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# Zwitterionic polymers with carbobetaine moieties

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A series of new monomeric and polymeric carbobetaines based on acrylamides has been synthesized and characterized. Due to long hydrocarbon substituents, the compounds have chemical structures of surfactants and polysoaps, respectively. Results are compared with those of analogous poly(sulfobetaine)s. The poly(carbobetaine)s are more hygroscopic and show improved solubility. Viscometric studies in ethanol show no, or only weak, polyelectrolyte behaviour. Thermal stability is decreased, and glass transitions occur at lower temperatures. X-ray diffractograms indicate the presence of superstructures whose detailed forms depend on the polymers' geometry. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: polyzwitterions; ammoniocarboxylates; synthesis)**

## INTRODUCTION

Stable zwitterionic polymers represent highly dipolar materials with a wide spectrum of unique and specific properties[1,2]. As modifications of precursor polymers are never 100% efficient, leaving some ionic groups unbalanced, fully zwitterionic polymers in which the individual macromolecules have no residual net charge are best obtained by polymerization of zwitterionic polymers. Most studies so far have focused on poly(ammoniopropane sulfonate)s and poly(ammoniobutanane sulfonate)s as they are easily accessible via alkylation of tertiary amines by propanesultone and butanesultone respectively[3–9]. This route has the particular advantage that the presence of low molecular weight salt in the final reaction mixture is avoided, and thus can be excluded for the polymers. In fact, salt impurities are tenaciously held by polyzwitterions, but the complete removal of bound salt is crucial for a number of studies such as thermal stability, viscometry, electrical conductivity, etc. However, a major problem for fundamental studies is that the distance between the cationic and the anionic moiety is fixed in these polymers, i.e. the number of methylene units $n$ always equals 3 or 4, or exceptionally 2 (ref. 10) (*Scheme 1*).

Although being the oldest known synthetic poly(betaine)s[11], poly(carbobetaine)s posed problems for a long time in fundamental studies as standard synthetic pathways could not exclude the presence of residual low molecular weight salt in the polymers. But recently, for non-polymerizable zwitterions, this problem was resolved by the use of anionic ion-exchange resins as a key step in the synthesis[12–15]. This strategy allows any desired distance to be achieved between the cationic and the anionic moiety in the carbobetaine groups, i.e. the number of methylene units $n$ can be adjusted to any value (*Scheme 1*). The exception is the case of $n = 2$, as those adducts of acrylic acid and tertiary amines are not stable[14,16].

Stimulated by this work on low molecular weight carbobetaines, we have tried to extend the synthesis towards carbobetaine monomers, and to study the resulting polymers.

The newly synthesizd monomers are listed in *Figure 1*. They all are tertiary acrylamides which were chosen due to their improved resistance to hydrolysis by bases, compared to polymerizable esters. The alternative choice of secondary acrylamides or aromatic polymerizable moieties such as styrene or pyridines was avoided because of the known poor solubility of such poly(betaine)s[8,9,17]. In addition, analogous poly(acrylamide)s containing sulfobetaine groups have been described previously enabling instructive comparisons[9,17,18].

Within the compounds studied, the spacer group separating the polymer backbone and zwitterionic moiety ($C_2$ for **7** and **8** *versus* $C_{11}$ for **5** and **6**) is varied, as is the number of methylene groups $n$ separating the cationic ammonium moiety from the anionic carboxylate group ($n = 1$ for **5** and **7** *versus* $n = 3$ for **6** and **8**, cf. *Scheme 1*). This structural variation implies a change of the acidity of the carboxyl groups, too[13,16]: the $pK_a$ of ammonioacetates is *c*. 1.8 whereas the $pK_a$ of ammoniobutyrates is *c*. 4. Note that pairs **5** / **7** and **6** / **8** are positional isomers.

## EXPERIMENTAL

### *Materials/solvents*

All solvents used were distilled prior to use. Flash chromatography was performed on Silicagel (Merck, 230–400 mesh).

The water used to dissolve the betaines was purified using a Millipore water purification system.

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**Scheme 1** General structure of ammonioalkanesulfonates and ammonioalkanecarboxylates ($n \geq 1$)

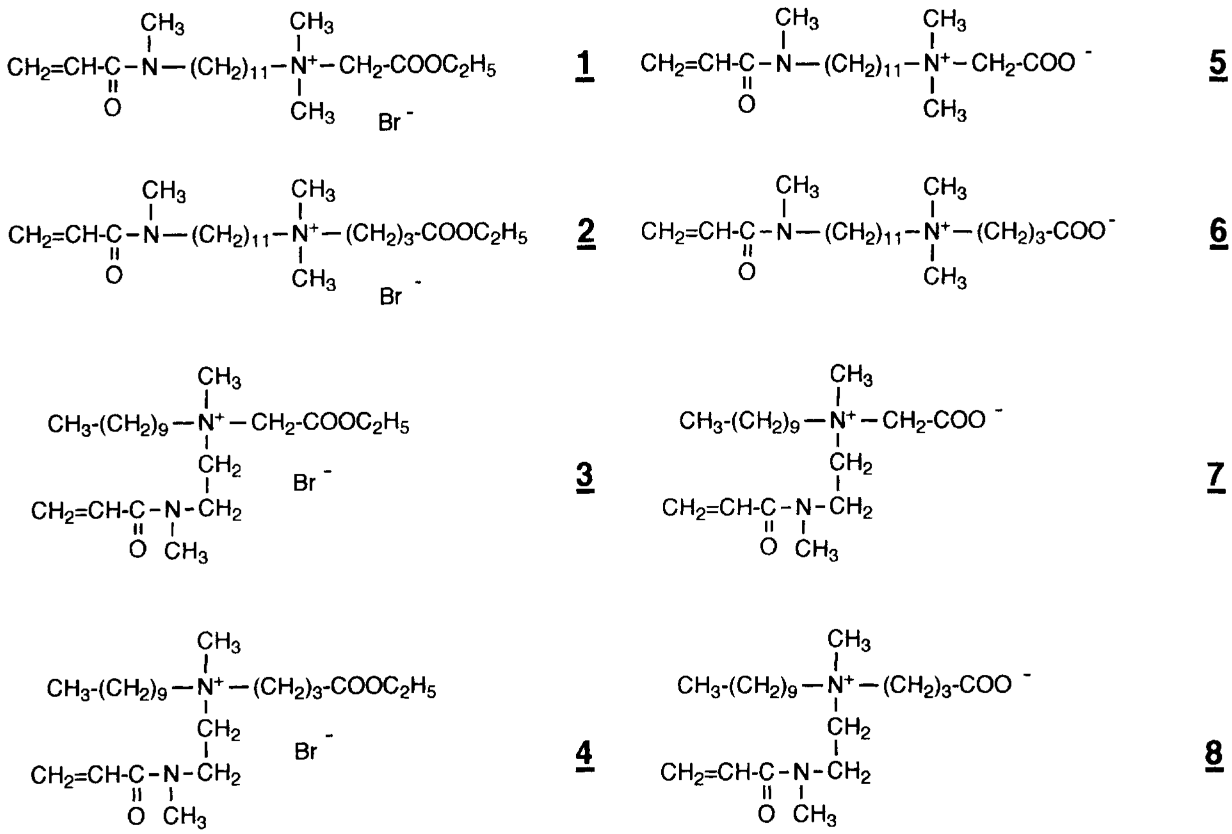


**Figure 1** Cationic and zwitterionic monomers synthesized

The saponification of ammonium bromides bearing ester groups was achieved by use of an $OH^-$ loaded anion exchange resin (Amberlist A26) conditioned by 2 M aqueous NaOH. The $OH^-$ content of the resin was $6.27 \times 10^{-4}$ mol g$^{-1}$ as determined by 0.1 M HCl standard solution.

*Monomers*

N,N′-*Dimethyl*-N-*11-(*N-*methylacrylamidyl)undecyl*-N-*(ethyloxycarbonyl)methyl-ammonium bromide* **1**. A total of 5 g (1.77 mmol) of *N*-methyl, *N*-11-(dimethylamino)undecyl acrylamide[18], 4.49 g (2.70 mol) of ethyl 2-bromoacetate and 100 mg of 2,6-di-t-butyl-*p*-cresol (DBPC) were refluxed in 50 ml of acetonitrile for 72 h under argon. The solvent was evaporated, the oily residue dissolved in water and lyophilized.

Yield: 7.22 g (91%), of slightly yellowish oil.

$^1$H nuclear magnetic resonance (n.m.r.) (200 MHz, $D_2O$) : $\delta$ (in ppm): 1.1–1.3 m (17H, –$(CH_2)_7$–, –COO–C–$CH_3$), 1.38–1.72 m (4H, $^+$N–C–$CH_2$–, –CON–C–$CH_2$–), 2.9 s/2.98 s (3H, –CO–N($CH_3$) *trans* and *cis* conformers), 3.2–3.38 m (2H, $CH_2$–NCO), 3.5 s (6H, $>N^+$ $(CH_3)_2$–), 3.69 m (2H, –$CH_2$–$N^+$), 4.17 q (2H, –COO–$CH_2$), 4.78 m (2H, $^+$N–$CH_2$–COO–), 5.58 m (1H, CH=C–CON–*trans*), 6.2 m (1H, CH=C–CON–*cis*), 6.5 m (1H, =CH–CON–).

N,N-*Dimethyl*–N-*11-(*N-*methylacrylamidyl)undecyl*-N-*(ethyloxycarbonyl)propyl ammonium bromide* **2**. A total of 5 g (1.77 mmol) of *N*-methyl-*N*-11-(dimethylamino)undecyl acrylamide[18], 4.49 g (2.30 mmol) of ethyl 4-bromobutyrate and 100 mg of DBPC were refluxed in 57 ml of acetonitrile for 72 h under argon. After removal of the solvent, the crude product was redissolved in water and lyophilized.

Yield: 8.14 g (96%), slightly yellowish oil.

$^1$H n.m.r. (200 MHz, $CDCl_3$): $\delta$ (in ppm): 1.15–1.4 m (17H, –COO–C–$CH_3$, –$(CH_2)_7$–), 1.4–1.75 m (4H, –$C_7$–$CH_2$–C–$N^+$–, –CON–C–$CH_2$–), 1.96 m (2H, $N^+$–C–$CH_2$–C–COO–), 2.48 t (2H, –$CH_2$–COO–), 2.93 s/3.02 s (3H, –CONC$H_3$ *trans* and *cis* conformer), 3.22–3.65 m (12H, $(CH_3)_2N^+(CH_2$–$R)_2$, $CH_2$–NCO), 4.08 q (2H, –COO–$CH_2$–), 5.62 m (1H, CH=C–CON–*trans*), 6.24 m (1H, CH=C–CON–*cis*), 6.52 m (1H, =CH–CON–).

N-*Decyl*-N-*(2*-N-*methylacrylamidyl)ethyl*-N-*(ethyloxycarbonyl)methyl*-N-*methylammonium bromide* **3**. A total of 7.35 g (2.6 mol) of *N*-methyl-*N*-(*N*′-methyl-3-azatridecyl)acrylamide[17], 5.75 g (3.44 mmol) of ethyl 2-bromoacetate and 100 mg of DBPC were dissolved in 80 ml of acetonitrile, and refluxed for 40 h under nitrogen. After evaporating the solvent, the oily crude product was repeatedly extracted with diethylether at room temperature, redissolved and precipitated into ether at 0°C.

Yield: 9.12 g (82%), colourless, hygroscopic wax.

$^1$H n.m.r. (200 MHz, $CDCl_3$): $\delta$ (in ppm): 0.90 t (3H, $CH_3$–), 1.25–1.4 m (17H, –$(CH_2)_7$–, –COO–C–$CH_3$), 1.7–1.9 m (2H, –$C_7$–$CH_2$–C–$N^+$), 3.3 s (3H, –CON–$CH_3$), 3.63 s (3H, –$N^+$–$CH_3$), 3.8–3.92 m (2H, –$C_7$–$CH_2$–$N^+$), 4.0–4.35 m (6H, –$N^+$–$CH_2$–$CH_2$–NCO–, –COO–$CH_2$–), 4.7–4.9 m (2H, –$N^+$–$CH_2$–COO–), 5.8 m (1H, CH=C–CON–*trans*), 6.35 m (1H, CH=C–CON–*cis*), 6.6 m (1H, =CH–CON–).

*N-Decyl-N-(2-(N-methyl)acrylamidyl)ethyl-N-3-(ethyloxycarbonyl)propyl-N-methylammonium bromide* **4**. A total of 10.49 g (3.71 mmol) of *N*-methyl-*N*-(*N'*-methyl-3-azatridecyl) acrylamide[17], 9.46 g (4.85 mmol) of ethyl 4-bromobutyrate and 100 mg of DBPC were dissolved in 120 ml of acetonitrile. The mixture was refluxed for 7 days under nitrogen. The acetonitrile was evaporated and the crude product purified by flash chromatography (Silicagel, eluent acetone).

Yield: 6.78 g (38%), slightly brownish oil.

$^1$H n.m.r. (200 MHz, $CDCl_3$): $\delta$ (in ppm): 0.78 t (3H, –$CH_3$), 1.15–1.30 m (17H, –$(CH_2)_7$–, –COO–C–$CH_3$), 1.62–1.80 m (2H, –$C_7$–$CH_2$–C–$N^+$), 2.01 m (2H, $N^+$–C–$CH_2$–C–COO–), 2.44 t (2H, $CH_2$–COO–) 3.15 s / 3.23 s (3H, $CH_3$–NCO), 3.3 s (3H, $N^+$–$CH_3$), 3.32–3.45 m (2H, $C_7$–C–$CH_2$–$N^+$), 3.5–3.63 m (2H, $N^+$–$CH_2$–C–C–COO–), 3.8–3.9 m (4H, $N^+$–$CH_2$–$CH_2$–NCO), 4.05 q (3H, –COO–$CH_2$–), 5.68 m (1H, CH=C–CON–*trans*), 6.22 m (1H, CH=C–CON–*cis*), 6.50 m (1H, =CH–CON–).

*2-(N,N-Dimethyl-N-(11-(N-methylacrylamidyl)-undecyl)ammonioacetate* **5**. A total of 3 g (0.67 mol) of **1** were dissolved in water at room temperature, adding a slight excess (125%) of $OH^-$ loaded anion exchange resin. The mixture was stirred for 90 min, the resin filtered off, and the aqueous solution lyophilized.

Yield: 2.2 g (quantitative), very hygroscopic oil.

$^1$H n.m.r. (200 MHz, $D_2O$): $\delta$ (in ppm): 1.05–1.25 m (14H, $(CH_2)_7$), 1.4–1.63 m (4H, CON–C–$CH_2$, $N^+$–C–$CH_2$), 2.82 s, 2.95 s (3H, $CH_3$–NCO), 3.04 s (6H, $(CH_3)_2N^+$), 3.2–3.42 m (4H, CON–$CH_2$, $N^+$–$CH_2$–C–$C_7$), 3.7 s (2H, $N^+$–$CH_2$–$COO^-$), 5.63 m (1H, CH=C–CON–*trans*), 6.0 m (1H, CH=C–CON–), 6.58 m (1H, =CH–CON–).

Fast atom bombardment (FAB) mass spectrum: mass at 341.3 $(M+1)^+$, 363.2 $(M+Na)^+$.

*4-(N,N-(Dimethyl)-N-11-(N-methylacrylamidyl)-undecyl)ammoniobutyrate* **6**. A total of 3 g (0.63 mmol) of **2** were dissolved in water at room temperature. Then, a slight excess (125%) of $OH^-$ loaded anion exchange resin was added and the mixture stirred for 90 min. The resin was removed by filtration, and the aqueous solution lyophilized.

Yield: 2.3 g (quantitative), very hygroscopic oil.

$^1$H n.m.r. (200 MHz, $D_2O$): $\delta$ (in ppm): 0.95–1.27 m (14H, –$(CH_2)_7$–), 1.32–1.65 m (4H, $N^+$–C–$CH_2$–$C_7$–, –CON–C–$CH_2$–), 1.78 m (2H, $N^+$–C–$CH_2$–C–$COO^-$), 2.04 t (2H, –$CH_2$–$COO^-$), 2.78 s, 2.85 s, 2.9 s (9H, $(CH_3)_2N^+$, –CONCH$_3$ *trans* and *cis* conformer), 3.0–3.3 m (6H, –$CH_2$–$N^+$–$CH_2$–, –CON–$CH_2$–), 5.6 m (1H, CH=C–CON–*trans*), 5.95 m (1H, CH=C–CON–*cis*), 6.53 m (1H, =CH–CON–).

FAB mass spectrum: mass at 369.5 $(M+1)^+$, 391.2 $(M+Na)^+$.

*2-(N-Decyl-N-2-(N-methylacrylamidyl)ethyl-N-methyl)ammonioacetate* 7. A total of 2.83 g (0.63 mmol) of **3** was dissolved in water at room temperature. An equimolar amount of $OH^-$ loaded anion exchange resin was added and the mixture was stirred for 90 min. After filtering the resin off, the aqueous solution was lyophilized.

Yield: 2.10 g (quantitative), very hygroscopic oil.

$^1$H n.m.r. (200 MHz, $D_2O$): $\delta$ (in ppm): 0.72 t (3H, $CH_3$–), 1.1–1.4 m (14H, –$(CH_2)_7$–), 1.6–1.8 m (2H, –$CH_2$–C–$N^+$), 2.88 s, 2.98 s (3H, –CONCH$_3$ *trans* and *cis* conformer), 3.08 s (3H, $CH_3$–$N^+$), 3.3–3.55 m (2H, –$C_7$–$CH_2$–$N^+$), 3.55–3.9 m (6H, –CON–$CH_2$–$CH_2$–$N^+$–$CH_2$–$COO^-$), 5.65 m (1H, CH=C–CON–*trans*), 6.05 m (1H, CH=C–CON–*cis*), 6.55 m (, 1H, =CH–CON–).

FAB mass spectrum: mass at 341.4 $(M+1)^+$, 363.2 $(M+Na)^+$.

*4-(N-Decyl-N-2-(N-methylacrylamidyl)ethyl-N-methyl)ammoniobutyrate* **8**. A total of 3.78 g (0.79 mmol) of **4** were dissolved in water and an excess (125%) of $OH^-$ loaded anion exchange resin was added. The mixture was stirred for 4 h at room temperature, the resin filtered off, and the solution lyophilized. (The recovered resin contained substantial amounts of side product which could be extracted with $CHCl_3/CH_3OH$ 1/1; according to n.m.r. analysis, the side product consisted of 4-(*N*-decyl-*N*2-(*N*-methyl-2'-hydroxy-propionamidyl)ethyl-*N*-ethyl)ammoniobutyrate, i.e. the product of $H_2O$ addition to the acrylamide moiety of **8**.)

Yield: 1.7 g (63%), very hygroscopic oil.

$^1$H n.m.r. (200 MHz, $D_2O$): $\delta$ (in ppm): 0.73 t (3H, $CH_3$–), 1.08–1.28 m (14H, –$(CH_2)_7$–), 1.52–1.74 m (2H, –$C_7$–$CH_2$–C–$N^+$), 1.85 m (2H, $N^+$–C–$CH_2$–C–$COO^-$), 2.12 t (2H, $CH_2$–$COO^-$), 2.3–2.45 m (impurities), 2.7–3.45 m (12H, –$N^+$–$CH_3$, $CH_3$–N–CO, –$N^+(CH_2$–R$)_3$–), 3.76 m (2H, –$CH_2$–NCO), 5.7 m (1H, CH=C–CON–*trans*), 6.08 m (1H, CH=C–CON–*cis*), 6.6 m (1H, =CH–CON–).

### *Polymers*

Monomer solutions of 5–10% by weight in water were purged with argon for 40 min, sealed and reacted for 16–48 h at 60°C, using 2 mol% azobisisobutyronitrile (AIBN) as initiator. The solubility of AIBN in the mixtures is attributed to micellar solubilization by the monomers.

Water-insoluble polymers were filtered off and washed several times with water. Then, they were dissolved in $CH_3OH/CHCl_3$ (1/1 v/v), precipitated into water, recovered, and washed in excess water. Reaction mixtures containing water-soluble polymers were lyophilized. The residue was dissolved in isopropanol, precipitated into acetone and collected. Polymers were dried *in vacuo* at 60°C.

### *Analysis*

N.m.r. spectra were taken by a Gemini 100 MHz spectrometer. I.r. spectra were recorded by an *FT*i.r. apparatus (Nicolet 205). FAB mass spectroscopy was

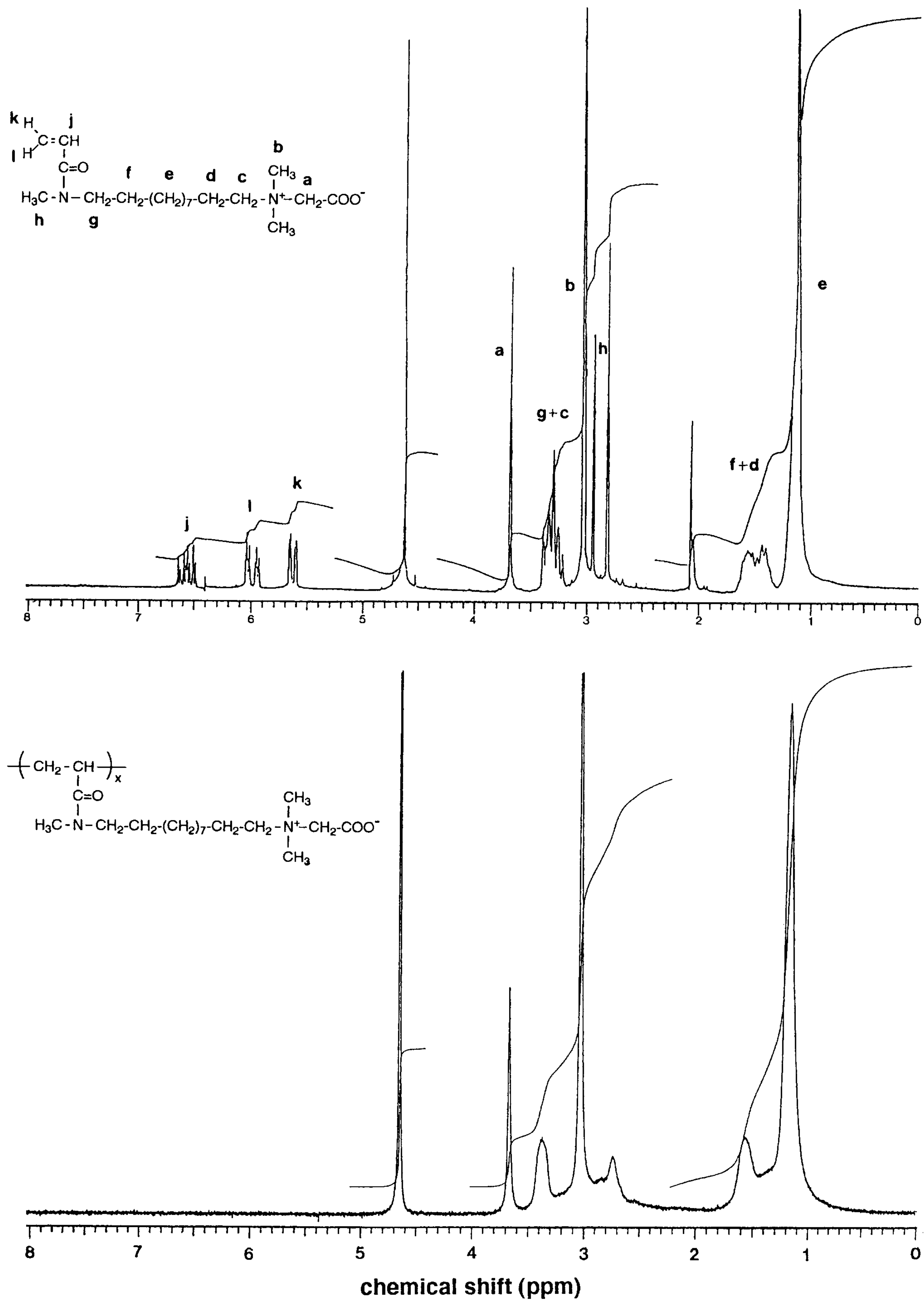



**Figure 2** $^1$H n.m.r. spectra of monomeric carbobetaines **5** and **8**, and of their polymers in $D_2O$ and $CD_3OD$

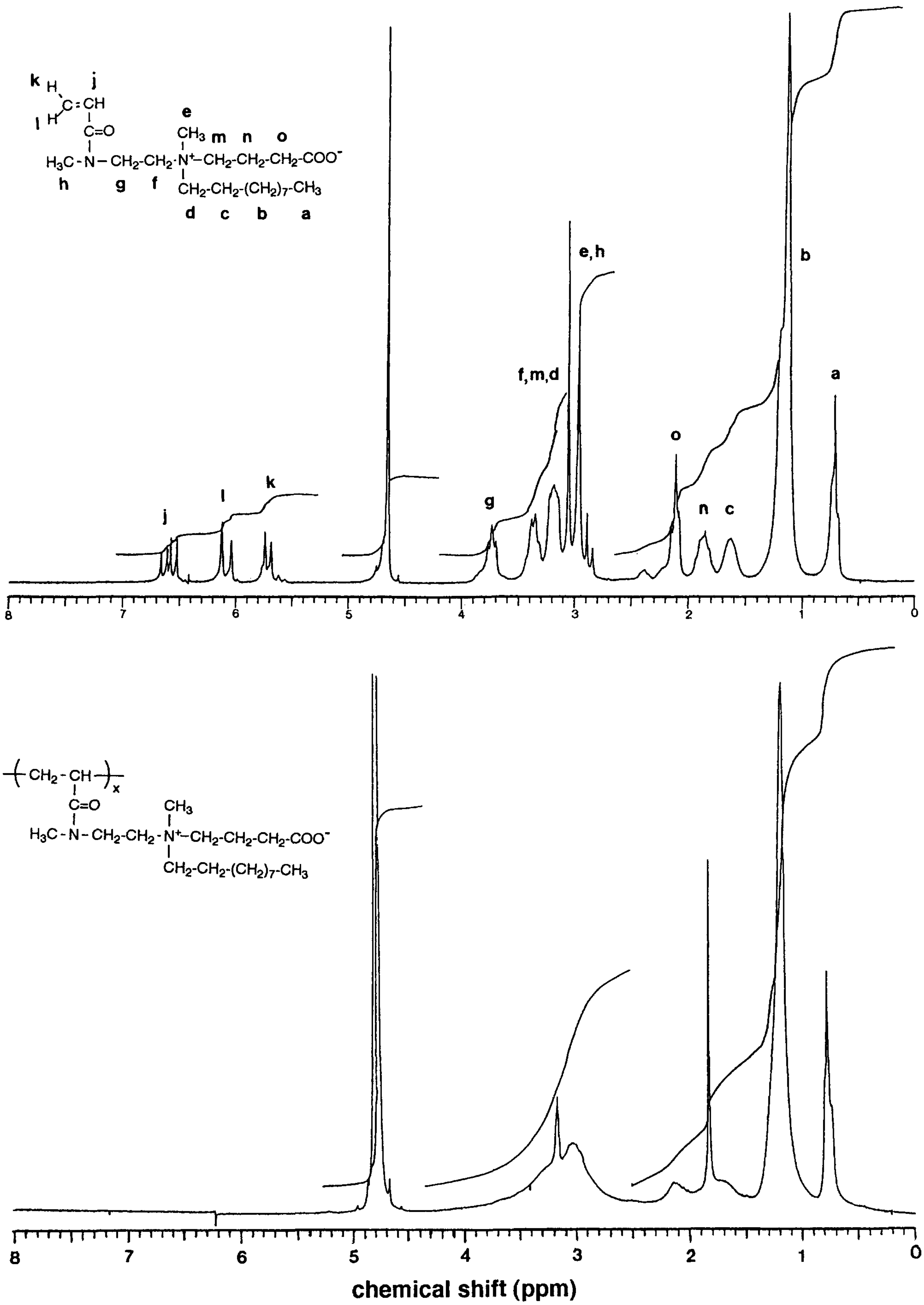



**Figure 2** (Continued)

kindly performed by the laboratory of E. De Hoffmann (Université Catholique de Louvain) using an *m*-nitrobenzyl alcohol matrix. Elemental analysis was performed by the Chemistry Department, University College London.

Viscometry was performed by a semi-automatic Ubbelohde capillary viscometer (Schott) in ethanol at 25°C.

Thermogravimetry was performed on a thermogravimetric analyser (TGA-500 SETARAM), with a heating rate of $10°C min^{-1}$ in nitrogen atmosphere. Differential scanning calorimetry (d.s.c.) was performed with a Perkin-Elmer DSC7, applying heating and cooling rates of $20°C min^{-1}$. X-ray scattering experiments were done with a diffractometer (Siemens D-500), using the Ni-filtered Cu-K$\alpha$ line ($\lambda = 0.1541$ nm).

## RESULTS AND DISCUSSION

### *Monomer synthesis*

The cationic precursor monomers **1**–**4** are prepared in three steps: (i) preparation of the mixed secondary–tertiary diamine; (ii) conversion to the tertiary acrylamide; (iii) alkylation of the tertiary amine group by a $\omega$-bromoester. The latter reaction takes place much faster with ethyl bromoacetate than with ethyl 4-bromobutyrate, requiring an appropriate choice of solvent. Acetonitrile proved to be satisfactory whereas both nitromethane and ethanol are not suited as they add partially to the double bond of the acrylamide moiety. Presumably, this side reaction is catalysed by the tertiary amine groups.

The key step in the synthesis of the zwitterionic monomers **5–8** is the conversion of the cationic precursors **1–4** to carbobetaines. Following the preparation mode for simple analogues, the cationic compounds were passed over an $OH^-$ loaded anion exchange resin, resulting in exchange of the bromide counterions, and subsequently in the rapid basic hydrolysis of the ester to give ammoniocarboxylate and the corresponding alcohol. This strategy allows the preparation of carbobetaines free of salt[12–15].

Whereas this method provides non-functionalized betaines in good yields, in the case of the acrylamides **1**–**4** an important side reaction takes place: $^1H$ and $^{13}C$ n.m.r. spectra indicate the successful hydrolysis of the ester bond while preserving the amide moiety; however, the signals of the acryl moiety are nearly absent after the reaction, and a new signal at 2.5–2.6 ppm appears (in $CDCl_3$) with an intensity corresponding to two protons. Additionally, the integral of the complex multiplet signal between 3.4 and 4 ppm, which is primarily attributed to the methylene groups in the $\alpha$-positions of the ammonium and the amide nitrogens, is too intense, the difference amounting to roughly two additional protons. All other signals which are present in the original cations and which should also be present in the carbobetaines are preserved. These findings can be explained by the formation of $\beta$-hydroxypropionamides, i.e. by the addition of water onto the acrylic double bond.

*N,N*-Dimethylacrylamide and tertiary amine acrylamide precursors do not react under these conditions; the amide bond is not hydrolysed, nor is the acrylic double bond attacked. The surprisingly facile addition of water onto the double bond in the case of **1**–**4** is attributed to the proximity of the hydroxide ions intermediately bound to the ammonium group to the acrylamide moiety. In fact, a similar neighbouring group effect may be responsible for the efficient addition of ethanol and nitromethane onto the acrylamide moiety during the alkylation of the tertiary amine intermediates. In agreement with this reasoning, the acrylamide moieties in **3** and **4**, which are separated by two methylene groups only from the ammonium group, are more sensitive towards the addition reaction than the acrylamide moieties in **1** and **2**.

Despite the problems discussed above, carbobetaines **5–8** could be prepared in pure form when the precursor cations were slowly titrated with stoichiometric equivalents of the ion exchange resin, or a slight excess only. Under these conditions, no addition product was observed. As already observed for the quaternization reaction, ammoniumacetates react more rapidly than ammoniumbutyrates. Representative n.m.r. spectra of the monomeric carbobetaines are shown in *Figure 2* for monomers **5** and **8** in $D_2O$.

### *Surfactant properties of the monomers*

The structures of the newly prepared cationic and zwitterionic monomers **1**–**8** are those of surfactants, as for related betaine monomers[8,18,19]. Indeed, their aqueous solutions are foaming, show strongly reduced surface tensions, and form lyotropic mesophases when concentrated. The surfactant properties of the monomers are exploited for their polymerization in homogeneous aqueous solutions despite the use of basically water-insoluble AIBN as initiator, due to the solubilization capacity of the micelles formed. From their aqueous polymerization mixtures, poly (**7**) and poly (**8**) precipitate in the course of the reaction.

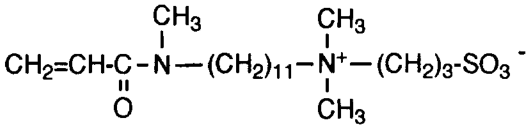
### *Solubilities of the polymers*

Hydrophobized betaine polymers are advantageously classified by their geometry: 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[8]. Within this classification, polymers of **5** and of **6** belong to the 'tail-end' type, whereas polymers of **7** and of **8** fall into the 'head' type.

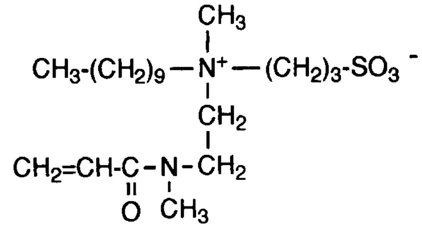
The solubility of the newly prepared carbobetaine-bearing poly(acrylamides)s is controlled by their geometry, in agreement with previous studies of analagous polymers[8,17,18]. Thus, the tail-end type polymers, poly (**5**) and poly (**6**), dissolve in highly polar solvents such as water or formamide, but not in less polar solvents such as $CHCl_3$. In contrast, the head type polymers poly (**7**) and poly (**8**) dissolve in $CHCl_3$, but do not dissolve in water. Compared to analogous sulfobetaine-bearing poly(acrylamides)s[17,18], such as poly (**9**) or poly (**10**) (*Figure 3*), the choice of possible solvents is considerably enlarged; for example, both types of polymer geometry dissolve in trifluoroethanol, methanol and ethanol as solvents of intermediate polarity. However, acetone, ethylacetate and tetrahydrofuran are non-solvents for all the polymers.

### *Viscometric studies*

Viscosities of solutions of polymeric carbobetaines poly (**7**) and poly (**8**) and of the analogous polymeric sulfobetaine poly (**10**) in ethanol were studied, the results being depicted in *Figure 4*. This set of polymers varies in



**9**



**10**

**Figure 3** Poly(sulfobetaines) used as references

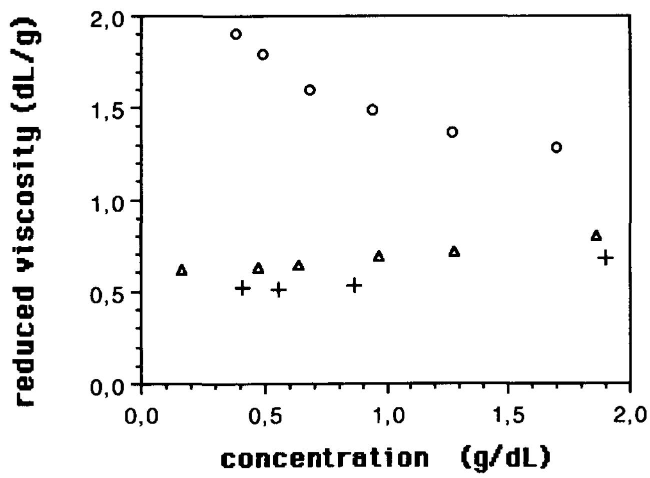



**Figure 4** Reduced viscosity of solutions of polyzwitterions in ethanol at 25°C in dependence on the concentration: $\Delta$ = poly (**7**), $\bigcirc$ = poly (**8**), + = poly (**10**)

the nature of the zwitterionic group, either with respect to the anionic group used ($-COO^-$ *versus* $SO_3^-$), or to the number of methylene groups $n$ separating the cationic and the anionic group ($-(CH_2)-$ *versus* $-(CH_2)_3-$, cf. Scheme 1).

*Figure 4* illustrates the absence of polyelectrolyte behaviour for poly (**7**) and poly (**10**), both exhibiting approximate linear dependence of the reduced viscosity on the polymer concentration. This finding is in agreement with a fully zwitterionic character of the polymers, i.e. the number of cationic and anionic groups in the macromolecules is identical. This implies the full deprotonation of the strongly acidic ammoniopropane sulfonate and ammonioacetate moieties. In contrast, the reduced viscosity of ethanolic solutions of ammoniobutyrate poly (**8**) shows a marked increase upon dilution, which is characteristic for polyelectrolytes. The result can be easily rationalized by the reduced acidity of the ammoniobutyrate group compared to the ammonioacetate group[13,16]; the partial protonation of the carboxylates in protic solvents such as ethanol converts the polybetaine into a weak polycation.

In the case of polyzwitterions poly (**7**) and poly (**10**), the missing polyelectrolyte character allows the extrapolation of the reduced viscosity to zero concentration, thus providing the intrinsic viscosities. The values of $0.6\,dl\,g^{-1}$ for poly (**7**) and of $0.5\,dl\,g^{-1}$ for poly (**10**) point to high molar masses.

*General bulk properties*

The polymeric carbobetaines are very hygroscopic. Exposed even for short periods to air, they readily adsorb substantial amounts of water. Water uptake under ambient atmosphere continues for tail-end polymers poly (**5**) and poly (**6**) with prolonged exposure to air until the polymers finally dissolve in the water adsorbed, in contrast to their poly(sulfobetaine) analogue poly (**9**). The adsorbed water is fully removed only by extensive drying at elevated temperatures.

The *FT*i.r. spectra of the poly(ammoniobutyrate)s poly (**6**) and poly (**8**) taken as KBr pellets exhibit two intense sharp peaks at 1635–1640 and $1575\,cm^{-1}$ (see *Figure 5*). These peaks are attributed to the carbonyl stretching modes of the tertiary amide and the carboxylate moiety. The *FT*i.r. spectra of the poly(ammonioacetate)s poly (**5**) and poly (**7**) exhibit only one intense broadened peak at $1635–1640\,cm^{-1}$. These peaks are attributed to the superposition of the carbonyl stretching modes of the tertiary amide and the carboxylate moiety. The spectral differences between the ammoniobutyrates and the ammonioacetates are in good agreement with the known dependence of the carboxylate band in carbobetaines on the distance from the ammonium group[13]. It is noteworthy that for all polymers, no peak in the region $1760–1680\,cm^{-1}$, indicative of the protonated carboxyl groups, is observed, and neither are their characteristic very broad bands in the range of 3000 and $960–875\,cm^{-1}$. Therefore we conclude that all the poly(carbobetaine)s investigated exist in bulk in their zwitterionic form, in contrast to the results obtained in solution (cf. *Figure 4*).

*Thermal properties*

Thermogravimetric experiments revealed distinct differences in the thermal stability of the poly(carbobetaine)s, which is controlled by the betaine moiety. Whereas the ammonioacetates poly (**5**) and poly (**7**) begin to decompose above 200°C, and thus are only slightly less stable than their sulfobetaine analogues such as poly (**9**) and poly (**10**), the ammoniobutyrates poly (**6**) and poly (**8**) begin to decompose around 140°C (*Table 1*). This reduced thermal stability limits the use of polymeric ammoniobutyrates considerably.

The origin of the low thermal stability of the polymeric ammoniobutyrates is not fully clear. It might be due a conformationally facilitated intramolecular nucleophilic attack of the carboxylate moiety on the ammonium group, thus eliminating butyrolactone. This hypothesis is backed by an *FT*i.r. analysis of the insoluble pyrolysis products (*Figure 5*): whereas the carbonyl signal of the tertiary amide at $1635\,cm^{-1}$ is preserved, the carboxylate stretching modes at 1575 and $1405\,cm^{-1}$ are lost upon heating to 150°C. In parallel, new signals appear at 2765, 2780 and $2815\,cm^{-1}$ which would match with a newly formed $-CH_2-N(CH_3)_2$ moiety as produced by the loss of butyrolactone.

Owing to the high density of charged groups,

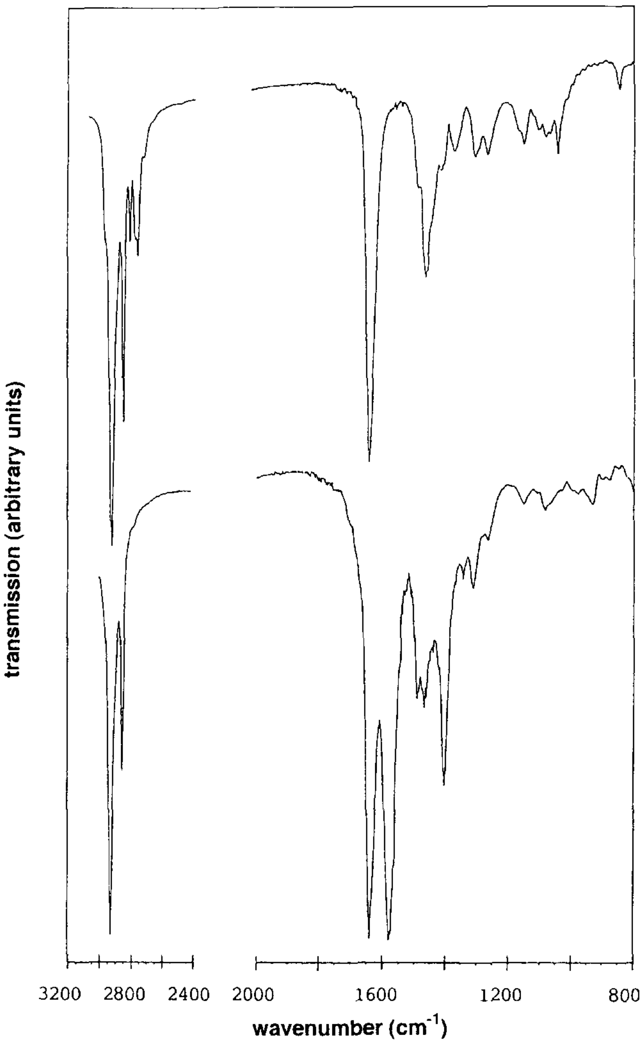



**Figure 5** *FT*i.r. spectra of ammoniobutyrate poly (**8**) before heating (bottom) and after heating (top) to 150°C (KBr pellets)

**Table 1** Thermal properties of polyzwitterions

| Polymer | Glass transition temperature, $T_g$ (°C) | Onset of thermal decomposition (°C) |
|---|---|---|
| poly (**5**) | 140 | 200 |
| poly (**6**) | – | 145 |
| poly (**7**) | 163 | 200 |
| poly (**8**) | – | 140 |
| poly (**9**) | – | 230 |
| poly (**10**) | – | 210 |

zwitterionic homopolymers of vinyl compounds do generally not exhibit glass transitions below their decomposition temperatures[1,7]. This also applies to the extensively studied alkyl-substituted poly(sulfobetaine)s[9], although in general alkyl substituents lower the glass transition temperatures ($T_g$) of acrylic and methacrylic polymers efficiently[20]. In order to reduce $T_g$ values of poly(sulfobetaine)s sufficiently, complex substitution patterns or particular substituents are needed[8,9,21–23].

In the case of the hydrophobized poly(carbobetaine)s, however, glass transitions are found in some cases (*Table 1*). For the ammoniobutyrates poly (**6**) and poly (**8**), no $T_g$ could be found below 130°C by d.s.c. measurements after extensive drying (small amounts of water act as an efficient plasticizer[22]). However, for the ammonioacetates poly (**5**) and poly (**7**), glass transitions are observed at 140 and 163°C respectively. Accordingly, head-type polymers have higher $T_g$s than their tail-end analogues, which might be due to the increased steric crowding close to the backbone of the former. Note also the lower $T_g$s of poly(carbobetaine)s in comparison to their poly(sulfobetaine) analogues poly (**9**) and poly (**10**). How the distance between the ammonium and the carboxylate moiety will influence $T_g$, remains an open question owing to the low thermal stability of the ammoniobutyrates under investigation.

*Bulk structures*

The dried poly(carbobetaine)s were investigated by small- and wide-angle X-ray diffraction at ambient temperature (*c.* 22°C). Although not crystalline, polymers poly (**5**)–poly (**8**) exhibit small-angle reflections indicative of a superstructure. The diffraction patterns are characteristic for the respective polymer geometries, as illustrated in *Figure 6*. The powder diffractograms show many similarities with those of analogous hydrophobized poly(sulfobetaine)s[9,17,24].

The diffraction patterns observed are of two types. Head-type polymers poly (**7**) and poly (**8**) give patterns with only one intense peak at 3.0° and 3.1° respectively, with calculated Bragg distances of 2.94 and 2.85 nm (cf. pattern 'C' in ref. 9). Tail-end type polymers poly (**5**) and poly (**6**) exhibit one peak with much lower intensity compared to the halo at 5.4 and 5.5°, with calculated Bragg distances of 16.4 and 16.0 nm. The pattern observed is somewhat similar to their sulfobetaine analogues such as poly (**9**) (cf. pattern 'A' in ref. 9), although a second small peak at smaller angles is missing in the diffractograms. Since for both tail-end and head-type poly(sulfobetaine)s–exhibiting diffraction patterns A and C–, the presence of complex lamellar structures has been demonstrated[24], we assume a lamellar superstructure in the case of the poly(carbobetaine)s poly (**5**)–poly (**8**), also.

The results for the poly(carbobetaine)s poly (**5**)–poly (**8**) corroborate that polymer geometry is the most important factor determining the type of superstructure of the polymers. Nevertheless, the chemical nature of the zwitterionic group chosen is of importance too. This is exemplified by comparing the diffraction patterns of poly(ammoniobutyrate)s poly (**6**) and poly (**8**) with those of the analogous poly(ammoniopropanesulfonate)s poly (**9**) and poly (**10**), i.e. comparing polymers with different anionic group but identical distance between the cationic and anionic group[9]; not only is the detailed position of the scattering peak markedly influenced, but also the general appearance of the diffraction pattern. This means that the organization of the fragments is sensitive to whether a sulfonate or a carboxylate moiety is used as anionic group. In contrast, in the case of the poly (carbobetaine)s, the distance between the anionic and the cationic groups seems to be of less importance, as for the analogous pairs of poly(ammonioacetate)s and poly-(ammoniobutyrate)s poly (**5**)/poly (**6**) of the tail-end geometry and poly (**7**)/poly (**8**) of the head geometry, the diffraction patterns and the position of the peaks are identical within the experimental accuracy.

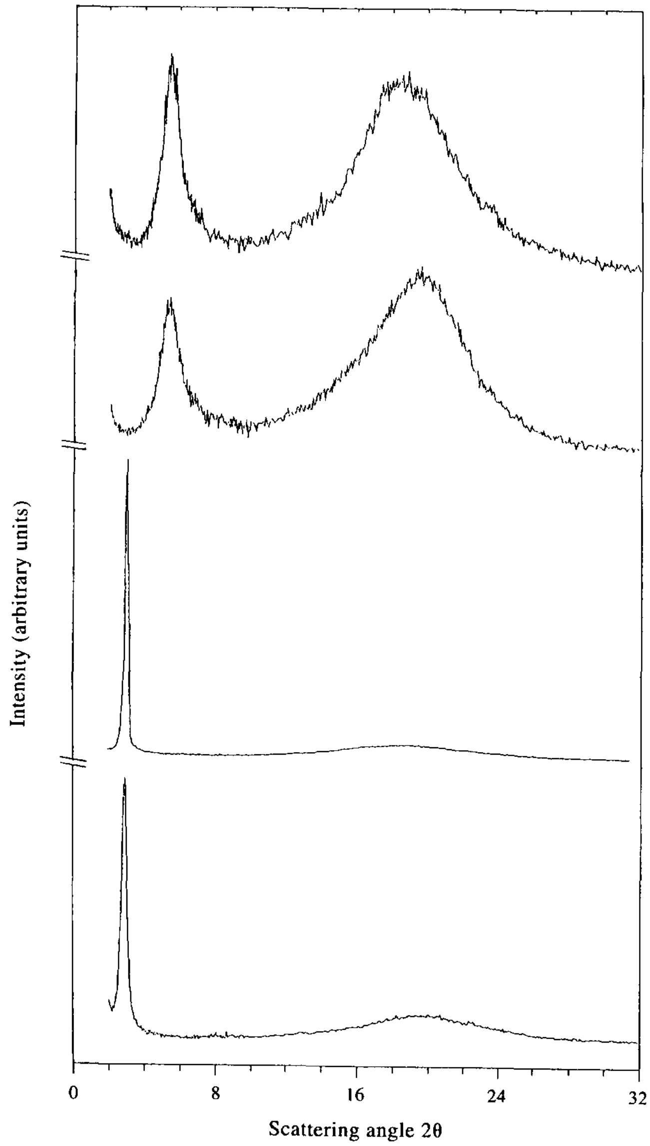



**Figure 6** X-ray powder diffractograms of polymeric carbobetaines poly (**5**)–poly (**8**) (top to bottom)

## CONCLUSIONS

Despite some particular side reactions, carbobetaine acrylamides and their polymers are accessible via a synthetic route avoiding the presence of salt. The hydrophobized monomeric and polymeric carbobetaines prepared exhibit many similarities to their sulfobetaine analogues. In more detailed comparison, the poly(carbobetaine)s are more hygroscopic and show improved solubility. Viscometric studies in ethanol show no, or only weak, polyelectrolyte behaviour, depending on the proximity of the carboxyl group to the ammonium moiety. Concerning bulk properties, thermal stability is decreased, in particular in the case of ammoniobutyrates, and glass transitions occur at lower temperatures. X-ray diffractograms show similar diffraction patterns indicating the presence of superstructures whose detailed forms depend on the polymer geometry. This dependence follows the established rules for polymeric sulfobetaines.

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