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Synthesis and investigation of new amphiphilic poly(carbobetaine)s made from diallylammonium monomers

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Abstract

A series of new hydrolytically stable poly(carbobetaine)s was synthesised varying the length and the position of the hydrophobic side chains, together with their cationic analogues. The synthetic strategy avoids the presence of residual salt in the polybetaines, thus making them well suited for model studies. The betaine monomers as well as their cationic analogues bearing the equivalent of an undecyl chain exhibit surfactant properties ("surfmers"). The corresponding polymers, however, which are formed by cyclopolymerisation, are insoluble in water, though hygroscopic. In contrast, the hydrophobic chains favour the solubility in alcohols and allow the formation of superstructures in bulk. The poly(carbobetaine)s form homogeneous blends with selected inorganic salts, to provide organic–inorganic hybrid materials.

Keywords: Polyzwitterions; Poly(carbobetaine)s; Diallylammonium monomers

1. Introduction

Stable zwitterionic polymers are highly dipolar materials with some specific and unique properties [1,2]. Also, they may serve as models for ampholytic natural polymers, such as proteins in the vicinity of the isoelectric point, or DNA at low pH. Moreover, homogeneous blends can be prepared from certain zwitterionic polymers by mixing with an equimolar amount of inorganic salts, thus providing new organic–inorganic hybrid materials [3–5].

Up to now, most studies have focused on poly(ammoniopropane sulfonate)s [3–11], and on polymeric phosphatidylcholines [12–14]. They are conveniently prepared by ring-opening alkylation of tertiary amines, avoiding the presence of residual salt. Poly(carbobetaine)s [15–25] are an alternative class of polyzwitterions, which offer in comparison good molecular variability of the zwitterionic moiety and good stability. Typically, however, stable poly(carbobetaine)s are not accessible by ring-opening alkylation, so that low molar mass salts are by-products of their synthesis. The salts, however, stick tenaciously to the polymers and are difficult to remove completely. Therefore, possible interferences in model studies resulting from residual salt cannot be excluded (e.g. in solubility or conductivity studies).

Recently, we have presented a synthetic strategy to prepare salt-free poly(carbobetaine)s, which also allows us to vary easily the distance between the cationic and the anionic groups [18,21]. The key step is the anion exchange of an intermediate cationic species by hydroxide [16,26,27]. As the reaction conditions are strongly basic for this approach, the polymerisable moieties must be stable towards hydrolysis. In this respect, diallylammonium compounds (Fig. 1) are very attractive as they are inherently resistant not only to hydrolysis, but also to other base mediated side-reactions such as Michael additions, which can cause problems, e.g. for acrylic monomers [18]. The chemical stability of diallylammonium polymers in aqueous media as such has attracted most recently the interest of several research groups for the preparation of polyzwitterions [21–25], but typically, the synthetic paths chosen do not exclude the presence of salt [23–25]. Characteristically, diallylammonium monomers undergo cyclopolymerisation without cross-linking leading to a backbone containing predominantly five-membered rings [28–30].

The monomers of the polymers studied are listed in Fig. 1, together with their cationic precursors. Monomers **3a-b**, **4a-b**, **8a-b**, **9a-b** and **10** are new compounds whereas the other monomers were described before [21]. Monomers **1** and **6** can be defined as parent compounds of the series. The sulfobetaine analogue **5** [11,21] served as reference.

Because numerous hydrophobic polyzwitterions are

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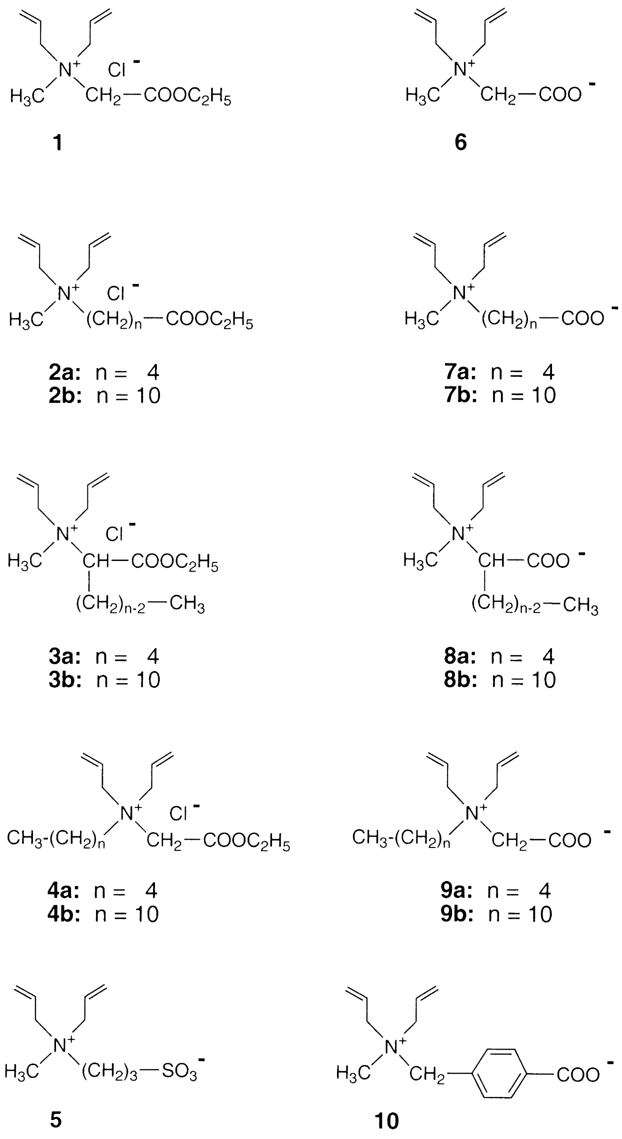

Fig. 1. Zwitterionic monomers studied and their cationic analogues.

known to self-organise into micellar, liquid-crystalline or other self-organised superstructures [4,12,13,31], we wanted to study the role of hydrophobic substituents on the parent compound **6**, by attaching hydrophobic chains of different length (cf. series **6**, **8a** and **8b**, etc.) at different positions relative to the ammonium group (cf. series **7a**, **8a** and **9a**, etc.). Also, we have varied the length of the spacer group between the cationic and anionic group (cf. monomers **6**, **7a**, **7b**) and its rigidity (cf. monomers **7a** and **10**), as the acidity of the carboxyl group, and the tendency to form ion pairs within the same fragment will depend on the distance between the ammonium and the carboxylate group, as well as on the rigidity of this spacer. As these cyclopolymers have a rigidified backbone compared to the previously studied amphiphilic vinyl and vinylidene polymers, it is not clear whether this stiffening will interfere with the self-organisation of the side chains, or whether it will favour structure formation.

2. Experimental

2.1. Materials

All solvents were distilled prior to use. The water used to dissolve the betaines was purified using a Elgastat maxima (18.2 mΩ) purification system. The synthesis of monomers **1**, **2**, **5**, **6** and **7a-b**, and of the corresponding polymers was reported previously [21]. Ammonium iodides bearing ester groups were saponified by using an OH^- loaded anion exchange resin (IRA-400) conditioned by 1 M aqueous NaOH, as described before [21]. The loaded resins were tested with silver nitrate before use [26]. Ammonium iodides were converted into the chlorides by use of the exchange resin (IRA-400) loaded with Cl^-. 2,2′-dimethyl-2,2′-azopropionitrile (AIBN), 2,2′-azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide (VA-086, gift from WAKO), $K_2S_2O_8$ and benzoylperoxide were recrystallised before use.

2.2. Monomers

Ethyl-2-(N,N-diallylamino)valerate. 25.56 g (0.26 mol) of diallylamine and 25.00 g (0.12 mol) of ethyl-2-bromovalerate in 250 ml of ethanol were refluxed for 3 days under argon. The solvent was evaporated and the residue dissolved in CH_2Cl_2, washed three times with saturated aqueous K_2CO_3 and dried over $MgSO_4$. The residue was distilled in vacuo (1 mmHg) at 62°C. Yield: 20.37 g (75.3%), colourless liquid, $n_D^{21} = 1.4448$

^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.90$ (t; 3H, CH_3), 1.23–1.50 (m; 5H, CH_2–C–C–COO, COO–C–CH_3), 1.62 (m; 2H, CH_2–C(–N)–COO), 2.97–3.45 (m; 5H, =C–CH_2, N–CH–COO), 4.13 (q; 2H, COO–CH_2), 5.07–5.22 (dd; 4H, CH_2=C), 5.80 (m; 2H, C=CH).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.7$ (*C*H_3), 14.4 (COO–C–*C*H_3), 19.4 (*C*H_2–C–C–COO), 31.8 (*C*H_2–C–COO), 53.3 (=C–*C*H_2), 59.7 (COO–*C*H_2), 61.6 (*C*H(–N)–COO), 116.6 (*C*H_2=C), 136.7 (C=*C*H), 173.4 (*C*OO).

Ethyl-2-(N,N-diallyl-N-methylammonio)valerate chloride (3a). 15.00 g (0.066 mol) of ethyl-2-(*N*,*N*-diallylamino) valerate and 8.53 g (0.0605 mol) of CH_3I were stirred at ambient temperature in 66 ml of dry dimethylformamide (DMF) for 4 days under argon. Diethyl ether was added until an oil separated that was washed with ether until no trace of the reagents or solvent could be detected by thin layer chromatography (TLC) or by NMR, respectively. The oil was dissolved in water and lyophilised, to yield 19.66 g (83.55%) of ethyl-2-(*N*,*N*-diallyl-*N*-methylammonio)valerate iodide as a yellowish viscous oil. 11.71 g (0.032 mol) of the iodide salt were dissolved in water at room temperature. An equimolar amount of Cl^- loaded anion exchange resin was added. The mixture was stirred for 20 min before the resin was filtered off. After repeating the operations, the aqueous solution was lyophilised. Yield: 7.84 g (90%), viscous, hygroscopic oil.

^{1}H NMR (200 MHz, D$_2$O): $\delta = 0.96$ (t; 3H, C–C–CH$_3$), 1.03–1.44 (m; 5H, CH$_2$–C–C–COO, COO–C–CH$_3$), 2.04–2.12 (m; 2H, CH$_2$–C–COO), 3.18 (m; 3H, N$^+$–CH$_3$), 4.06–4.24 (m; 5H, =C–CH$_2$, CH(–N$^+$)–COO), 4.42 (q; 2H, COO–CH$_2$), 5.70–5.81 (m; 4H, CH$_2$=C), 6.10 (m; 2H, C=CH). The complex shape of the signal at 4.06–4.24 ppm compared to the signals of the allylic protons in the analogous compounds **1** [21] or **4a-b** is attributed to the non-equivalence of the two diastereotopic allylic protons due to the asymmetric carbon of the methine group, and to hindered rotation of the allyl groups.

^{13}C NMR (50 MHz, D$_2$O): $\delta = 17.4$ (*C*H$_3$), 17.7 (COO–C–*C*H$_3$), 23.1 (*C*H$_2$–C–C–COO), 32.3 (*C*H$_2$–C–COO), 50.1 (N$^+$–*C*H$_3$), 67.8, 68.1, 68.5 (COO–*C*H$_2$, =C–*C*H$_2$), 75.8 (*C*H(–N$^+$)–COO), 128.4 (C=*C*H), 134.1 (*C*H$_2$=C), 172.8 (*C*OO). The two signals at 67.8 and 68.1 ppm of the allylic carbons are attributed to hindered rotation of the allyl groups.

Elemental analysis of $C_{14}H_{26}ClNO_2$ (275.82):
calc.: C, 60.97%; H, 9.50%; N, 5.08%; Cl, 12.85%;
calc. + 0.7·H$_2$O: C, 58.30%; H, 9.09%; N, 4.86%; Cl, 12.29%;
found: C, 58.24%; H, 9.94%; N, 4.79%; Cl, 12.97%;
C/N ratio calc.: 12.00; found, 12.16.

Mass spectrometry (FAB): $m/z = 240.2$ (M–Cl$^-$)$^+$.

*N,N-diallyl-N-methyl-2-ammoniovalerate (**8a**).* Yield after ion exchange: quantitative; viscous hygroscopic oil.

^{1}H NMR (200 MHz, D$_2$O): $\delta = 0.95$ (t; 3H, CH$_3$), 1.02–1.41 (m; 2H, CH$_2$–C–C–COO), 1.88–1.97 (m; 2H, CH$_2$–C–COO), 3.10 (m; 3H, N$^+$–CH$_3$), 3.68–3.76 (m; 1H, CH(–N$^+$)–COO), 3.89–4.16 (m; 4H, =C–CH$_2$), 5.66–5.76 (m; 4H, CH$_2$=C), 6.05 (m; 2H, C=CH). The complex shape of the signal at 3.89–4.1 ppm compared to the signals of the allylic protons in the analogous compounds **6** [21] or **9a-b** is attributed to the non-equivalence of the two diastereotopic allylic protons due to the asymmetric carbon of the methine group, and to hindered rotation of the allyl groups.

^{13}C NMR (50 MHz, D$_2$O): $\delta = 13.0$ (*C*H$_3$), 18.8 (*C*H$_2$–C–C–COO), 27.6 (*C*H$_2$–C–COO), 44.7 (N$^+$–*C*H$_3$), 62.0, 62.7 (=C–*C*H$_2$), 74.9 (*C*H(–N$^+$)–COO), 124.3 (C=*C*H), 128.6 (*C*H$_2$=C), 171.8 (*C*OO). The two signals at 62.0 and 62.7 ppm of the allylic carbons are attributed to hindered rotation of the allyl groups.

Elemental analysis of $C_{12}H_{21}NO_2$ (211.30):
calc.: C, 68.21%; H, 10.02%; N, 6.63%;
calc. + 0.8·H$_2$O: C, 63.86%; H, 9.38%; N, 6.21%;
found: C, 63.84%; H, 10.42%; N, 6.16%;
C/N ratio calc.: 10.29; found, 10.36.

Mass spectrometry (FAB): $m/z = 212.2$ (M + 1)$^+$.

Monomers **3b** and **8b** were prepared in analogy to their homologues **3a** and **8a**.

Ethyl-2-(N,N-diallylamino)undecanoate. Yield: 54.0%, colourless liquid, $n_D^{21} = 1.4550$.

^{1}H NMR (200 MHz, CDCl$_3$): $\delta = 0.86$ (t; 3H, CH$_3$), 1.23–1.37 (m; 17H, (CH$_2$)$_7$–C–C–COO, COO–C–CH$_3$), 1.64 (m; 2H, CH$_2$–C(–N)–COO), 2.98–3.40 (m; 5H, =C–CH$_2$, CH(–N)–COO), 4.09–4.17 (m; 2H, COO–CH$_2$), 5.05–5.19 (dd; 4H, CH$_2$=C), 5.75 (m; 2H, C=CH).

^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 14.0$ (*C*H$_3$), 14.4 (COO–C–*C*H$_3$), 22.6 (C–*C*H$_2$–C–), 26.2, 29.2, 29.3, 29.5, 29.7 ((*C*H$_2$)$_6$–C–C–COO), 31.9 (*C*H$_2$–C–COO), 53.4 (=C–*C*H$_2$), 59.8 (COO–*C*H$_2$), 61.9 (*C*H(–N)–COO), 116.7 (*C*H$_2$=C), 136.7 (C=*C*H), 173.4 (*C*OO).

Ethyl-2-(N,N-diallyl-N-methylammonio) undecanoate iodide. Yield: 33%, slightly yellowish viscous oil.

*Ethyl-2-(N,N-diallyl-N-methylammonio) undecanoate chloride (**3b**).* Yield: quantitative, viscous, hygroscopic oil.

^{1}H NMR (200 MHz, D$_2$O): $\delta = 0.90$ (t; 3H, CH$_3$), 1.20–1.50 (m; 17H, (CH$_2$)$_7$–C–C–COO, COO–C–CH$_3$), 2.00–2.25 (m; 2H, CH$_2$–C(–N$^+$)–COO), 3.20 (m; 3H, N$^+$–CH$_3$), 4.08–4.22 (m; 5H, =C–CH$_2$, CH(–N$^+$)–COO), 4.35 (q; 2H, COO–CH$_2$), 5.72–5.83 (m; 4H, CH$_2$=C), 6.10 (m; 2H, C=CH). The complex shape of the signal at 4.08–4.22 ppm compared to the signals of the allylic protons in the analogous compounds **1** [21] or **4a-b** is attributed to the non-equivalence of the two diastereotopic allylic protons due to the asymmetric carbon of the methine group, and to hindered rotation of the allyl groups.

^{13}C NMR (50 MHz, D$_2$O): $\delta = 15.4$ (*C*H$_3$), 15.7 (COO–C–*C*H$_3$), 21.3 (C–*C*H$_2$–C–), 24.5, 27.5, 27.8, 30.7, 31.4 ((*C*H$_2$)$_6$–C–C–COO), 33.7 (*C*H$_2$–C–COO), 47.7 (N$^+$–*C*H$_3$), 65.2, 65.3 (=C–*C*H$_2$), 68.5 (COO–*C*H$_2$), 73.1 (*C*H(–N$^+$)–COO), 125.9 (C=*C*H), 131.6 (*C*H$_2$=C), 169.7 (*C*OO). The two signals at 65.2 and 65.3 ppm of the allylic carbons are attributed to hindered rotation of the allyl groups.

Elemental analysis of $C_{20}H_{38}ClNO_2$ (359.98):
calc.: C, 66.73%; H, 10.64%; N, 3.89%; Cl, 9.85%;
calc. + 1.3·H$_2$O: C, 62.66%; H, 9.99%; N, 3.65%; Cl, 9.25%;
found: C, 62.73%; H, 10.82%; N, 3.61%; Cl, 10.13%;
C/N ratio calc.: 17.15; found, 17.38.

Mass spectrometry (FAB): $m/z = 324.2$ (M–Cl$^-$)$^+$.

*N,N-diallyl-N-methyl-2-ammonioundecanoate (**8b**).* Yield: 95%, viscous hygroscopic oil.

^{1}H NMR (200 MHz, D$_2$O): $\delta = 0.89$ (t; 3H, CH$_3$), 1.20–1.50 (m; 14H, (CH$_2$)$_7$–C–C–COO), 1.90 (m; 2H, CH$_2$–C(–N$^+$)–COO), 3.11 (m; 3H, N$^+$–CH$_3$), 3.68 (m; 1H, CH(–N$^+$)–COO), 3.82–4.28 (m; 4H, =C–CH$_2$), 5.65–5.77 (m; 4H, CH$_2$=C), 6.08 (m; 2H, C=CH). The complex shape of the signal at 3.82–4.28 ppm compared to the signals of the allylic protons in the analogous compounds **6** [21] or **9a-b** is attributed to the non-equivalence of the two diastereotopic allylic protons due to the asymmetric carbon of the methine group, and to hindered rotation of the allyl groups.

^{13}C NMR (50 MHz, D$_2$O): $\delta = 13.7$ (*C*H$_3$), 22.4 (C–*C*H$_2$–C–), 25.6, 25.8, 28.9, 29.0, 29.2 ((*C*H$_2$)$_6$–C–C–COO), 31.6 (*C*H$_2$–C–COO), 45.0 (N$^+$–*C*H$_3$), 62.0, 62.9 (=C–*C*H$_2$), 75.1 (N$^+$–*C*H–COO), 124.6 (C=*C*H), 128.6

(*C*H_2=C), 171.0 (*C*OO). The two signals at 62.0 and 62.9 ppm of the allylic carbons are attributed to hindered rotation of the allyl groups.

IR (film) selected bands: 3084 cm^{-1} (=CH), 1629 cm^{-1} (broad –COO, C=C).

Elemental analysis of $C_{18}H_{33}NO_2$ (295.46):
calc: C, 73.17%; H, 11.26%; N, 4.74%;
calc. + 0.6·H_2O: C, 70.59%; H, 10.86%; N, 4.57%;
found: C, 70.38%; H, 11.31%; N, 4.60%;
C/N ratio calc.: 15.44; found, 15.30.

Mass spectrometry (EI): $m/z = 296.3\ (M+1)^+$.

N,N-diallyl-n-pentyl amine. 38.47 g (0.40 mol) of diallylamine and 35.62 g (0.18 mol) of 1-iodopentane in 180 ml of ethanol were refluxed for 1 day under argon. The solvent was evaporated and the residue dissolved in CH_2Cl_2, washed three times with saturated aqueous K_2CO_3 and dried over $MgSO_4$. The residue was distilled at 191°C. Yield: 19.45 g (65.0%), colourless liquid, $n_D^{21} = 1.4430$.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.86$ (t; 3H, CH_3), 1.18–1.50 (m; 6H, $(CH_2)_3$–C–N), 2.35 (m; 2H, CH_2–N), 3.03 (d; 4H, =C–CH_2), 5.07–5.22 (dd; 4H, CH_2=C), 5.80 (m; 2H, C=CH).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.0$ (*C*H_3), 22.6 (N–C–C–C–*C*H_2), 26.6 (N–C–*C*H_2), 29.7 (N–C–C–*C*H_2), 53.3 (C–*C*H_2–N), 56.8 (=C–*C*H_2), 116.9 (*C*H_2=C), 135.9 (C=*C*H).

*Ethyl-2-(N,N-diallyl-N-pentylammonio) acetate chloride (**4a**).* 10.10 g (0.060 mol) of *N,N*-diallyl-*n*-pentyl amine and 10.10 g (0.060 mol) of ethyl bromoacetate were stirred at ambient temperature in 60 ml of dry DMF for 4 days under argon. Then, diethyl ether was added until a slightly yellowish oil precipitated. The oil was washed with ether until no trace of the reagents or solvent could be detected by TLC or by NMR, respectively. The oily residue was dissolved in water and lyophilised to yield 15.06 g (74.5%) of ethyl-2-(*N,N*-diallyl-*N*-pentylammonio) acetate bromide, as hygroscopic viscous oil. 6.00 g (0.018 mol) of the bromide salt were dissolved in water at room temperature and an equimolar amount of Cl^- loaded anion exchange resin was added. The mixture was stirred for 20 min before the resin was filtered off. The operations were repeated, and the aqueous solution was lyophilised. Yield: 5.03 g (96.7%), hygroscopic, white solid.

^{1}H NMR (200 MHz, D_2O): $\delta = 0.98$ (t; 3H, CH_3), 1.28–1.42 (m; 7H, COO–C–CH_3, $(CH_2)_2$–C–C–N^+), 1.90 (m; 2H, CH_2–C–N^+), 3.52–3.60 (m; 2H, $(C)_4$–CH_2–N^+), 4.22–4.44 (m; 8H, N^+–CH_2–COO, =C–CH_2, COO–CH_2), 5.75–5.86 (m; 4H, CH_2=C), 6.11 (m; 2H, C=CH).

^{13}C NMR (50 MHz, D_2O): $\delta = 13.0$ (*C*H_3), 13.1 (COO–C–*C*H_3), 20.9, 21.3, 27.5 ((*C*H_2)$_3$–C–N^+), 56.2, 59.8 (*C*H_2–N^+, COO–*C*H_2), 62.1, 63.4 (N^+–*C*H_2–COO, =C–*C*H_2), 123.6 (C=*C*H), 129.4 (*C*H_2=C), 165.2 (*C*OO).

IR (KBr) selected bands: 3085 cm^{-1} (=CH), 1740 cm^{-1} (C=O), 1654 cm^{-1} (C=C).

Elemental analysis of $C_{15}H_{28}ClNO_2$ (289.84):
calc: C, 62.16%; H, 9.74%; N, 4.83%; Cl, 12.23%;
calc. + 0.7·H_2O: C, 59.57%; H, 9.33%; N, 4.63%; Cl, 11.72%;
found: C, 59.52%; H, 10.00%; N, 4.60%; Cl, 12.59%;
C/N ratio calc.: 12.87; found, 12.94.

Mass spectrometry (FAB): $m/z = 254.2\ (M{-}Cl^-)^+$.

*N,N-diallyl-N-pentyl-ammonioacetate (**9a**).* Yield after ion exchange: quantitative; viscous hygroscopic oil.

^{1}H NMR (200 MHz, D_2O): $\delta = 0.93$ (t; 3H, CH_3), 1.35–1.39 (m; 4H, $(CH_2)_2$–C–C–N^+), 1.80 (m; 2H, CH_2–C–N^+), 3.45 (m; 2H, CH_2–N^+), 3.78 (s; 2H, N^+–CH_2–COO^-), 4.15–4.20 (m; 4H, =C–CH_2), 5.66–5.98 (m; 4H, CH_2=C), 6.05 (m; 2H, C=CH).

^{13}C NMR (50 MHz, D_2O): $\delta = 12.9$ (*C*H_3) 20.8, 21.3, 27.6 ((*C*H_2)$_3$–C–N^+), 58.0, 58.6, 60.7 (*C*H_2–N^+, N^+–*C*H_2–COO, =C–*C*H_2), 124.3 (C=*C*H), 128.5 (*C*H_2=C), 167.8 (*C*OO).

Elemental analysis of $C_{13}H_{23}NO_2$ (225.33):
calc: C, 69.30%; H, 10.29%; N, 6.22%;
calc. + 1.1·H_2O: C, 63.69%; H, 9.46%; N, 5.76%;
found: C, 63.59%; H, 10.54%; N, 5.80%;
C/N ratio calc.: 11.14; found, 10.96.

Mass spectrometry (EI): $m/z = 224.2\ (M-1)^+$.

N,N-diallyl-n-undecyl amine. 37.91 g (0.39 mol) of diallylamine and 50.00 g (0.18 mol) of 1-iodoundecane in 180 ml of ethanol were refluxed for 2 days under argon. The solvent was evaporated and the residue dissolved in CH_2Cl_2, washed three times with saturated aqueous K_2CO_3 and dried over $MgSO_4$. The residue was distilled in vacuo (1 mmHg) at 62°C. Yield: 39.02 g (87.0%), colourless liquid, $n_D^{21} = 1.4530$.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (t; 3H, CH_3), 1.25–1.46 (m; 18H, $(CH_2)_9$–C–N), 2.39 (m; 2H, CH_2–N), 3.08 (d; 4H, =C–CH_2), 5.10–5.18 (dd; 4H, CH_2=C), 5.85 (m; 2H, C=CH).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (*C*H_3), 22.7 (C–*C*H_2–C–), 26.9, 27.5, 29.3, 29.6, 31.9 (N–C–(*C*H_2)$_8$), 53.4 (C–*C*H_2–N), 56.9 (=C–*C*H_2), 117.1 (*C*H_2=C), 135.9 (C=*C*H).

*Ethyl-2-(N,N-diallyl-N-undecylammonio) acetate chloride (**4b**).* 26.60 g (0.106 mol) of *N,N*-diallyl-*n*-undecyl amine and 17.69 g (0.106 mol) of ethyl-bromoacetate were stirred at ambient temperature in 60 ml of dry DMF for 4 days under argon. Then, diethyl ether was added until a slightly yellowish oil precipitated. The oil was washed with ether until no trace of the reagents or solvent could be detected by TLC or by NMR, respectively. The oily residue was dissolved in water and lyophilised to yield 22.31 g (50.4%) of ethyl-2-(*N,N*-diallyl-*N*-undecylammonio) acetate bromide, as slightly yellowish hygroscopic viscous oil. 10.00 g (0.024 mol) of the bromide were dissolved in water at room temperature and an equimolar amount of Cl^- loaded anion exchange resin was added. The mixture was stirred for 20 min before the resin was filtered off. Another equimolar amount of Cl^- loaded anion exchange resin was added to the aqueous solution. After stirring for 20 min and filtering the resin off, the aqueous solution was lyophilised. Yield: 8.43 g (94.3 %), viscous, hygroscopic oil.

^{1}H NMR (200 MHz, D_2O): $\delta = 0.95$ (t; 3H, CH_3), 1.20–1.50 (m; 19H, COO–C–CH_3, $(CH_2)_8$–C–C–N^+), 1.90 (m; 2H, CH_2–C–N^+), 3.55 (m; 2H, $(C)_{10}$–CH_2–N^+), 4.20–4.40 (m; 8H, N^+–CH_2–COO, =C–CH_2, COO–CH_2), 5.70–5.90 (m; 4H, CH_2=C), 6.00–6.25 (m; 2H, C=CH).

^{13}C NMR (50 MHz, D_2O): $\delta = 13.3$ (*C*H_3), 13.7 (COO–C–*C*H_3), 21.6 (C–CH_2–C–), 22.5, 25.9, 28.6, 29.2, 29.4, 29.5, 31.8 ($(CH_2)_8$–C –N^+), 56.1, 59.2, 62.5, 63.0 (*C*H_2–N^+, COO–*C*H_2, *C*H_2–COO, =C–*C*H_2), 123.6 (C=*C*H), 129.7 (*C*H_2=C), 165.2 (*C*OO).

Elemental analysis of $C_{21}H_{40}ClNO_2$ (374.01):
calc: C, 67.44%; H, 10.78%; N, 3.75%; Cl, 9.48%;
calc. + 2·H_2O: C, 61.51%; H, 9.83%; N, 3.42%; Cl, 8.65%;
found: C, 61.47%; H, 10.74%; N, 3.43%; Cl, 7.07%;
C/N ratio calc.: 17.98; found, 17.92.
Mass spectrometry (FAB): *m*/*z* = 338.3 $(M–Cl^-)^+$.

N,N-diallyl-N-undecyl-ammonioacetate (***9b***). Yield after ion exchange: quantitative; viscous hygroscopic oil.

^{1}H NMR (200 MHz, D_2O): $\delta = 0.95$ (t; 3H, CH_3), 1.30–1.50 (m; 16H, $(CH_2)_8$–C–C–N^+), 1.80 (m; 2H, CH_2–C–N^+), 3.50 (m; 2H, (CH_2–N^+), 3.78 (s; 2H, N^+–CH_2–COO–), 4.10–4.30 (m; 4H, =C–CH_2), 5.70–5.80 (m; 4H, CH_2=C), 5.95–6.20 (m; 2H, C=CH).

^{13}C NMR (50 MHz, D_2O): $\delta = 13.8$ (*C*H_3), 21.5 (C–CH_2–C–), 22.5, 26.1, 28.9, 29.3, 29.5, 29.6, 31.9 ((*C*$H_2)_8$–C–N^+), 58.1, 58.3, 60.9 (=C–*C*H_2, *C*H_2–N^+, N^+–*C*H_2–COO), 124.3 (C=*C*H), 128.7 (*C*H_2=C), 168.1 (*C*OO).

Elemental analysis of $C_{19}H_{35}NO_2$ (309.49):
calc.: C, 73.74%; H, 11.40%; N, 4.53%;
calc. + 0.8·H_2O: C, 70.46%; H, 10.89%; N, 4.32%;
found: C, 70.54%; H, 11.41%; N, 4.31%;
C/N ratio calc.: 16.28; found, 16.37.
Mass spectrometry (EI): *m*/*z* = 308.2 $(M - 1)^+$.

Ethyl-(4-bromomethyl)benzoate. 15.00 g (0.069 mol) of (4-bromomethyl)benzoic acid and 0.60 g of dimethylaminopyridine were added to 70 ml ethanol. The solution was cooled at 0°C and 13.08 g (0.063 mol) of *N*,*N*-dicyclohexylcarbodiimide dissolved in 70 ml ethanol were added dropwise. The reaction mixture was stirred during 3 days at room temperature. The precipitated was filtered, redissolved in CH_2Cl_2, washed with water and dried over $MgSO_4$. The residue was distilled in vacuo (1 mmHg) at 147°C. Yield: 9.22 g (54.0%), white solid, m.p. 38.9°C.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.36$ (t; 3H, CH_3), 4.35 (q; 2H, COO–CH_2), 4.46 (s; 2H, CH_2–Br), 7.70, 8.05 (d; 2H, +d; 2H, aryl).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (*C*H_3), 32.1 (*C*–Br), 60.9 (COO–*C*), 128.8 (*C*H=C–C–Br), 129.9 (*C*H=C–COO), 130.3 (*C*–COO), 142.4 (*C*–C–Br), 165.9 (*C*OO).

Ethyl-(4-N,N-diallylaminomethyl)benzoate. 8.07 g (0.08 mol) of diallylamine and 9.18 g (0.04 mol) of ethyl-(4-bromomethyl)benzoate in 83 ml of ethanol were refluxed for 1 day under argon. The solvent was evaporated and the residue dissolved in CH_2Cl_2, washed three times with saturated aqueous K_2CO_3 and dried over $MgSO_4$. The residue was distilled in vacuo (1 mmHg) at 130°C. Yield: 6.73 g (68.7%), colourless liquid, $n_D^{21} = 1.5165$.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.34$ (t; 3H, *C*H_3), 3.02 (d; 4H, =C–*C*H_2–N), 3.57 (s; 2H, aryl-*C*H_2–N), 4.32 (q; 2H, COO–*C*H_2), 5.07–5.19 (dd; 4H, C=*C*H_2), 5.83 (m, 2H, *C*H=C), 7.38, 7.96 (d; 2H, +d; 2H, aryl).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.1$ (*C*H_3), 32.1 (*C*–Br), 56.4, 57.1 (=C–*C*H_2–N, C–*C*H_2–N), 60.5 (COO– *C*H_2), 117.3 (C=*C*H_2), 128.4 (*C*H=C–C–N), 129.0 (*C*–COO), 129.3 (*C*H=C–COO), 135.5 (N–C–*C*H=), 145.0 (*C*–C–N), 166.3 (*C*OO).

Ethyl-4-(N,N-diallyl-N-methylammonio) benzoate iodide. 6.62 g (0.026 mol) of ethyl-(4-*N*,*N*-diallylaminomethyl)-benzoate and 3.27 g (0.0232 mol) of CH_3I were stirred at ambient temperature in 26 ml of dry DMF for 1 day under argon. Then, diethyl ether was added until a slightly yellowish oil precipitated. The oil was washed with ether until no trace of the reagents or solvent could be detected by TLC or by NMR, respectively. The oily residue was dissolved in water and lyophilised. Yield: 8.01 g (86.0%), of slightly yellowish viscous oil.

^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.15$ (t; 3H, *C*H_3), 2.95 (s; 3H, *C*H_3–N^+), 3.85–4.20 (m; 6H, COO–*C*H_2, =C–*C*H_2–N), 4.85 (s; 2H, aryl-*C*H_2–N^+), 5.50–5.70 (dd; 4H, C=*C*H_2), 5.92 (m, 2H, *C*H=C), 7.65 (d; 2H, *C*H=C–C–N^+), 7.85 (d; 2H, *C*H=C–COO).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 13.7$ (*C*H_3), 46.5 (*C*H_3–N^+), 60.8 (COO–*C*H_2), 63.0, 63.5 (=C–*C*H_2–N^+, aryl-*C*–N^+), 123.9 (*C*H=CH_2), 129.2 (C=*C*H_2), 129.5 (*C*H=C–COO), 131.0 (*C*–COO), 132.0, 132.9 (*C*–C–N^+, *C*H=C–C–N^+), 164.8 (*C*OO).

IR (film) selected bands: 3079 cm^{-1} (=CH), 1718 cm^{-1} (C=O).

Elemental analysis of $C_{17}H_{24}INO_2$ (401.29):
calc.: C, 50.88%; H, 6.08%; N, 3.49%; I, 31.62%;
found: C, 49.09%; H, 5.84%; N, 3.32%; I, 38.30%;
C/N ratio calc.: 14.58; found, 14.79.
Mass spectrometry (FAB): *m*/*z* = 274.3 $(M–I^-)^+$.

4(-N,N-diallyl-N-methyl-ammoniomethyl)benzoate (***10***). Yield after ion exchange: 90%; viscous hygroscopic oil.

^{1}H NMR (200 MHz, D_2O): $\delta = 2.90$ (s; 3H, *C*H_3–N^+), 3.82 (m; 4H, =C–*C*H_2–N), 4.36 (s; 2H, aryl-*C*H_2–N^+), 5.60–5.80 (dd; 4H, C=*C*H_2), 6.08 (m, 2H, *C*H=C), 7.49 (d; 2H, *C*H=C–C–N^+), 7.89 (d; 2H, *C*H=C–COO).

^{13}C NMR (50 MHz, D_2O): $\delta = 46.5$ (*C*H_3–N^+), 63.5, 64.7 (=C–*C*H_2–N^+, aryl-*C*H_2–N^+), 124.1 (*C*H=CH_2), 128.9, 129.1 (C=*C*H_2, *C*–COO), 129.4 (*C*H=C–C–N^+), 132.7 (*C*H=C–COO), 139.0 (*C*–C–N^+), 174.0 (*C*OO).

Elemental analysis of $C_{15}H_{19}NO_2$ (245.32):
calc.: C, 73.44%; H, 7.81%; N, 5.71%;
calc. + 0.8·H_2O: C, 69.37%; H, 7.73%; N, 5.39%;
found: C, 69.39%; H, 8.06%; N, 5.39%;
C/N ratio calc.: 12.86; found, 12.87.
Mass spectrometry (EI): *m*/*z* = 246.0 $(M + 1)^+$.

Table 1
Micellar behaviour of hydrophobised diallylammonium monomers

Monomer	cmc ($g\,l^{-1}$)	cmc (10^{-3} $mol\,l^{-1}$)	Surface tension at cmc ($mN\,m^{-1}$)
2b	32	89	37
4b	6.3	19	29
7b	–	–	45[a]
9b	13	42	33

[a] Surface tension at concentration of $50 g\,l^{-1}$.

2.3. Polymerisation

Aqueous solutions of the zwitterionic monomers (50% by weight) were degassed by three freeze/thaw cycles, sealed and reacted for 48 h at 80°C, using 4 mol% of initiator. Solutions of the ammonium monomers of 50% by weight in a mixture of ethanol and acetonitrile (1:1, v/v) were degassed by three freeze and thawing cycles, sealed and reacted for 48 h at 60°C, using 4 mol% of initiator. The polymers were purified by dialysis (Spectra/Por® membrane, nominal cut-off of 6000–8000 Da, The Spectrum Company, Gardena CA) and freeze dried.

2.4. Methods

NMR spectra were recorded using Gemini 200- or 300-MHz spectrometers. Dioxane or 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt were used as references for ^{13}C spectrums in D_2O. Viscometry was performed with a semi-automatic Ubbeholde capillary viscometer (Schott AVS 350) at 30°C. Thermogravimetry was performed on a model TGA-500 thermogravimetric analyser (SETARAM), with a heating rate of $10°C\,min^{-1}$ in a nitrogen atmosphere. Differential scanning calorimetry (DSC) studies applied heating and cooling rates of $20°C\,min^{-1}$ (Perkin–Elmer DSC7). X-ray scattering experiments used the Ni-filtered Cu-K_α line ($\lambda = 0.1541$ nm, diffractometer Siemens D-5000). The surface tensions of aqueous solutions of the monomers were measured by a manual tensiometer (Krüss 8501, de Noüy).

3. Results and discussion

3.1. Monomer synthesis and surfactant properties

The key step in the salt-free synthesis of the zwitterionic monomers is the conversion of the cationic precursor to the betaine. Following the preparation mode for simple aliphatic analogues [27], the cationic diallylammonium compounds bearing an ester group are treated with an OH^- loaded anion exchange resin. The iodide counterions are exchanged by OH^-, which subsequently hydrolyses the ester to yield the ammoniocarboxylate.

At first glance, the direct alkylation of diallylmethylamine with a bromoalkanoic acid seemed to be the more direct synthetic route to the diallylammonium ester intermediates. However, the reaction of *N*,*N*-diallyl-*N*-ethyloxycarbonylmethylamine with the alkylating agents proved to be sluggish, requiring high temperatures, which led to side products that were difficult to eliminate completely. The cationic precursor monomers were therefore prepared in two steps: (i) preparation of the functional tertiary amine by reacting diallylamine with an ester of a bromoalkanoic acid; and (ii) alkylation of the tertiary amine with methyl iodide at ambient temperature. Using this sequence, pure cationic diallylammonium ester intermediates are obtained.

For comparison, the cationic precursor monomers were polymerised and studied, too. All monomers were used as chlorides, as the corresponding iodide salts degrade rapidly in air or under daylight, and have only limited solubility in water. The hydrophilicity of the ammonium chloride monomers is reflected by their marked hygroscopy, which parallels the behaviour of the carbobetaine monomers.

The structure of the cationic monomers **2b**, **3b** and **4b** and of their analogues **7b**, **8b** and **9b** are characteristic for polymerisable surfactants (often referred to as “surfmers”), such as *N*,*N*-diallyl-*N*-methyl-dodecyl ammonium choride [32]. All these molecules give strongly foaming aqueous solutions, underlining their surfactant character. The behaviour of monomers **2b** and **7b**, however, is not directly evident as the two polar groups, namely the ammonium and the carboxyl group, are located at opposite ends of the molecules. Therefore, we performed surface tension vs. monomer concentration measurements (Table 1). Monomers **2b**, **4b** and **9b** form micelles with a defined critical micelle concentration (cmc) as indicated by a sharp break point in the curves, whereas despite marked surface activity, no cmc could be detected for monomer **7b**, at least below concentrations of 5 wt% (Table 1). Accordingly, the cmc values of the zwitterionic ammonioacetate surfactants **7b** and **9b** are somewhat higher than those of their cationic ethyl ester analogues **2b** and **4b**. The solubilities of monomers **3b** and **8b** in water are too low at room temperature to determine a cmc. However, at higher temperatures they are sufficiently soluble and form lyotropic liquid-crystalline phases in concentrated solutions, as indicated by the birefringence in the polarisation microscope. The oily streak textures found for **3b** and the broken fan textures seen for **8b** suggest the formation of lamellar and hexagonal phases, respectively.

The cmc values of **2b** and of **4b** compare well with the value of $0.031\ mol\,l^{-1}$ reported for dodecyldimethylammonium chloride [33]. Cationic monomer **2b** exhibits a substantially higher cmc than its structural analogue **4b**, which may result from the position of the ester group at the end of the hydrophobic chain. If the latter is converted into the strongly hydrophilic carboxylate group, the compound becomes a “bola-type” surfactant, a class which is known for its high cmc values [34]. So the lack of a cmc at moderate concentrations of **7b** is not too surprising.

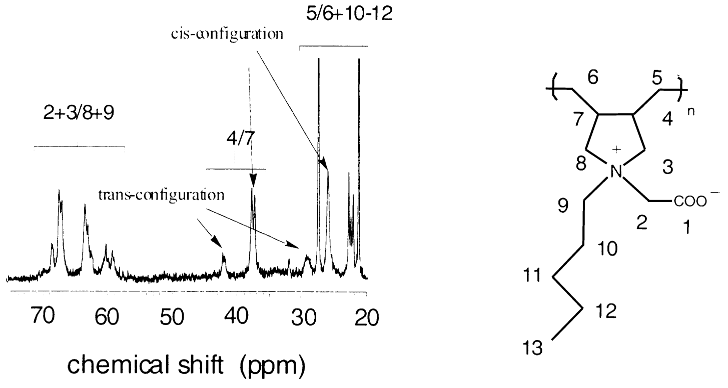

Fig. 2. Selected region of the ^{13}C NMR spectrum of poly(betaine) **P-9a** in D_2O.

3.2. Polymerisation and polymer structure

Polymers were prepared by free-radical polymerisation in homogeneous solution. High monomer (40–65% weight) and initiator concentrations (at least 4%) were necessary for obtaining polymers, in agreement with the literature on diallylammonium monomers [25,35,36]. Also, as described before, we did not succeed in polymerising the diallylammonium iodides, only the chlorides [21]. The failure is attributed to the presence of small amounts of iodine due to the rapid oxidation of iodide by oxygen, which acts as an inhibitor.

The polymerisation of the different betaine and cationic analogues was not straightforward. Whereas monomers **1**, **2a-b**, **5**, **6**, **7a-b** and **10** could be polymerised with azo initiators, no polymer could be isolated for **3a-b**, **4a-b**, **8a-b** and **9a-b**. Polymerisations were attempted in different solvents, but without success. In contrast, we polymerised these monomers at 80°C with persulfate, hydrogen peroxide or benzoyl peroxide initiators. Polymerisation also occurred when using persulfate at ambient temperature in the presence of tertiary amines. Nevertheless, polymer yields were always as low as 10%. These results suggest that when four bulky substituents are attached to the nitrogen atom, the polymerisability of the diallylammonium monomers is seriously hampered. Anton et al. already encountered a similar problem for the polymerisation of (*N*,*N*-diallyl-*N*-decyl)ammoniopropanesulfonate [37]. Also in agreement with our observations, the sensitivity of the polymerisation of diallylammonium compounds on the initiator employed has been reported occasionally [25,38]. Consequently, the cationic diallylmonomers with bulky substituents were polymerised by persulfate initiators, whereas benzoyl peroxide was used for the analogous zwitterionic monomers, in order to provide salt-free poly(betaine)s.

Owing to the lack of other sensitive groups, the polycations can be converted into the corresponding poly(carbobetaine)s by hydrolytic cleavage of the ester groups [15,16,20,23–25,39,40]. However, this alternative and convenient pathway neither guarantees 100% cleavage of the ester groups in the polymers [25,40] nor excludes rigorously the presence of some residual salt in the obtained polyzwitterions.

Information about the structure of the polymers by ^{1}H NMR is limited because of the superposition of many broad signals. ^{13}C NMR spectra are more instructive as the individual signals are better resolved (Figs. 2 and 3). According to the assignment of the different signals, based on coupled ^{1}H–^{13}C NMR spectra and on data from literature [28–30,41], cyclopolymerisation occurred for all monomers leading to the kinetically favoured five-membered rings at least in majority. Because the ^{13}C NMR signals are rather broad, presumably due to the rather rigid polymer backbone,

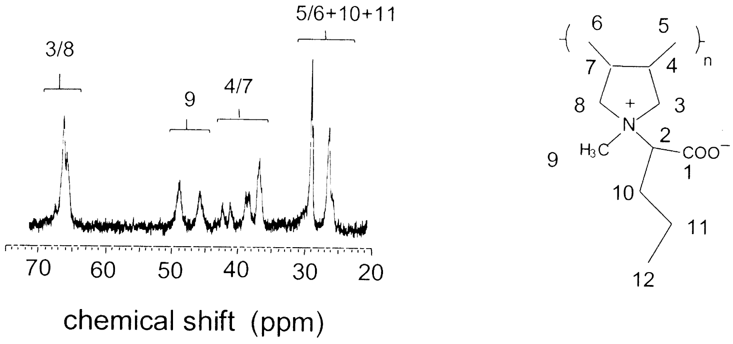

Fig. 3. Selected region of the ^{13}C NMR spectrum of poly(betaine) **P-8a** in D_2O.

Table 2
Solubility of poly(carbobetaine)s (+ = soluble, − = insoluble)

Solvent	Polymer								
	P5	**P6**	**P7a**	**P7b**	**P8a**	**P8b**	**P9a**	**P9b**	**P10**
Water	−	+	+	−	+	−	+	−	−
Brine[a]	−	+	+	+	+	−	+	−	+
Acetic acid				+		−		−	+
Ethanol	−	−	−	−	−	+	−	+	−
$CHCl_3$	−	−	−	−	−	−	−	−	−
THF	−	−	−	−	−	−	−	−	−

[a] Approximately 10 g NaCl l^{-1}.

a more detailed analysis is difficult. Nevertheless, the relative intensities of the signals at 26/29 and 38/42 ppm, which are attributed to *cis*/*trans* isomers [28,30] at positions 5/6 and 4/7 (see Figs. 2 and 3), respectively, suggest that the majority of the rings in the polymers have *cis* configuration [29,30,41,42]. The methine carbon peaks 4 and 7 at higher field give rise to doublets. This splitting could be the result of configurational differences between adjacent rings due to the lack of tacticity [30].

The spectrum of **P-9a** in Fig. 2 has a very similar pattern to that of poly(diallyldimethylammonium) chloride with regard to carbons 4, 7 and 5, 6 [41]. This is, however, not true for **P-8a** for which chemical shifts and patterns differ for carbons 4, 7 (Fig. 3), as found for **P-6** [21]. Hypothetically, we attribute these changes not only to the tacticity of the polymer backbone as described above, but also to the presence of two different substituents on the ammonium group in the five-membered rings, thus creating an additional stereocentre. The situation is particularly complex for **P-8a** because the presence of an asymmetric methine carbon in the side chain increases the number of possible stereoisomers. Note that the polycation analogues display virtually the same ^{13}C NMR patterns.

The complex microstructure of the new zwitterionic diallylammonium polymers is not surprising. The structure and the configuration of the poly(*N*,*N*-diallyl-*N*,*N*-dialkylammonium halide)s has been reported to be sensitive to the nature of the *N*-alkyl substituents, of the anion of the quaternary ammonium salt and of the solvent, though increasing the concentration of diallylammonium monomers in water or in methanol during the polymerisation did not change the polymer structure [29,43].

3.3. Polymer properties

The polymeric carbobetaines and their polycation analogues are very hygroscopic. Exposed even for short periods to air, they readily adsorb substantial amounts of water. All polycations are soluble in ethanol, except for the most hydrophobic ones **P-3b** and **P-4b**, which dissolve in $CHCl_3$. Polycations **P-1**, **P-2a**, **P-3a** and **P-4a** are also soluble in water, in contrast to **P-2b**, **P-3b** and **P-4b** bearing long alkyl chains.

The solubilities of the poly(carbobetaine)s in some polar solvents are summarised in Table 2. The parent polymer **P-6** is known to be soluble in pure water whereas the analogous polymeric sulfobetaine **P-5** was only found to be soluble in mixtures of water and CF_3COOH [21]. Adding pentyl substituents as in **P-8a** and **P-9a** still results in water-soluble polymers, as does the separation of the ammonium group from the carboxylate by a tetramethylene spacer in **P-7a**. In contrast, polymer **P-10** is not soluble in pure water. Because the benzyl group of **P-10** equals the tetramethylene group of **P-7a** as regards their hydrophobicity, the reduced solubility may be related to the rigidity of the benzyl spacer, possibly favouring intermolecular over intramolecular ion pairing. However, the addition of salt or the addition of an acid (e.g. acetic acid) renders **P-10** water-soluble. Polymer **P-7b** with the long hydrophobic decamethylene spacer behaves analogously to **P-10**, i.e. being insoluble in pure water but soluble in brine or in acetic acid. The salting-in of poly(betaine)s is a well-known phenomenon [1–4,7,17]. The addition of acetic acid dissolves **P-7b** and **P-10** presumably by protonating the carboxylate moiety and thus converting the polyzwitterions into polycations. These polymers are soluble neither in ethanol nor in methanol.

The hydrophobic poly(carbobetaines)s **P-8b** and **P-9b** did not dissolve either in pure water or in brine, but did in methanol and in ethanol. As for their cationic analogues **P-3b** and **P-4b** (as for **P-2b**) this can be rationalised by the geometry of these polymerised surfactants (so-called “polysoaps”) in agreement with previous work [34,37]: in hydrophobic polyelectrolytes and poly(zwitterions) with a constitutional C_2– repeat unit, the ionic groups close to the polymer backbone are hidden from the solvent by the densely attached, pendent hydrocarbon chains (“head geometry”). The anchoring of the charged groups to the polymer backbone blocks the amphilicity of the repeat units, and thus renders such polymers more lipophilic than expected from their hydrophilic–hydrophobic balance.

The viscosity of solutions of poly(carbobetaine)s and of their analogous polycations was studied in water, in ethanol or in chloroform, depending on their solubility. As reported for **P-6** and **P-7a** [21], Fig. 4 illustrates the absence of polyelectrolyte behaviour for the new poly(carbobetaine)s **P-8a**, **P-8b**, **P-9a** and **P-9b**, which shows a linear dependence of the reduced viscosity on the polymer concentration. This finding is consistent with the zwitterionic character of the polymer and suggests the full deprotonation of the ammonioacetate group, as found previously, in agreement with the low pK_a of trimethylammonioacetate [17]. Note that **P-6** exhibits a marked higher intrinsic viscosity of $[\eta] = 28$ ml g^{-1} in water than poly(betaine)s **P-8a** and **P-9a**. Their lower values may reflect substantially lower molar masses, or alternatively, they may originate from an intramolecular hydrophobic interaction of the alkyl side chains.

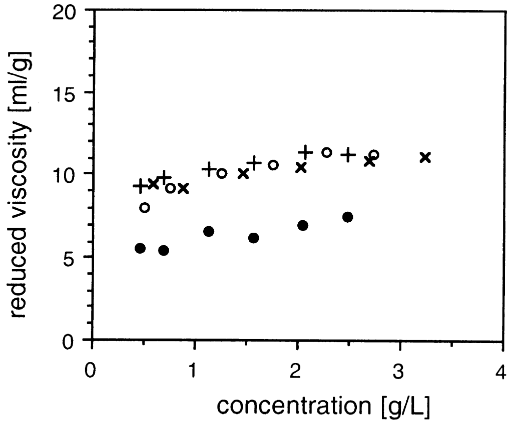

Fig. 4. Reduced viscosities of solutions of polyzwitterions at 30°C. (+) **P-8a** in water; (O) **P-9a** in water; (×) **P-8b** in ethanol; and (●) **P-9b** in ethanol.

Fig. 5 presents the reduced viscosity of the polycations **P-3a**, **P-3b**, **P-4a** and **P-4b**. The curves do not exhibit a pronounced polyelectrolyte behaviour at low concentrations, i.e. a marked increase of the reduced viscosity with decreasing concentration, but show only a very weak effect. In view of these results, we verified by infrared spectroscopy that the ester groups were not hydrolysed during viscometry thus yielding the poly(betaine): no change in the FT-IR spectrum could be observed after the viscometric studies. Therefore, we attribute the unusual viscometric behaviour to the stiffened polymer backbone, and/or to a low degree of dissociation in the organic solvents used [44,45].

The thermal stability of the polycations is determined by the dealkylation of the ammonium group, which depends on the nucleophilicity of the counter ion, and on the alkyl substituents. The stability of the polycations was reported to increase in the series **P-1**, **P-2a**, **P-2b** with increasing length of the alkyl chain separating the ester group from the ammonium, decompositions starting at 180, 200 and 225°C, respectively. Thermal decomposition of polycations **P-3a**, **P-3b** **P-4a** and **P-4b** starts in the range between 170 and 180°C, i.e. at about the same temperature as for **P-1**. This reflects the similar substitution pattern of the ammonium by the ethyl acetate group.

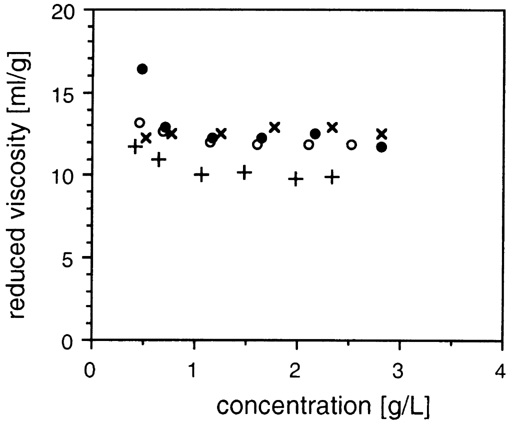

Fig. 5. Reduced viscosities of solutions of polycations at 30°C. (+) **P-3a** in water; (O) **P-4a** in ethanol; (×) **P-3b** in ethanol; and (●) **P-4b** in $CHCl_3$.

The thermal stability of the carbobetaines differs from the behaviour of their polycation analogues due to the different nucleophilicity of the carboxylate group compared to chloride. All new polymers bearing the ammonioacetate unit, i.e. **P-8a**, **P-8b**, **P-9a** and **P-9b**, decompose at temperatures of about 250°C. The benzoate bearing **P-10** starts to decompose at a similarly high temperature of 240°C. These values compare well with the onset of thermal degradation of the parent polymer **P-6**, whereas the poly(betaine)s **P-7a** and **P-7b** begin already to decompose around 210 and 185°C, respectively [21]. These findings support our previous hypothesis that the low thermal stability of poly(carbobetaine)s with a long flexible spacer between the ammonium and the carboxylate group may derive from a conformationally facilitated intramolecular or intermolecular nucleophilic attack of the carboxylate moiety on the ammonium group, presumably yielding a lactone or an ester [18,21].

The cationic and the zwitterionic polymers do not exhibit a glass transition in the dry state below their decomposition temperatures. This is attributed to the combination of the rather rigid polymer backbone containing cyclic structures with the high density of charged groups. The lack of an observable glass transition is also true for the polymers bearing long alkyl chains, which could act as intramolecular plasticisers. These observations are in agreement with those for most zwitterionic vinyl polymers that rarely exhibit a glass transition below their decomposition temperature [4,46,47].

The dry poly(carbobetaine)s and their polycation analogues were studied in bulk at ambient temperature (ca. 22°C) by X-ray powder diffraction. All polymers show only a broad halo at about $2\theta = 21°$ in the wide-angle range, demonstrating that the polymers are not crystalline. However, the polymers **P-2b**, **P-7b**, **P-3b**, **P-8b**, **P-4b** and **P-9b**, which bear a long alkyl fragment, exhibit one additional sharp and intense signal at small angles (Table 3). The general pattern of these diffractograms is similar to the ones reported previously for polymerised surfactants of the "head-type" [4]. The signals at small angles indicate the presence of a superstructure.

The presence of a single signal precludes assigning a particular superstructure to the diffraction patterns. Hypothetically, we assume a lamellar structure on the basis of previous results of structurally similar poly(sulfobetaine)s [31]. It is noteworthy that the Bragg distance found for the poly(betaine) **P-7b** is much smaller than that of the other polymers. This may point to an interdigitation of the alkyl side chains driven by the interaction of the well-separated cationic and anionic groups, whereas the other polymers may be arranged in a simple 'bilayer' structure,

Table 3
Characteristic peaks in X-ray powder diffractograms of diallylammonium polymers bearing long alkyl fragments

	Polymer					
	P-2b	**P-3b**	**P-4b**	**P-7b**	**P-8b**	**P-9b**
Angle 2θ of signal	3.1	3.5	3.5	4.5	3.2	3.2
Bragg distance (nm)	2.9	2.5	2.5	2.0	2.8	2.8

as found for structurally analogous poly(sulfobetaine)s [31] (see Fig. 6).

3.4. Inorganic–organic hybrid materials

The interaction of polycations and polyzwitterions in solution with various salts is well documented, also for diallyammonium polymers [11,23–25]. Such interactions are effective in bulk, too. In contrast to polycations, which may only undergo ion exchange, poly(sulfobetaine)s have been shown to form homogeneous mixtures with stoichiometric amounts of many inorganic [3–5] and organic salts [5]. Initial studies indicated analogous behaviour for the poly(carbobetaine)s [21]. We have therefore extended such miscibility studies to the new polymers. In fact, all the new poly(carbobetaine)s give homogeneous blends when mixed with equimolar amounts of NaI: no peak indicative of residual NaI was visible in the diffractograms, demonstrating the full miscibility. In the case of the poly(carbobetaine)s with long alkyl chains, **P-7b**, **P-8b** and **P-9b**, the mixing affects the small-angle peak in the powder diffractograms, corroborating the formation of homogeneous blends. However, the small angle disappeared upon mixing for **P-7b**, thus indicating the loss of the superstructure. For poly(betaine)s **P-8b** and **P-9b**, the small-angle peaks are preserved, but they become less intense and are shifted from $2\theta = 3.2$ to 3.5°. The difference in behaviour between **P-7b**, in which the cationic and the anionic group are separated by the long alkyl chain, and polymers **P-8b** and **P-9b**, which have the cationic and the anionic group next to each other but bear lateral alkyl chains, can be understood by assuming a different type of superstructure, as proposed in Fig. 6.

Poly(carbobetaine)s **P-6**, **P-7a** and **P-10** were selected for further study varying the anion and the cation of the admixed salts. The poly(sulfobetaine) analogue **P-5** was employed for comparison. The results listed in Table 4 demonstrate that both anions and cations are important to obtain homogeneous blends. With regard to the anions, the observed selectivity in admixing their sodium salts with the poly(betaine)s is in agreement with the Hofmeister series [4,48]: perchlorate, iodide and nitrate admix well for all four polyzwitterions, whereas chloride and sulfate do not. Bromide is the borderline case. Its miscibility depends on the detailed polymer structure. Polymers **P-6**, **P-7a** and reference **P-5** give homogeneous equimolar blends, whereas **P-10** gives blends containing some phase-separated NaBr. The rigid spacer between the ammonium and the carboxylate group seems to disfavour miscibility. The role of the spacer is further illustrated by comparing the blends of **P-6** and **P-7a** with some nitrates of multivalent cations. **P-6** with the short spacer between the cationic and the anionic group is miscible in equimolar amounts with $Pd(NO_3)_2$ and $Bi(NO_3)_3$, but not with $Pb(NO_3)_2$, whereas **P-7a** is miscible

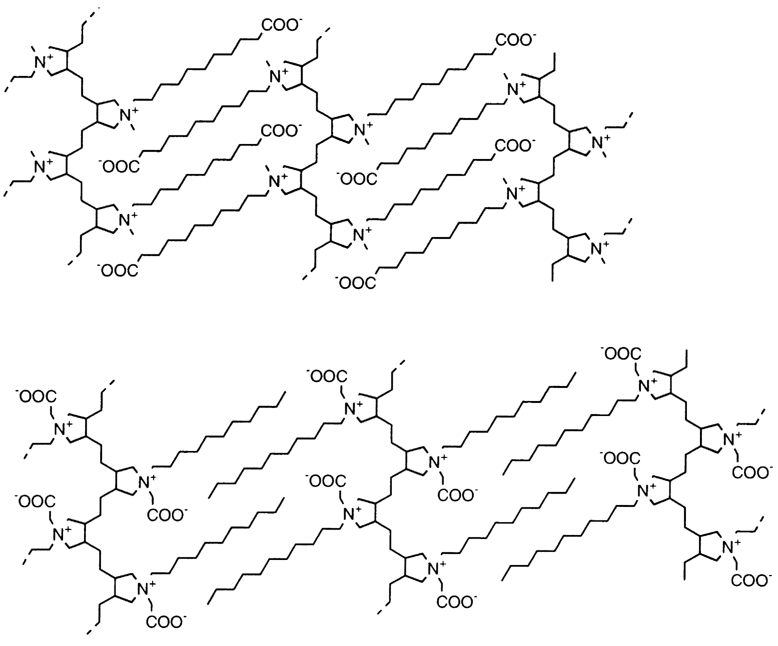

Fig. 6. Two possibilities for superstructures of amphiphilic poly(carbobetaine)s in bulk, depending on the relative positions of the cationic and of the anionic groups (schematic illustration for polymers **P-7b** and **P-9b**).

Table 4
Miscibility of poly(betaine)s with equimolar amounts of inorganic salts (+ = homogeneous blend, − = heterogeneous blend)

Admixed salt	Polymer			
	P5	**P6**	**P7a**	**P10**
Na_2SO_4	−	−	−	−
NaCl	−	−	−	−
NaBr	+	+	+	−
NaI	+	+	+	+
$NaClO_4$	+	+	+	+
$NaNO_3$	+	+	+	+
$Pd(NO_3)_2$		+	+	
$Pb(NO_3)_2$		−	+	
$Bi(NO_3)_3$		+	+	

in equimolar amounts with all three salts. Studies to exploit such homogeneous organic–inorganic hybrids for the preparation of metallic catalysts are under way.

The ability to form homogeneous hybrid materials is a remarkable feature of poly(betaine)s. Most probably, the simultaneous binding of the anions and the cations of the inorganic salt to the ammonium and carboxylate group is at the origin of this behaviour [4,5]. Still, such a simplistic "ion-pairing model" does not explain the possibility of dissolving even more than the stoichiometric amount of inorganic salt in a polymer matrix in some cases [49], as exemplified here by **P-7a** and $Pd(NO_3)_2$, $Pb(NO_3)_2$ or $Bi(NO_3)_3$.

4. Conclusions

We have developed a pathway to salt-free poly(carbobetaine)s by radical homopolymerisation of zwitterionic diallyl ammonium monomers. The preparation of zwitterionic monomers without contamination of inorganic salt is essential for fundamental studies. The diallyl ammonium unit can be substituted easily, to enable the variation the distance between the cationic and the anionic group, and to incorporate hydrophobic fragments at various positions of the monomers. The monomers and their polymers are inherently resistant to hydrolysis. Nevertheless, the monomers with four bulky substituents suffer from limited polymerisability. The initiator must be chosen with care and preferably, peroxides should be employed.

As for cationic diallyl ammonium polymers, the carbobetaines undergo cyclopolymerisation. The detailed microstructure of the polymers depends sensitively on the substituents. Compared to analogous poly(sulfobetaine)s, the new poly(carbobetaine)s are more hygroscopic and show better solubility. Their thermal stability increases with decreasing length of the spacer between the ammonium and carboxylate groups, and its rigidity, whereas lateral alkyl chains do not seem to have a great influence. Despite the high density of charged groups, the polymers are amorphous. DSC gave no indication of glass transitions below thermal decomposition, even when the polymers bear long alkyl chains, which could behave as plasticisers. In these cases, however, X-ray studies of the poly(carbobetaine)s and of the analogous polycations reveal the formation of superstructures in bulk. In contrast to their polycation analogues, all poly(betaine)s can form stoichiometric homogeneous blends with selected inorganic salts. For some MeX_2 and MeX_3 salts, the amount of homogeneously admixed salt can even reach equimolarity.

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