$-CH_3$
31	$-(CH_2CH_2O)_3-$	$-CO\underset{CH_3}{C}=CH_2$	$-CH_3$

or acryloyl chloride by methacryloyl chloride, respectively. Acrylates **5**–**8** were prepared by analogy[11] with monomer **4**, replacing dimethylamine by diethylamine or methylbutylamine or propanesultone by butanesultone in the case of **5** and **7**. By similar modifications, methacrylates **9** and **11**–**14** were prepared by analogy[11] with monomer **10**. Reaction conditions and yields were comparable for all ammoniopropanesulfonates; however, in the case of ammoniobutanesulfonates the yields of 50% of the final alkylation step were considerably lower despite prolonged reaction times. This is attributed to the lower reactivity of butanesultone. Methacrylate **16** was prepared analogously[20] with monomer **31**, replacing *N*-methyldecylamine by dimethylamine.

2: ^{13}C-NMR (100.6 MHz, CD_3OD, spin-echo) δ 7.7 ($-N^+CCH_3$), 19.1 ($-N^+CCH_2CSO_3$), 22.6 ($-CCH_2CN^+-$), 27.4, 27.5, 27.9, 29.7, 30.1, 30.3, 30.4, 30.5 ($-(CH_2)_8-$), 34.4, 36.0 ($-CONCH_3$ cis + trans), 51.1 ($-CH_2SO_3$), 54.5 ($-N^+CH_2CH_3$), 57.2 ($-N^+CH_2CCSO_3$), 58.7 ($-CCCH_2N^+$), 128.15, 128.25 ($CH_2=CCON<$), 129.0, 129.4 ($C=CHCON<$), 168.4, 168.6 ($-CON<$).

3: ^{13}C-NMR (100.6 MHz, $CDCl_3$, spin-echo) δ 19.3 ($-N^+CCH_2CSO_3$), 20.2, 20.7 ($=(CH_3)CON<$, amide cis + trans) 22.6 ($-CCH_2CN^+-$), 26.3, 26.6, 29.1, 29.2, 29.3, 29.35 ($-(CH_2)_8-$), 32.0, 36.4 ($-CONCH_3$), 46.7 ($-CONCH_2-$), 47.8 ($-CH_2SO_3$), 50.7 ($-N^+CH_3$), 63.2 ($-N^+CH_2CCSO_3$), 64.4 ($-CCCH_2N^+$), 114.7 ($CH_2=CCON<$), 141.1 ($=CCON<$), 172.1, 172.6 ($-CON<$, cis + trans).

4: ^{13}C-NMR (100.6 MHz, CD_3OD, spin-echo) δ 19.9 ($-N^+CCH_2CSO_3$), 23.5 ($-CH_2CN^+$), 27.0, 27.4, 29.7, 30.1, 30.3, 30.5, 30.55 ($-(CH_2)_8-$), 48.8 ($-CH_2SO_3$), 51.3 ($-N^+CH_3$), 64.0, 65.7, 65.8 ($-CH_2N^+CH_2-$, $-COOCH_2-$), 129.7 ($=CHCOO-$, 131.3 ($CH_2=CCOO-$), 167.9 ($-COO-$).

5: ^{13}C-NMR (100.6 MHz, $CDCl_3$, spin-echo) δ 21.5, 22.3, 22.7 ($-CCH_2CN^+CCH_2CH_2CSO_3$), 25.8, 26.4, 28.5, 29.0, 29.1, 29.2, 29.3 ($-(CH_2)_8-$), 50.5 ($-CH_2SO_3$), 50.8 ($-N^+CH_3$), 63.8, 63.9 ($-CH_2N^+CH_2-$, 64.6 ($-COOCH_2-$), 128.6 ($=CHCOO-$), 130.4 ($CH_2=CCOO-$), 166.3 ($-COO-$).

7: ^{13}C-NMR (100.6 MHz, $CDCl_3$, spin-echo) δ 13.6 ($-CH_3$), 19.6, 21.0, 22.0 22.3 ($(-CCH_2C)_2N^+CCH_2CH_2CSO_3$), 24.1, 25.8, 26.3, 28.5, 29.1, 29.3, 29.35 ($-CH_2)_8-$, $-N^+CCCH_2CH_3$), 50.2 ($-CH_2SO_3$), 50.4 ($-N^+CH_3$), 60.85, 60.9 ($-CH_2N^+CH_2CCCSO_3$), 62.2 ($-N^+CH_2CCCH_3$), 64.6 ($-COOCH_2-$), 128.6 ($=CHCOO-$), 130.3 ($CH_2=CCOO-$), 166.3 ($-COO-$).

8: ^{13}C-NMR (100.6 MHz, $CDCl_3$, spin-echo) δ 7.7 ($-N^+CCH_3$), 18.6 ($-N^+CCH_2CSO_3$), 21.8 ($-CCH_2CN^+-$), 25.8, 26.4, 28.5, 29.0, 29.1, 29.2, 29.3 ($-(CH_2)_7-$), 47.2 ($-CH_2SO_3$), 53.6 ($-N^+CH_2CH_3$), 56.8, 57.7 ($-CH_2N^+CH_2CCSO_3$), 64.6 ($-COOCH_2-$), 128.6 ($=CHCOO-$), 130.4 ($CH_2=CCOO-$), 166.3 ($-COO-$).

9: ^{13}C-NMR (100.6 MHz, D_2O, spin-echo) δ 17.3 ($=C(CH_3)COO$), 18.1 ($-CH_2CSO_3$), 21.7 ($-CH_2CN^+-$), 24.7, 25.1, 27.5 ($-(CH_2)_3$), 47.3 ($-CH_2SO_3$), 50.5 ($-N^+CH_3$), 62.1, 64.2 ($-CH_2N^+CH_2-$), 65.4 ($-COOCH_2-$), 126.4 ($CH_2=CCOO$), 136.2 ($=CCOO$), 170.0 ($-COO-$).

11: ^{13}C-NMR (100.6 MHz, D_2O, spin-echo) δ 17.7 ($=C(CH_3)COO$), 20.9, 21.3, 22.1 ($-CCH_2CN^+CCH_2CH_2CSO_3$), 25.6, 25.9, 28.2, 28.7, 28.9, 29.05, 29.1 ($-(CH_2)_8-$), 50.0 ($-CH_2SO_3$), 50.7 ($-N^+CH_3$), 63.2, 63.9 ($-CH_2N^+CH_2-$), 65.0 ($-COOCH_2-$), 125.6 ($CH_2=CCOO$), 136.2 ($=CCOO$), 168.0 ($-COO-$).

12: ^{13}C-NMR (100.6 MHz, CD_3OD, spin-echo) δ 13.9 ($-CH_3$), 18.4 ($=C(CH_3)COO$), 19.6 ($-N^+CCH_2CSO_3$), 20.7, 23.1 ($-CCH_2CN^+CCH_2-$), 25.1, 27.0, 27.4, 29.7, 30.1, 30.3, 30.45, 30.5 ($-(CH_2)_8-$, $-N^+CCCH_2CH_3$), 48.6 ($-CH_2SO_3$), 49.9 ($-N^+CH_3$), 61.3 ($-N^+CH_2CCSO_3$), 62.8, 63.1 ($-CH_2N^+CH_2-$), 65.9 ($-COOCH_2-$), 125.9 ($CH_2=CCOO$), 137.9 ($=CCOO$), 168.9 ($-COO-$).

13: ^{13}C-NMR (100.6 MHz, CD_3OD, spin-echo) δ 13.9 ($-CH_3$), 18.4 ($=C(CH_3)COO$), 20.7, 22.0, 23.1, 23.2 ($(RCH_2C)_2N^+CCH_2CH_2CSO_3$), 25.1 27.0, 27.4, 29.7, 30.1, 30.3, 30.45, 30.5 ($-(CH_2)_8-$, $-N^+CCCH_2CH_3$), 49.9 ($-N^+CH_3$), 51.3 ($-CH_2SO_3$), 62.5, 62.7, 63.0 ($-N^+(CH_2R)_3$), 65.9 ($-COOCH_2-$), 125.9 ($CH_2=CCOO$), 137.9 ($=CCOO$), 168.9 ($-COO-$).

14: ^{13}C-NMR (100.6 MHz, CD_3Cl_3, spin-echo) δ 7.6 ($-N^+CCH_3$), 18.2 ($=C(CH_3)COO$), 18.4 ($-N^+CCH_2CSO_3$), 21.7 ($-CCH_2CN^+-$), 25.8, 26.4, 28.5, 29.0, 29.1, 29.3 ($-(CH_2)_8-$), 47.2 ($-CH_2SO_3$), 53.6 ($\mathrm{-N^+\mathit{C}H_2CH_3}$), 56.7 ($\mathrm{-N^+\mathit{C}H_2CCSO_3}$), 57.6 ($\mathrm{-CC\mathit{C}H_2N^+}$), 64.7 ($\mathrm{-COO\mathit{C}H_2-}$), 125.1 ($\mathrm{\mathit{C}H_2{=}CCOO}$), 136.5 ($\mathrm{{=}\mathit{C}COO}$), 167.5 ($\mathrm{-COO-}$).

16: ^{13}C-NMR (100.6 MHz, $\mathrm{CDCl_3}$) δ 18.4 ($\mathrm{{=}C\mathit{C}H_3}$), 19.8 ($\mathrm{-N^+C\mathit{C}H_2CSO_3}$), 47.9 ($\mathrm{-\mathit{C}H_2SO_3}$), 51.8 ($\mathrm{-N^+CH_3}$), 63.4, 63.7, 64.8, 64.9, 69.1, 70.3, 70.4 ($\mathrm{-OCH_2-}$, $\mathrm{-N^+CH_2-}$) 125.8 ($\mathrm{\mathit{C}H_2{=}CCOO}$), 136.2 ($\mathrm{{=}\mathit{C}COO}$), 167.2 ($\mathrm{-COO-}$).

Acrylamide **17** was prepared from *N*-methylpiperazine, acryloyl chloride, and propanesultone by the standard techniques described[11] (hygroscopic crystals). ^{13}C-NMR (100.6 MHz, $\mathrm{D_2O}$, spin-echo): δ 17.4 ($\mathrm{-N^+C\mathit{C}H_2CSO_3}$), 38.5, 39.6 ($\mathrm{-CON\mathit{C}H_2CN^+}$, amide cis + trans), 46.8 ($\mathrm{-N^+\mathit{C}H_3}$), 47.1 ($\mathrm{-\mathit{C}H_2SO_3}$), 59.3 ($\mathrm{-CONC\mathit{C}H_2N^+}$), 62.4 ($\mathrm{-N^+\mathit{C}H_2CCSO_3}$) 126.4 ($\mathrm{{=}\mathit{C}HCON{<}}$), 129.9 ($\mathrm{\mathit{C}H_2{=}CCON{<}}$), 168.1 ($\mathrm{-CON{<}}$).

3-[4-(11-Methacryloylundecyl)-1-methylpiperazinio]propanesulfonate (18) and 3-[1-(11-Methacryloylundecyl)-4-methyl-4-(3-sulfonatopropyl)piperazinio]propanesulfonate (19). Using conditions analogous to those for the synthesis of 11-(dimethylamino)undecanol,[11] waxy 1-(11-hydroxyundecyl)-4-methylpiperazine is prepared from 11-bromoundecanol and *N*-methylpiperazine in 65% yield, mp 63 °C. This alcohol is reacted with methacryloyl chloride in dichloromethane/powdered anhydrous $\mathrm{Na_2CO_3}$ to give the ester in 86% yield (slightly brownish oil, $n_D{}^{26}$ = 1.4742). ^{1}H-NMR (200 MHz, $\mathrm{CDCl_3}$): δ 1.1–1.5 (m, 16H, $\mathrm{-(CH_2)_8-}$), 1.68 (m, 2H, $\mathrm{-COOCCH_2}$), 1.9 (s, 3H, $\mathrm{CH_3C(COO){=}C}$), 2.15–2.6 (m, 13H, $\mathrm{-CH_2N(CH_2CH_2)_2\text{-}NCH_3)_2}$), 4.10 (t, 2H, $\mathrm{-COOCH_2-}$), 5.5 (m, 1H, $\mathrm{CH{=}CCOO-}$ trans), 6.05 (m, 1H, $\mathrm{CH{=}CCOO-}$ cis).

A total of 2 g (5.9 mmol) of 1-(11-methacryloylundecyl)-4-methylpiperazine, 1.59 g (13 mmol) of propanesultone, and 0.1 mL of nitrobenzene in 100 mL of acetonitrile are refluxed under nitrogen. After 2 days, colorless crystals of the double alkylation product **19** begin to precipitate from the reaction mixture. After 7 days, the reaction is stopped. The hot mixture is filtered and the crude **19** collected, which is purified by repeated extraction with boiling acetonitrile. The compound is very poorly soluble; the best solvents found were concentrated aqueous salt solutions. Yield: 0.4 g (10%) of colorless, hygroscopic powder. FD-MS: peak at 583.7 ($\mathrm{M + 1^+}$).

19: ^{1}H-NMR (400 MHz, $\mathrm{D_2O}$ + 3% KI): δ 1.4–1.8 (m, 14H, $\mathrm{-(CH_2)_7-}$), 1.8–1.9 (m, 4H, $\mathrm{-COOCCH_2}$, $\mathrm{-CH_2CN^+{<}}$), 2.1 (s, 3H, $\mathrm{CH_3C(COO){=}C}$), 2.4–2.6 (m, 4H, $\mathrm{-N^+CCH_2CSO_3}$), 3.25–3.4 (m, 4H, $\mathrm{-CH_2SO_3}$), 3.6–3.9 (m, 5H, $\mathrm{N^+CH_3}$, $\mathrm{-CH_2N^+{<}}$), 3.95–4.35 (m, 14H, $\mathrm{N^+(CH_2CH_2)_2N^+-}$, $\mathrm{-N^+CH_2CCSO_3}$, $\mathrm{-COOCH_2-}$), 5.82 (m, 1H, $\mathrm{CH{=}CCOO-}$ trans), 6.28 (m, 1H, $\mathrm{CH{=}CCOO-}$ cis).

On cooling the filtrate, monoalkylation product **18** precipitates, which is purified by flash chromatography (silica gel, gradually changing the eluent from pure $\mathrm{CH_2Cl_2}$ to pure methanol). Yield: 1.8 g (66%) of colorless, hygroscopic powder. FD-MS: peaks at 461.2 ($\mathrm{M + 1^+}$) and 483.2 ($\mathrm{M + Na^+}$).

18: ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.1–1.5 (m, 16H, $\mathrm{-(CH_2)_8-}$), 1.65 (m, 2H, $\mathrm{-COOCCH_2}$), 1.9 (s, 3H, $\mathrm{CH_3C(COO){=}C}$), 2.25 (m, 2H, $\mathrm{-N^+CCH_2CSO_3}$), 2.40 (t, 2H, $\mathrm{-CH_2N{<}}$), 2.6–2.85 (m, 4H, $\mathrm{-N(CH_2C)_2}$), 2.90 (t, 2H, $\mathrm{-CH_2SO_3}$), 3.22 (s, 3H, $\mathrm{N^+CH_3}$), 3.4–3.6 (m, 4H, $\mathrm{N(CCH_2)_2N^+-}$), 3.75 (m, 2H, $\mathrm{-N^+CH_2CCSO_3}$), 4.09 (t, 2H, $\mathrm{-COOCH_2-}$), 5.5 (m, 1H, $\mathrm{CH{=}CCOO-}$ trans), 6.05 (m, 1H, $\mathrm{CH{=}CCOO-}$ cis).

3-[*N*-(2-Vinylbenzyl)-*N*-decyl-*N*-methylammonio)]propanesulfonate (25). A saturated solution of *N*-decyl-*N*-methyl-1,2,3,4-tetrahydroisoquinolinium iodide, which is prepared by successive alkylation of 1,2,3,4-tetrahydroisoquinoline with 1-bromodecane and iodomethane, in methanol/water (2:1, v/v) is passed through a column of strongly basic ion exchange resin (Amberlite). On evaporation of most of the solvent at 85 °C under reduced pressure (14 Torr), an oil phase separates on top of the residual aqueous phase, which consists of pure 2-(*N*-decyl-*N*-methylaminomethyl)styrene (yield: nearly quantitative, slightly yellowish oil, $n_D{}^{25}$ = 1.5052).

A total of 10 g (34.8 mmol) of the styrene and 0.5 mL of nitrobenzene in 100 mL of acetonitrile are refluxed with 4.22 g (34.6 mmol) of propanesultone under nitrogen for 5 days. The product which precipitates on cooling is collected and repeatedly recrystallized from acetonitrile. Yield: 2 g (85%) of colorless, hygroscopic crystals. Mp: 178 °C. ^{13}C-NMR (100.6 MHz, $\mathrm{CDCl_3}$, spin-echo): δ 14.0 ($\mathrm{\mathit{C}H_3-}$), 19.5 ($\mathrm{-N^+C\mathit{C}H_2CSO_3}$), 22.4, 22.5 ($\mathrm{CH_3\mathit{C}H_2-}$, $\mathrm{-C\mathit{C}H_2CN^+}$), 26.4 $\mathrm{-C\mathit{C}H_2CCN^+}$), 29.0, 29.1, 29.3, 29.4 ($\mathrm{-(\mathit{C}H_2)_4-}$), 31.8 ($\mathrm{CH_3C\mathit{C}H_2-}$), 47.5 ($\mathrm{-N^+\mathit{C}H_3}$), 47.9 ($\mathrm{-\mathit{C}H_2SO_3}$), 60.5, 61.5, 63.0 ($\mathrm{Ar\mathit{C}H_2N^+-}$, $\mathrm{-N^+\mathit{C}H_2CCSO_3}$), $\mathrm{-N^+\mathit{C}H_2R}$), 119.1, 124.8, 140.7 ($\mathrm{\mathit{C}H_2{=}CAr}$, $\mathrm{{=}\mathit{C}{<}}$ aryl), 127.7, 128.0, 131.0, 134.4, 134.6 ($\mathrm{C{=}\mathit{C}HAr}$, $\mathrm{{=}\mathit{C}H-}$ aryl).

Monomers **2**–**19** are strongly hygroscopic powders and waxes. No melting points are given as—like surfactants[23]—they are strongly decreased by small water contents and are difficult to reproduce; extensive drying in a vacuum oven gives rise to partial polymerization. Elemental analysis (C, H, N, S) of the dried samples was satisfactory.

Polymerization. Polymers of the newly described monomers are obtained by free-radical polymerization, generally in ethanol solutions (ca. 5% by weight) at 70 °C, using 1 mol % of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator.[11] Styrene **25** had to be polymerized in water under micellar conditions using the initiator 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)]propionamide for 24 h at 85 °C. All attempts to polymerize methacrylamide **3** failed. The poor polymerizability of *N*-methylmethacrylamides is known and may be caused by steric crowding. No suitable solvent for the polymerization of the very poorly soluble **19** containing two sulfobetaine moieties was found. UV irradiation or prolonged heating of the solid monomer produces an insoluble and infusible solid. Polymers are purified by extraction with hot acetone and reprecipitated from methanol/water mixtures into acetone/diethyl ether mixtures.

The polymerizations of the known monomers have been described previously.[11,12,20,21] The dienes **21** and **22** give 1,4-polymers; vinylcyclopropane **23** gives a 1,5-polymer, i.e., a poly(1,1-dialkoxycarbonyl-3-pentenylene), via ring opening.[21] Diallyl monomer **26** cyclopolymerizes, also when copolymerized with $\mathrm{SO_2}$. This is in agreement with the reported cyclopolymerization of another zwitterionic diallyl monomer, 2-(*N*,*N*-diallyl-*N*-methylammonio)ethanesulfonate.[24] Monomer **24** (ca. a 5:1 mixture of the trans and cis isomers) and monomer **27** do not homopolymerize but form 1:1, presumably alternating copolymers with *N*-methyl-*N*-vinylformamide (NMVF) and *N*-methylmaleimide (MMI), respectively.[21]

Preparation of Polymer–Salt Mixtures. For water-soluble polymers, aqueous solutions of the polymer and of the salt were mixed, frozen in liquid nitrogen, and lyophilized. For polymers insoluble in water, solutions of the polymer and of the salt in aqueous ethanol were mixed, and the solvent was removed in vacuo. If the mixing produces a precipitate, sufficient methanol is added to the residue to give a clear, homogeneous solution, and the solvent is evaporated in vacuo.

Methods. NMR spectra were recorded by AC200 (200 MHz; Bruker) and Aspect 3000 spectrometers (400 MHz; Bruker). Thermogravimetry was performed on a thermogravimetric analyzer TGS-2 (Perkin-Elmer), with a heating rate of 10 °C/min in a nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC2, with heating and cooling rates of 10 and 20 °C/min, respectively. Glass transition temperatures (T_g) were determined by the inflection point (midpoint) method from heating cycles. X-ray scattering experiments were done with a diffractometer Kristalloflex (Siemens), using the Ni-filtered Cu Kα line (λ = 0.1541 nm).

Surfactant Properties of the Monomers. As for related betaine monomers, the structures of most of the newly prepared monomers are those of surfactants.[11,18] Indeed, except for **9**, **16**, and **17**, their aqueous solutions are foaming, show strongly reduced surface tensions, and form lyotropic mesophases when concentrated. The broken fan textures in the polarizing microscope point to hexagonal mesophases. Notably high Krafft temperatures are observed for styrene **25** (67 °C) and for the ammoniobutanesulfonates (e.g., 27 °C for **11** compared to 16 °C for the analogous propanesulfonate **10**).

Polymer Geometry. Hydrophobized betaine polymers are advantageously classified by their geometry:[11] polymers of "head" type carry the betaine moiety close to the polymer backbone; polymers of "tail-end" type have the betaine groups separated from the backbone by the hydrophobic alkyl groups; polymers of "midtail" type bear the betaine moiety in intermediate positions (Figure 1). Within this classification, polymers of **1**–**14**, **18**, and **19**, i.e., most of the newly prepared polymers, belong to the tail-end type, polymers of **20**–**24** fall into the midtail type, and

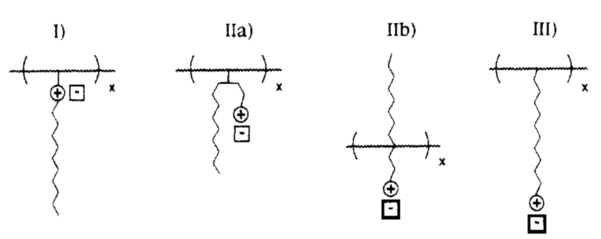


Figure 1. Schematic representation of geometries of hydrophobized poly(sulfobetaines): (I) head type; (IIa, IIb) midtail type; (III) tail-end type.

polymers of **25**–**31** are of the head type. Poly-**15** through poly-**17**, which do not bear hydrophobic chains, are used as references.

Solubilities of the Polymers. In agreement with a previously derived model, the solubility of the newly prepared vinyl polymers is controlled by their geometry.[12,21] Thus, the tail-end type polymers poly-**1**, poly-**2**, poly-**4** through poly-**14**, and poly-**18** dissolve only in highly polar solvents such as (hot) water or formamide but do not in less polar solvents such as ethanol or $CHCl_3$/methanol mixtures. The latter ones, however, are usually solvents for head type polymers which do not dissolve in water. But, polystyrene poly-**25** was only found to be soluble in trifluoroethanol, which is a general solvent for all poly(sulfobetaines) prepared, independent of the respective geometry, as indicated before.[19,22] The limited solubility of poly-**25** may be caused by simultaneous attractive interactions of both the betaine moiety and the aromatic group, in agreement with the high Krafft temperature found and as observed for other poly(sulfobetaines) with aromatic groups.[11]

Thermal Properties. The polymers are very hygroscopic. Handled even for short periods in air, they take up ca. 5% by weight of water. This corresponds to about 1 molecule of water per betain group, which can be removed by heating at 130 °C. Prolonged storage under ambient conditions can increase the water content considerably, depending on the detailed structure of the polymer.

The dried zwitterionic monomers and polymers do not show weight loss up to 210–250 °C in thermogravimetric experiments.

Exceptions are polystyrene poly-**25** whose decomposition starts above 185 °C, presumably due to the less stable benzyl ammonium moiety, and the aliphatic polysulfone co-**26**/SO_2 which decomposes above 140 °C. Hence, DSC studies were confined to temperatures below 210 °C (for poly-**25** below 175 °C; for co-**26**/SO_2 below 130 °C).

In general, the fully zwitterionic homopolymers reported so far do not show glass transitions.[1,7] This is also true for alkyl-substituted poly(sulfobetaines) studied previously,[11] although the decyl and undecyl substituents used are known to lower the glass transition temperatures T_g of acrylic and methacrylic polymers efficiently.[25] Notable exceptions in the literature are the polymer of 3-[*N*,*N*-diethyl-*N*-(5-methacryloyl-3-oxapentyl)-ammonio]propanesulfonate[7] and the analogous polyacrylate.[27] The standard way to obtain polyzwitterions with glass transitions has thus been random copolymerization of zwitterionic monomers with uncharged comonomers.[8,12–14,25,26] This method implies the dilution of the ionic groups, a less defined chemical structure, and sometimes the occurrence of two glass transitions as in ionomers.[14,26]

In agreement with the literature, the majority of the polymers studied do not show glass transitions up to 210 °C, i.e., up to the beginning of their thermal decomposition. But, nevertheless, by appropriate chemical variation, sulfobetaine homopolymers with accessible glass transitions can be prepared which are listed in Table 4. Just like the melting points of the monomers, T_gs are very sensitive to small amounts of water,[27] and the hygroscopic polymers have to be dried extensively at 130 °C to give reproducible values.

Comparing the various chemical modifications performed, three general pathways evolve to prepare polymers with low T_g:

(i) The elongation of the repeat unit of the polymer backbone, i.e., the reduction of density of the side chains, as exemplified by poly-**21** through poly-**23** and the alternating copolymer co-**24**/NMVF. This corresponds to the known random copolymerization[8,12] but produces well-defined polymer structures and reduces the amount of ionic groups in the polymers only marginally (e.g., compare analogs poly-**20** and poly-**21**). The efficiency of this strategy depends apparently on the nature of the backbone, presumably on the rigidity, as expected: analogous random copolymers based on tertiary acrylamides show much higher T_gs even at high nonionic comonomer content,[12] and for the alternating copolymer co-**27**/MMI, no T_g was found. There may be an additional effect of the different polymer geometries (head type vs midtail type), but considering the results for some random copolymers, this effect should be small.[12]

Table 4. Glass Transition Temperatures T_g of Poly(sulfobetaines) and of Their Stoichiometric Mixtures with NaI and NaCl

	glass transition temp T_g (K)		
polymer	pure polymer	NaI blend[a]	NaCl mixture[b]
poly-2	332	340	306
poly-6	316	322	307
poly-7	325	330	296
poly-8	320	331	
poly-12	342		
poly-13	355		
poly-14	358		
poly-16	355	360	327
poly-21	360		
poly-22	410		
poly-23	398		
co-24/NMVF	415		
poly-31	343		

[a] Stoichiometric amounts of polymer and salt, homogeneous blend. [b] Stoichiometric amounts of polymer and salt, heterogeneous mixture.

(ii) The separation of the betaine moiety from the backbone by a long alkyl chain (i.e., tail-end geometry), combined with an increase of the bulkiness of the substituents of the ammonium moiety. Comparing *N*,*N*-dimethylammonium derivatives **1**, **4**, and **10** with the *N*,*N*-diethylammonium analogs **2**, **8**, and **14** or with the *N*-butyl-*N*-methylammonium analogs **6** and **12**, the effect is striking: T_gs are lowered by more than 100 °C. Presumably, steric shielding of the cationic groups screens much of the interaction of the ionic groups, thus shifting T_gs toward the low values found for alkyl chain substituted polyacrylics and -methacrylics.[25] The steric effect seems predominant, as differences between acrylate, acrylamide, and methacrylate analogs, e.g., between poly-**2**, poly-**8** and poly-**14**, are small. Ammoniobutanesulfonates show slightly higher T_gs than the analogous ammoniopropanesulfonates, but again the differences are small. The higher values might derive from a stronger tendency to form "interside-chain" rather than cyclic "intraside-chain" ion pairs in the case of the larger separation of the anionic and the cationic groups (Table 1, $n = 4$ vs $n = 3$). Alternatively, the higher T_g values might be explained by the higher dipole moments realizable in ammoniobutanesulfonates ($\mu = 27.6$ D) than in ammoniopropanesulfonates ($\mu = 23.0$ D) due to the larger spacing between the cationic and the anionic groups.[28]

(iii) The incorporation of oligo(ethylene oxides). They might act as flexible side-chain spacers or as internal plasticizers. The efficiency of this strategy is demonstrated by the comparisons of poly-**15** with poly-**16** or of poly-**30** with poly-**31**. The low T_gs reported for poly[3-[*N*,*N*-diethyl-*N*-(5-methacryloyl-3-oxapentyl)ammonio]propanesulfonate][7] and the analogous polyacrylate[27] fit well into this scheme, combining the use of oligo(ethylene oxide) spacers and steric crowding.

Bulk Structures. The poly(sulfobetaines) were investigated by X-ray powder diffractograms at 300 K. In agreement with previous studies,[11,12,17] the polymers are not crystalline but exhibit small-angle reflections indicative of a superstructure when substituted by an alkyl chain, in contrast to the unsubstituted references poly-**15** through poly-**17** (Table 5). Samples of poly-**15** with very high molecular weight can be semicrystalline,[11] but the sample used here is fully amorphous as reported on other samples.[7,27] Poly-**9** carrying only a hexyl chain does not exhibit small-angle peaks either. The superstructures formed are attributed to microphase separation of the ionic groups and the

Table 5. X-ray Diffraction Patterns of Poly(sulfobetaines) Stored in Air, at 27 °C (Water Content ca. 5% by Weight)

polymer	diffraction pattern	small-angle peaks 2θ	small-angle peaks d (Å)	halo 2θ	halo d (Å)
poly-1	A	2.9/5.5	30/16	19.7	4.5
poly-2	A	3.0/5.8	29/15	19.6	4.5
poly-4	A	2.7/5.3	33/17	19.6	4.5
poly-5	A	2.8/5.4	32/16	19.6	4.5
poly-6	A	3.2/6.2	28/14	20.4	4.4
poly-7	A	3.1/5.6	29/16	20.3	4.5
poly-8	A	2.9/5.8	30/15	19.1	4.6
poly-9				19.2	4.6
poly-10	A	2.7/5.5	33/16	19.6	4.5
poly-11	A	2.8/5.5	32/16	19.8	4.5
poly-12	A	3.1/5.8	29/15	19.8	4.5
poly-13	A	3.0/5.7	29/15	19.6	4.5
poly-14	A	3.0/5.8	29/15	19.3	4.6
poly-15				19.8	4.5
poly-16				19.6	4.5
poly-17				18.0	4.9
poly-18	B	2.55/5.1	35/17	19.0	4.7
poly-20	C	3.0	29	19.8	4.5
poly-21	C	2.8	31	20.0	4.4
poly-22	C	2.1	42	19.7	4.5
poly-23	C	2.4	38	19.7	4.5
co-24/NMVF	B	2.3/4.6	39/19	19.0	4.6
poly-25	C	3.8	23	19.7	4.5
poly-26	C	3.8	23	19.4	4.5
co-26/SO_2	C	2.8	31	20.0	4.4
co-27/MMI	C	3.2	28	19.4	4.5
poly-28	C	3.4	26	19.4	4.5
poly-29	C	3.0	29	19.7	4.5
poly-30	C	3.7	24	19.7	4.5
poly-31	B	3.95/7.8	22/11	19.7	4.5

alkyl chains.[17,29] Characteristic diffraction patterns are shown in Figure 2.

The diffraction patterns are characteristic for the respective polymer geometry. Tail-end type polymers exhibit pattern A which is characterized by two peaks with low intensity compared to the halo. The peak at smaller angles is sharper but of lower intensity than the second one. Head type polymers give pattern C with only one intense peak. Midtail type polymers show pattern C as well, with the exception of copolymer co-**24**/NMVF. The latter exhibits, like poly-**18** and poly-**31**, several diffraction peaks of high intensity characteristic of pattern B: The intensity of the peaks decreases with the scattering angle, and the corresponding distances calculated by Bragg's equation are correlated by the factor $1/n$. Thus, the peaks may be assigned as first- and second-order reflections, etc., of a lamellar structure. For tail-end type and head type polymers showing patterns A and C, the presence of complex lamellar structures has also been recently demonstrated.[17]

Although the polymers studied can be subsumed into these four general classes (no small-angle peaks and patterns A–C), there are some gradual differences. Within the tail-end type polymers, the peaks of pattern A are more pronounced for the *N*,*N*-dimethylammonium derivatives **1**, **4**, **5**, **10**, and **11** than for the *N*,*N*-diethylammonium analogs and the *N*-butyl-*N*-methylammonium analogs **2**, **6–8**, and **12–14**, thus pointing to a better developed superstructure. This observation coincides with the much higher values of T_g found as discussed above.

Within the head type polymers, the single peak of pattern C tends to sharpen and gain intensity relative to the halo for less crowded backbones, such as for polydienes poly-**21** and poly-**23** or for poly(vinylcyclopropane) poly-**23**, pointing to improved microphase separation. Analogously, the peak found for the cyclopolymer of **26** is rather broad and weak but sharpens on copolymerization with SO_2. The simple lamellar pattern B for the alternating copolymer co-**24**/NMVF may be understood as the result of such improved ordering due to a less crowded bacbone, additionally supported by the structure IIb of Figure 1 favorable for microphase separation. The occurrence of pattern B for poly-**18** is attributed to favorable interactions between the piperazine rings, by analogy with the occurrence of pattern B for polymeric pyridiniobetaines.[11]

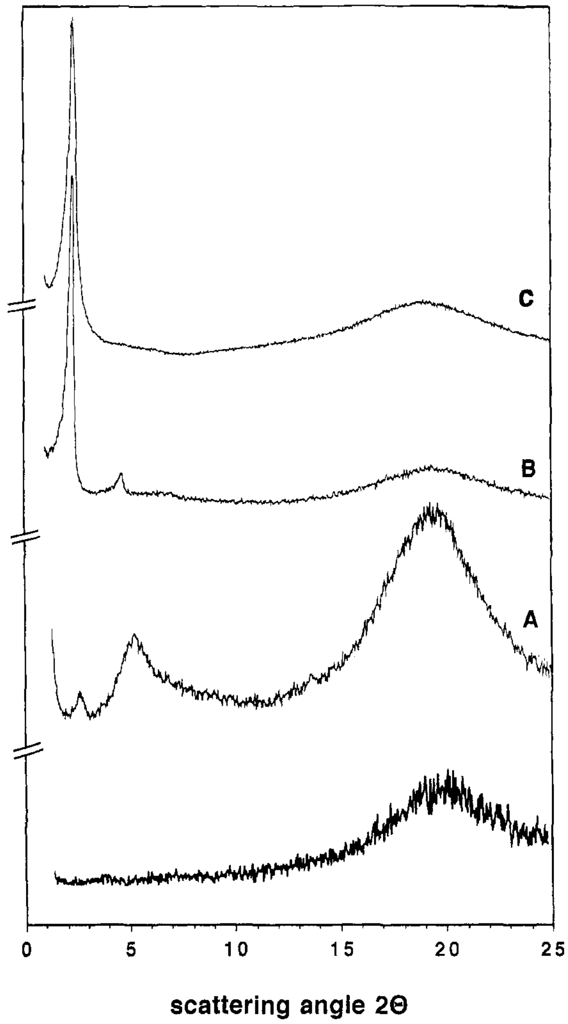


Figure 2. Representative X-ray powder diffractograms of poly(sulfobetaines) (300 K). From bottom to top: poly-**9**, poly-**5** (A), co-**24**/NMVF (B), poly-**23** (C).

Within the above discussion, the appearance of pattern B for poly-**31** is unexpected. In fact, this behavior is different from the other polymers of the head type, as—although not water-soluble—poly-**31** easily swells with moisture from the air to produce at temperatures above room temperature a lyotropic mesophase. The limiting water uptake is about 10% by weight; clearing temperatures are in the range of 85–115 °C depending on the water content. The mesophase is birefringent and mobile, but the textures observed in the polarizing microscope are nonspecific; the X-ray pattern is compatible with a lamellar mesophase or may be compatible with a hexagonal one. When the polymer is carefully dried at 130 °C, no mesophase is observed anymore, and the X-ray pattern C is observed (Table 6 and Figure 3a) also when the dry samples are cooled to 300 K.

An influence of small water contents on the X-ray diffraction pattern has been observed already in the past for another poly(sulfobetaine),[17] the tail-end type polyacrylate poly-**4**. Prolonged annealing with subsequent drying of the stored polymer induces a profound change of the diffraction pattern A to B-like. However, this behavior was not observed for the analogous polymethacrylate poly-**10**, which promoted us to look at the influence of absorbed water and elevated temperatures for some selected polymers.

Important changes of the diffraction patterns seem to be exceptional, as only in the case of polyacrylamide poly-**1** the loss of water induces changes similar to poly-**4**, yielding pattern B (Figure 3b and Table 6). The new structure lasts after cooling when stored dry but rearranges to the original pattern upon upon uptake of humidity. Neither the isomeric polymers poly-**28** and poly-**29** of the head type nor the analogous polyacrylates poly-**5**, poly-**6**, and poly-**8** with modified substitution patterns of the ammonium moiety exhibit such changes (Table 6).

Table 6. X-ray Diffraction Patterns of Poly(sulfobetaines) after Drying, at 127 °C

polymer	diffraction pattern	small-angle peaks 2θ	small-angle peaks d (Å)	halo 2θ	halo d (Å)
poly-1	B	2.8/5.6	32/16	19.6	4.5
poly-4	B[a]	3.3/6.3	27/14	19.0/21.0	4.7/4.2
poly-5	A	2.8/5.4	32/16	19.5	4.5
poly-6	A	3.2/6.2	28/14	19.9	4.5
poly-8	A	2.9/5.8	30/15	19.1	4.6
poly-10	A	2.7/5.5	33/16	19.6	4.5
poly-11	A	2.8/5.7	32/15	19.2	4.6
poly-28	C	3.4	26	19.5	4.5
poly-29	C	3.0	29	19.5	4.5
poly-30	C	3.7	24	19.5	4.5
poly-31	C	3.8	23	19.8	4.5

[a] More complex pattern; see ref 17.

Noteworthy, the phenomenon of changed diffraction patterns is independent of the glass transition (compare also ref 7). The last mentioned polymers pass through the glass transition on heating (see Table 4), which, however, does not modify the diffractograms substantially: the shape of the peaks is somewhat sharpened above T_g, but neither the pattern nor the position of the small-angle peaks changes.

Mixtures of Poly(Sulfobetaines) and Inorganic Salts: Salt Effects. In contrast to polycations or polyanions, zwitterionic polymers are capable of interacting simultaneously with all ions of added electrolytes. This was already indicated in early studies on copolymers of acrylonitrile, with zwitterionic monomers exhibiting improved uptake for both basic and acidic dyes.[30] As a result, some zwitterionic polymers produce homogeneous mixtures in the solid state with large quantities of inorganic salts, as shown recently.[7,9,10,15-17] Analogous polycations undergo anion exchange only.[16] This property is remarkable because salt uptake of organic polymers—even of well-complexing polymers such as poly(oxyethylene) or poly(dimethylacrylamide)—is usually very limited. In ideal cases, polyzwitterions can bind stoichiometric amounts of salt. However, in contrast to the early assumptions,[7] good miscibility with inorganic salts is not a general phenomenon but is confined to selected combinations of polymer and salt. The isomeric polymethacrylates **poly-10** and **poly-30**, for example, were shown to produce homogeneous mixtures with stoichiometric amounts of NaI, but not of NaCl.[16] A structural model for the salt blends was proposed,[29] implying a random location of the inorganic ions in the neighborhood of the polymer bound ionic groups.

Characteristically, in phase-separated mixtures, X-ray signals indicative of the added salt are superposed to the polymer diffraction pattern, whereas in homogeneous mixtures such signals are absent. Additionally, **poly-10** of the tail-end type underwent a change of its superstructure upon blending with NaI, resulting in X-ray diffraction pattern B of the blend (see Figure 4) instead of pattern A of the pure polymer. As the diffraction patterns observed do not vary with small water contents (Table 6), **poly-10** proved to be ideal to screen the selectivity of the binding toward various anions and cations. The results are presented in Table 7.

A number of salts failed to produce homogeneous blends in notable amounts, whereas others do so in stoichiometric amounts. The upper limits of mixing are not clear. Preliminary experiments show that mixtures of **poly-10** with 50% stoichiometric excess of NaI begin to exhibit salt signals in their diffractograms, but a 100% stoichiometric excess of $CaCl_2$ still produces homogeneous blends.

The series of sodium salts enables us to elucidate the influence of the anions on mixing. Miscibility in stoichiometric amounts is found for sodium iodide, bromide, and nitrate; salt signals at 23.8° and 27.5° or 25.8° and 29.1°, respectively, are missing in the diffractograms, and pattern A is changed to pattern B (Figure 4). But only small amounts of sodium acetate, oxalate, sulfate, fluoride, and chloride are miscible with **poly-10**, if at all. For these salts, diffraction pattern A of the pure polymer is unchanged, the salt signals being superposed. In the series of potassium salts the chloride is not miscible, and the bromide is only partially miscible: stoichiometric amounts of KBr produces superposed salt signals at 23.3° and 27.0° but nevertheless provoke a change of the diffractograms to pattern B. Variation of the amounts of salt revealed that phase separation occurs at about 40 mol % of KBr added. The change of diffraction pattern A to B occurs at addition of ca. 20 mol % of salt.

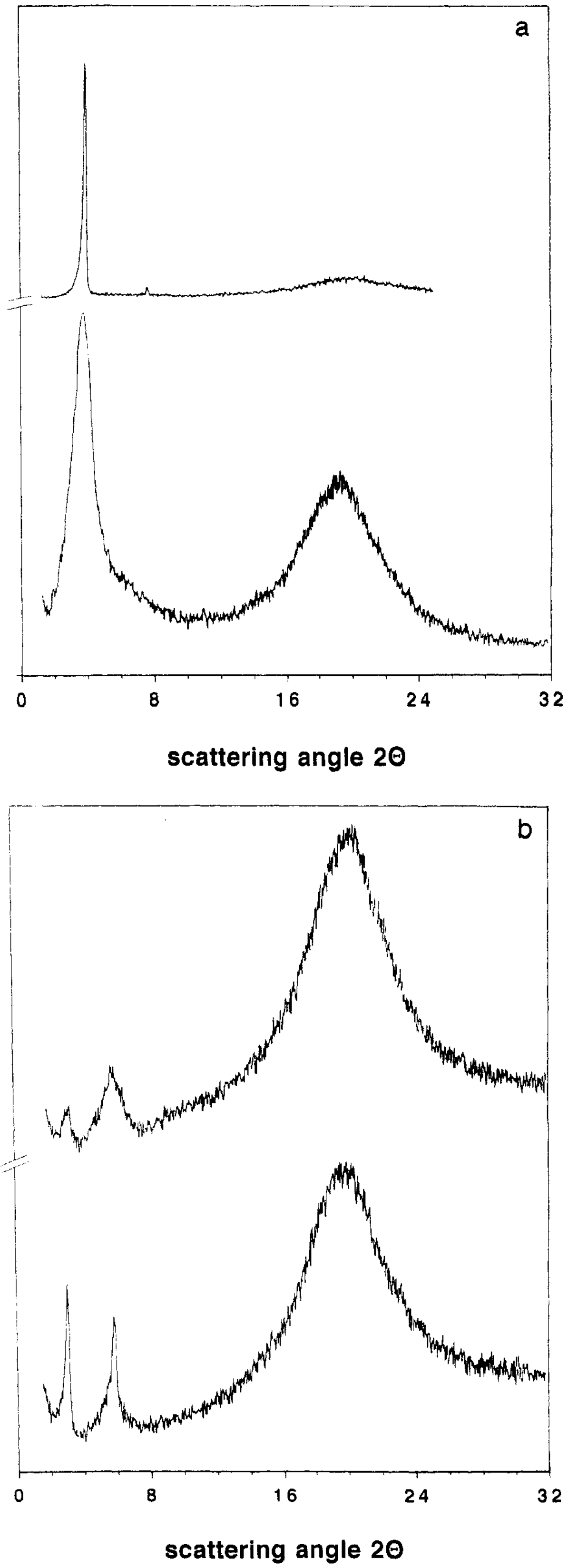


Figure 3. X-ray powder diffractograms of poly(sulfobetaines) at different temperatures and water content. (a) **Poly-31**: (top) 300 K, stored in air (water content ca. 7%); (bottom) 400 K, annealed at 420 K for 3 h. (b) **Poly-1**: (top) 300 K, stored in air (water content ca. 5%); (bottom) 400 K, annealed at 420 K for 3 h.

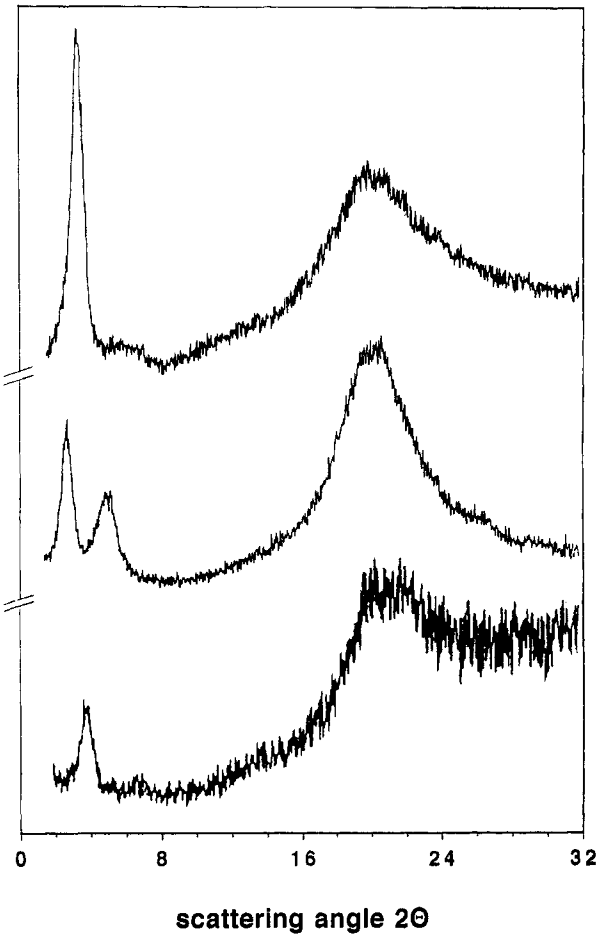


Figure 4. X-ray powder diffractograms of poly(sulfobetaines) mixed with stoichiometric amounts of salt. From top to bottom: poly-31 and NaBr; poly-10 and $LiClO_4$; poly-9 and NaI.

Table 7. Miscibility of Inorganic Salts with Poly-*10* in Stoichiometric Amounts[a]

	cation			
anion	**Li^+**	**Na^+**	**K^+**	**Ca^{2+}**
CH_3COO^-		–		
Ox^{2-}		–		
F^-		–		
Cl^-	+	–	–	++
NO_3^-		++		
Br^-		++	○	
I^-	++	++		
ClO_4^-	++			

[a] – = diffraction pattern unchanged, superposed salt signals. ○ = diffraction pattern changed, superposed salt signals. + = diffraction pattern unchanged, no salt signals visible. ++ = diffraction pattern modified, no salt signals visible.

There are not only differences between anions, but, as is exemplified above by sodium and potassium bromide, the cations influence the miscibility as well. Within the series of chlorides, miscibility in stoichiometric amounts is achieved for lithium and calcium chloride but not for sodium or potassium chloride. The case of lithium chloride is particular, as salt signals at 23.3° and 30.3° are missing in the diffractograms, but pattern A persists in the blend. Lithium perchlorate and iodide are miscible in stoichiometric amounts, too, but here the usual change to diffraction pattern B is observed. For all salt blends of poly-10 studied, the peak positions are in the region of 2.3–2.8° and 4.5–5.8°, which does not allow a detailed analysis of possible differences between the various salts within the limited accuracy of ±0.2°.

The results in Table 7 demonstrate marked selectivities of the miscibility for both cations and anions studied. The selectivity of the anions parallels the salting-in efficiencies in aqueous solution observed before,[3-6,16,19,31] agreeing with the empirical "Hofmeister lyotropic series":[32,33] homogeneous mixing is favored by "chaotropic" anions. The hard–soft–acid–bases (HSAB) concept[34,35] has been suggested to explain salt effects on polyzwitterions in solution,[4] but it fails to account for the successful binding of both soft anions such as iodide or bromide and hard anions such as nitrate or perchlorate, in contrast with the failures of "intermediate" anions such as chloride and other hard anions such as acetate, oxalate, or sulfate. The latter two anions disprove further a dominant role of charge density, as these doubly charged anions are surpassed by the several single charged ones. Concerning the effect of the cations with $K^+ < Na^+ < Li^+, Ca^{2+}$, the rules are less clear. Mixing may be favored by increasing charge density or may follow the empirical series of Schulze[36] and Hardy,[37] which had been correlated to the heats of hydration.[38] The energies of the crystal lattices may also be of importance.

Table 8. X-ray Diffraction Patterns of Poly(sulfobetaines) Mixed with Stoichiometric Amounts of Inorganic Salt, at 27 °C[a]

	miscibility			diffraction	small-angle peaks	
polymer	NaCl	NaBr	NaI	pattern	angle 2*θ*	distance *d* (Å)
poly-1	–		++	B	2.3/4.7	38/19
poly-2	–		++	B	2.55/5.0	35/18
poly-4	–	++	++	B	2.35/4.6	38/19
poly-5			++	B	2.4/4.5	37/19
poly-7	–		++	B	2.5/(4.8)[b]	35/(18)
poly-8			++	B	2.5/4.8	35/18
poly-9	–		++	C	3.4	26
poly-10	–	++	++	B	2.5/4.8	35/18
poly-11	–	○	++	B	3.2/4.6	39/19.5
poly-12	–		++	B	2.4/4.5	37/19
poly-13	–		++	B	2.5/4.5	35/19
poly-14			++	B	2.6/(5.0)[b]	34/(18)
poly-15	–		+			
poly-16	–	–	++	C	3.7	24
poly-17	–		+			
poly-18	–		+	B	2.2/4.2	40/21
poly-28	–	–	+	C	2.5	35
poly-30	–	–	+	C	3.1	28
poly-31	–	+	+	C	3.0	29

[a] – = diffraction pattern unchanged and superposed salt signals present. ○ = diffraction pattern changed, but superposed salt signals present. + = diffraction pattern unchanged, no superposed salt signals. ++ = diffraction pattern modified, no superposed salt signals.

Mixtures of Poly(sulfobetaines) and Inorganic Salts: Polymer Effects. To study the influence of the polymer structure on mixing, the well-mixing salt NaI and the poorly mixing NaCl were employed for mixtures with various polymers (Table 8).

Results show a general incompatibility of stoichimetric amounts of NaCl (peaks at 27.3° and 31.7°) and a general miscibility of stoichiometric amounts of NaI. This is not only true for the tested polymers of the tail-end type but for the polymers of the head-type as well, and even the references poly-15 through poly-17 without hydrophobic chains. The transition from pattern A to B is observed for all the tail-end type polymers on successful blending with NaI. In the case of the head type polymers, pattern C persists, but the single peak may be notably shifted to lower values; i.e., the *d*-spacings of the lamellar structures are increased by the incorporation of the salt.

Whereas the homogeneous blends of the reference polymers poly-15 and poly-17 with NaI show the original diffraction pattern without the small-angle peak, poly-9 with a hexyl chain and poly-16 with a triethylene oxide spacer show a particular behavior: the pure polymers show no small-angle signal, but the NaI blends do (Figure 4). The single peaks observed, though weak compared to the halo, indicate the presence of a superstructure. A similar induction of a superstructure was reported for the homogeneous blend of $LiClO_4$ and 3-[*N*,*N*-diethyl-*N*-(5-methacryloyl-3-oxapentyl)ammonio]propanesulfonate.[7] Apparently, added salt promotes microphase separation between the ionic fragments and the residual parts in polymers with a polar spacer or with a spacer of intermediate length, separating the betaine moieties and the backbone.

NaBr is better suited than NaCl for homogeneous blends, but less so than NaI according to Table 7. Thus, mixing studies with NaBr can reveal additional differences between various polymer structures (Table 8). For example, the polymer geometry contributes to the mixing behavior. Polymethacrylate poly-**10** of the tail-end type forms homogeneous blends with NaBr in stoichiometric amounts, but the isomeric poly-**30** of the head type does not: strong NaBr signals are present in the mixtures. The NaBr mixture of the polyacrylamide poly-**28** which is analogous to poly-**30** also exhibits residual salt signals, but they are much weaker and the small-angle peak is notably shifted from 3.4° to 2.8°, pointing to an improved, partial miscibility. Thus, the polymer backbone also influences the mixing behavior.

Alternatively, miscibility is improved by incorporation of an oligo(ethylene oxide) spacer, as exemplified by polymethacrylate poly-**31** of the head type. Homogeneous blends with stoichiometric amounts of NaBr are formed, in contrast to poly-**30**. However, the spacer group on its own does not seem to be sufficient to promote mixing, because the analogous poly-**16** without an alkyl chain does not form stoichiometric blends with NaBr. The additional presence of the alkyl chain is needed, perhaps because it promotes microphase separation.

A further factor is the separation between the ammonium and the sulfonate group: whereas ammoniopropanesulfonate poly-**10** forms stoichiometric blends with NaBr, the analogous ammoniobutanesulfonate poly-**11** does not (Table 8). Similar to the stoichiometric mixtures of poly-**10** and KBr, the diffractogram of the mixture exhibits pattern B, but residual signals of NaBr persist, indicating only partial miscibility.

Clearly, good miscibility of polyzwitterions and inorganic salts depends on both the salt and polymer chosen. The nature of the inorganic salts seems to be dominant, but in borderline cases the polymer structure is decisive. The detailed betaine moiety, the presence of alkyl groups, the polymer geometry, the nature of the backbone, and the presence of polar spacer groups all contribute to successful mixing. The studies suggest that, within the variations carried out, polyacrylamides of the tail-end type bearing the ammoniopropanesulfonate moiety are best suited for homogeneous blends.

Thermal Properties of the Polymer–Salt Mixtures. For selected polymers exhibiting glass transitions, the influence of mixing with salts on the thermal properties was studied. Some care must be taken, as the presence of strongly nucleophilic anions reduces the thermal stability of the ammonium group,[39] e.g., in the case of iodide down to 180 °C. The results are listed in Table 4.

Figure 5 illustrates two different trends seen in the table. Stoichiometric amounts of NaCl yielding a phase-separated system depress T_g, whereas stoichiometric amounts of NaI yielding homogeneous blends increase T_g. The latter effect is similar to the influence of $LiClO_4$ on the glass transition of poly-[3-[*N,N*-diethyl-*N*-(5-methacryloyl-3-oxapentyl)ammonio]propanesulfonate] in homogeneous blends,[7] indicating strong attractive interactions between the low molecular weight ions and the polymer-bound betaine moieties which presumably are responsible for the high values of T_g. In this context, the very large depressions of T_g (>100 °C) reported[10] for blends of NaI, e.g., with poly-**15**, are difficult to understand. Considering our TGA results, the onset of decomposition of the polymers by the strongly nucleophilic iodide during the thermal treatment or incomplete drying might be responsible for the effect.

The decrease of T_g found in NaCl mixtures points to a small, but partial, miscibility with the polymers. The weakly interacting salt may act as a plasticizer as described for liquid ethylammonium nitrate in some zwitterionic random copolymers.[26]

Conclusions

Zwitterionic poly(sulfobetaines) offer a spectrum of interesting solid-state properties, in particular a variety of microphase-separated systems, and a most remarkable miscibility with many inoorganic salts in stoichiometric amounts. In selected cases, miscibility can even be enhanced beyond that. Well-miscible salts are characterized by chaotropic anions and cations of high charge density. Miscibilities and bulk properties of the polybetaines are notably influenced by modification of the different structural elements of the polymer. This demonstrates that the presence of betaine groups in large amounts, accounting for ca. 30–40% by weight of the polymers, does not level the structural differences but still allows fine tuning of the required properties.

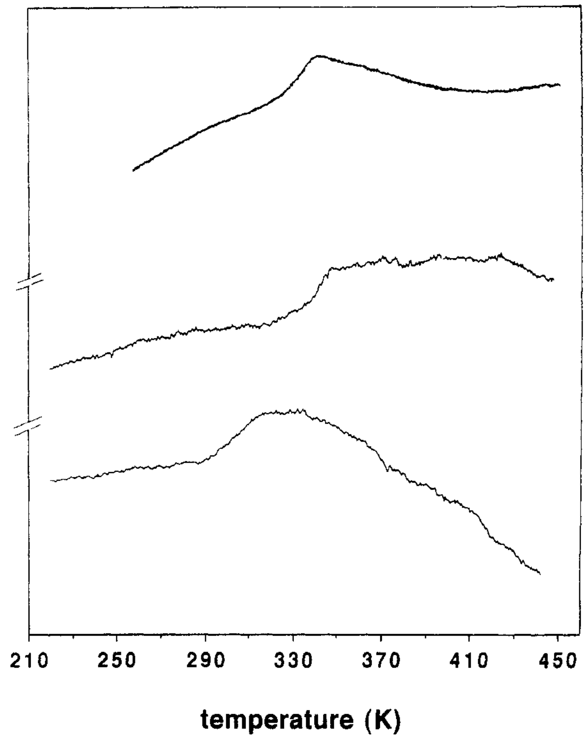


Figure 5. DSC traces of poly-**2**. From top to bottom: pure polymer, stoichiometric mixture with NaI, stoichiometric mixture with NaCl.

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