

Zwitterionic polymers with carbobetaine moieties

Nelly Bonte and André Laschewsky*

Université Catholique de Louvain, Dépt. de Chimie, Place L. Pasteur 1,
 B-1348 Louvain-la-Neuve, Belgium
 (Received 23 June 1995)

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(ammonio propane sulfonate)s and poly(ammonio butane 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)s¹¹, 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 synthesized 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 ammonioacetates 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.

* To whom correspondence should be addressed

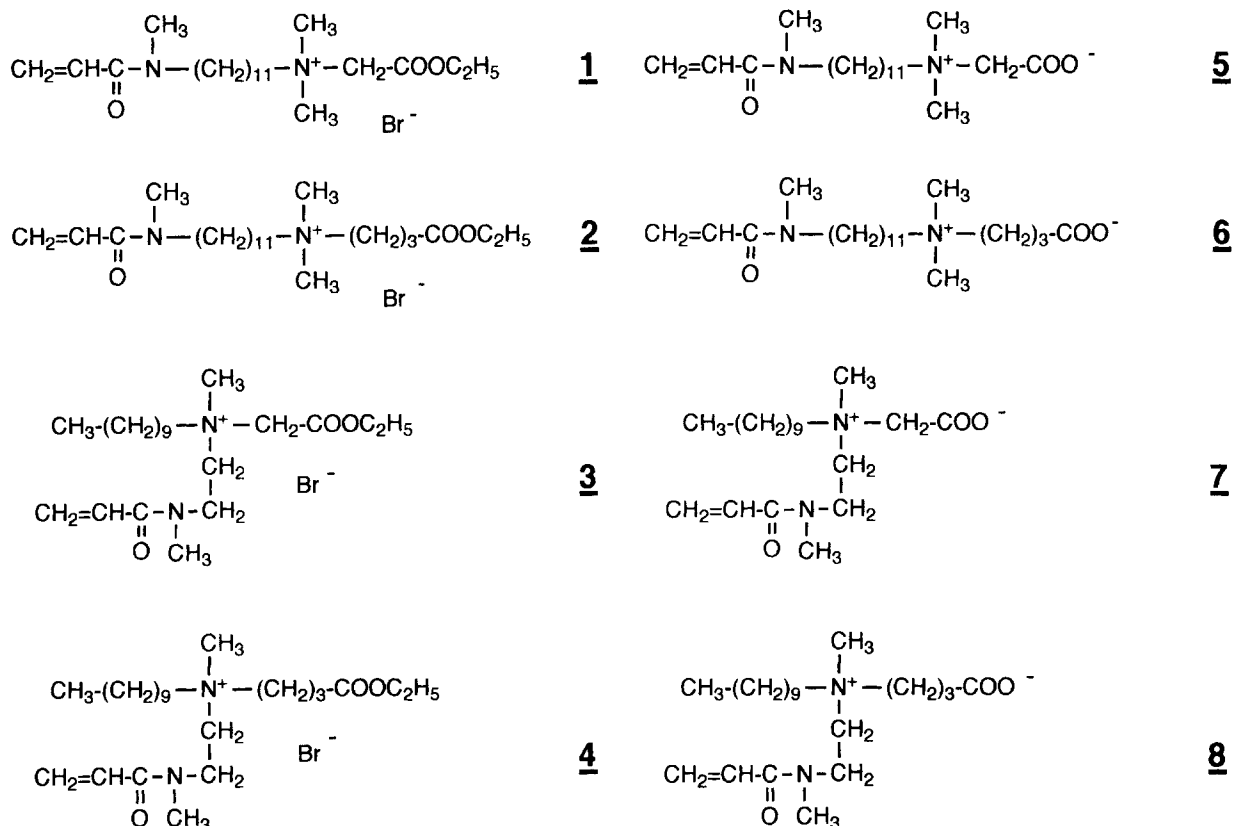
Scheme 1 General structure of ammonioalkanesulfonates and ammonioalkancarboxylates ($n \geq 1$)

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 $6.27 \times 10^{-4} \text{ mol g}^{-1}$ 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 acrylamide¹⁸, 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.

^1H nuclear magnetic resonance (n.m.r.) (200 MHz, D_2O): δ (in ppm): 1.1–1.3 m (17H, $-(\text{CH}_2)_7-$, $-\text{COO}-\text{C}-\text{CH}_3$), 1.38–1.72 m (4H, $^+\text{N}-\text{C}-\text{CH}_2-$, $-\text{CON}-\text{C}-\text{CH}_2-$), 2.9 s/2.98 s (3H, $-\text{CO}-\text{N}(\text{CH}_3)$ *trans* and *cis* conformers), 3.2–3.38 m (2H, CH_2-NCO), 3.5 s (6H, $>\text{N}^+(\text{CH}_3)_2-$), 3.69 m (2H, $-\text{CH}_2-\text{N}^+$), 4.17 q (2H, $-\text{COO}-\text{CH}_2$), 4.78 m (2H, $^+\text{N}-\text{CH}_2-\text{COO}-$), 5.58 m (1H, $\text{CH}=\text{C}-\text{CON}-\text{trans}$), 6.2 m (1H, $\text{CH}=\text{C}-\text{CON}-\text{cis}$), 6.5 m (1H, $=\text{CH}-\text{CON}-$).

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 acrylamide¹⁸, 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.

^1H n.m.r. (200 MHz, CDCl_3): δ (in ppm): 1.15–1.4 m (17H, $-\text{COO}-\text{C}-\text{CH}_3$, $-(\text{CH}_2)_7-$), 1.4–1.75 m (4H, $-\text{C}_7-\text{CH}_2-\text{C}-\text{N}^+$, $-\text{CON}-\text{C}-\text{CH}_2-$), 1.96 m (2H, $\text{N}^+-\text{C}-\text{CH}_2-\text{C}-\text{COO}-$), 2.48 t (2H, $-\text{CH}_2-\text{COO}-$), 2.93 s/3.02 s (3H, $-\text{CONCH}_3$ *trans* and *cis* conformer), 3.22–3.65 m (12H, $(\text{CH}_3)_2\text{N}^+(\text{CH}_2-\text{R})_2$, CH_2-NCO), 4.08 q (2H, $-\text{COO}-\text{CH}_2-$), 5.62 m (1H, $\text{CH}=\text{C}-\text{CON}-\text{trans}$), 6.24 m (1H, $\text{CH}=\text{C}-\text{CON}-\text{cis}$), 6.52 m (1H, $=\text{CH}-\text{CON}-$).

N-Decyl-*N*-(2-*N*-methylacrylamidyl)ethyl-*N*-(ethyl-oxycarbonyl)methyl-*N*-methylammonium bromide **3**. A total of 7.35 g (2.6 mol) of *N*-methyl-*N*-(*N'*-methyl-3-azatridecyl)acrylamide¹⁷, 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

Download English Version:

<https://daneshyari.com/en/article/5198692>

Download Persian Version:

<https://daneshyari.com/article/5198692>

[Daneshyari.com](https://daneshyari.com)