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Synthesis and solution properties of a new pH-responsive polymer containing amino acid residues

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Abstract

The amine salt, *N*,*N*-diallyl-*N*-carboethoxymethylammonium chloride was cyclopolymerized in water using ammonium persulfate as an initiator to afford a cationic polyelectrolyte which on acidic hydrolysis of the pendant ester groups gave the corresponding cationic acid salt (CAS). The CAS was converted into an anionic polyelectrolyte (APE) and polybetaine (PB). The solution properties of the APE having two basic functionalities were investigated in detail by potentiometric and viscometric techniques. Basicity constants of the amine as well as the carboxylate groups in APE are 'apparent' and as such follow the modified Henderson–Hasselbalch equation; as the degree of protonation (α) of the whole macromolecule increases, the protonation of the amine nitrogens and carboxylate groups becomes increasingly more difficult and easier, respectively. While the APE, PB and CAS were found to be soluble in salt-free water, the corresponding PB and CAS of the SO_2 copolymers of the amine salt **1** were found to be insoluble in water. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Polybetaine; Poly(amine salt)

1. Introduction

The discovery of cyclopolymerization of *N*,*N*-diallyl quaternary ammonium salts by Butler [1] led to the synthesis of an array of water-soluble cationic polyelectrolytes (CPEs) [2–4] of tremendous scientific and technological interest. The ammonium salts have also been successfully copolymerized [5–7] with sulfur dioxide to give copolymers. These CPEs have found extensive industrial and commercial applications [8,9] as paper additives, de-emulsifier of dispersed oil, paint thickeners, flocculants and coagulant aid in potable water and waste water treatment. Poly(diallyldimethylammonium chloride) alone accounts for over 1000 patents and publications. Modifications of Butler's monomers have provided entries [10–17] into the amphoteric polymers containing zwitterions on the same monomer (i.e. betaines) or along the same backbone (i.e. ampholytes). Amphoteric polymers have also found many applications in various fields [18,19] including their use as a simple model [20,21] for understanding the complex behavior of proteins. Amphoteric polymers, unlike polyelectrolytes, can exhibit 'anti-polyelectrolyte behavior' [11,22–26], i.e. enhancement in viscosity and solubility in the presence of added electrolytes (e.g. NaCl) due to the neutralization of the ionically cross-linked network in a collapsed coil conformation of the polyampholytes.

Quaternary ammonium salts having carboxy group in the pendant have been cyclopolymerized to polybetaines (PBs) which show pH-responsive solution behavior due to the incorporation of the pH-triggerable carboxybetaine functionality [13,15–17,27]. However, the use of amine salt (instead of a quaternary salt) with a carboxy pendant should permit generation of a trivalent nitrogen in the resultant polymer. The presence of strongly basic trivalent nitrogen as well as weakly basic carboxy functionalities would indeed demonstrate interesting pH-responsive solution behavior in a wider spectrum of the pH scale. In this context, we have recently reported [28,29] the synthesis of the amino acid–sulfur dioxide copolymers **2** from the diallyl amine salt monomers **1** (Scheme 1). Modification of Butler's monomers (diallyl quaternary ammonium salts), thus, allowed us to convert the CPE **2** into the cationic acid salt (CAS) **3**, PB **4**, and anionic polyelectrolyte (APE) **5** which exhibited interesting solution properties. To our knowledge, the homopolymers from amine salts of the type **1** have not been reported before. In our continuing studies of zwitterionic polymers, we now report the synthesis and solution properties of the homopolymers from the amine salt **1a**. The study would provide us with the opportunity to compare the solution properties in absence of SO_2 spacer in the polymeric backbone.

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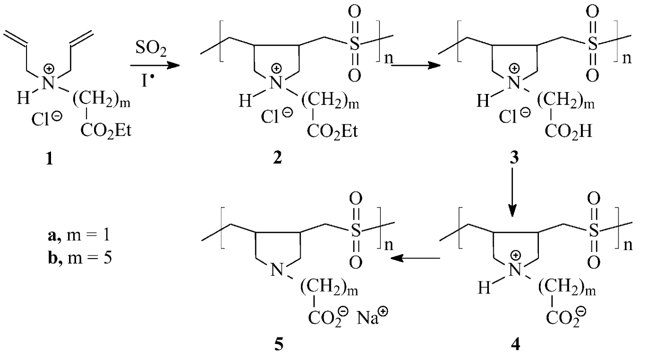


Scheme 1.

2. Experimental

2.1. Physical methods

Melting points are recorded in a calibrated Electrothermal IA9100 Digital Melting Point Apparatus using heating rates of 1 °C/min in the vicinity of the melting points. Elemental analyses were carried out in a Carlo-Erba elemental analyzer Model 1102. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer (Spectral resolution, 4 cm^{-1}; Number of scans, 19). ^{1}H and ^{13}C NMR spectra of the polymers were measured in D_2O using dioxane as internal standard on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made by an Ubbelohde viscometer (having Viscometer Constant of 0.005718 cSt/s all temperatures) using CO_2-free water under N_2 in order to avoid CO_2 absorption which may affect the viscosity data.

2.2. Materials

AIBN from Fluka was purified by recrystallization from a chloroform–ethanol mixture. Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK) and *t*-butylhydroperoxide (TBHP; 80% in ditertiarybutylperoxide) from Fluka Chemie AG (Buchs, Switzerland) were used as received. All glassware were cleaned using deionized water. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a bp of 64–65 °C (4 mmHg). For dialysis, Spectra/Por membrane with MWCO of 6-8000 was purchased from Spectrum Laboratories Inc.

2.3. General procedure for the polymerization of **1a**

A solution of the monomer **1a** [28] in deionized water (or DMSO) (of appropriate concentration) in a 10 cm^3 round bottomed flask was purged with N_2, and after adding the required amount of the initiator (as listed in Table 1), the mixture was stirred in the closed flask at the specified temperature and time. The reaction mixture remained transparent throughout the process. At the end of the specified time, the ^{1}H NMR spectra of the crude reaction mixture revealed the composition of the polymer and unreacted monomer. The reaction mixture was cooled, transferred to a dialysis bag and dialyzed against deionized water for 12 h in order to remove the unreacted monomer (checked with $AgNO_3$ test). The polymer solution was then freeze-dried and subsequently dried to a constant weight at 70 °C under vacuum. The ^{1}H NMR revealed significant (~50%) hydrolysis of the ester group in the polymer both during polymerization and dialysis. The hygroscopic white polymer was thus found to be composed of **6**, **7** and **8**, and their approximate compositions were used to calculate the yields of the polymers (Scheme 2). Since the polymer was a mixture of **6**, **7** and **8**, the elemental and spectral analyses are not presented.

2.4. Acidic hydrolysis of the mixture containing **6**, **7** and **8** to obtain polybetaine **8**

The reaction mixture (entry 6, Table 1), repeated on a large scale using 18 g (81.9 mmol) of the monomer **1a**, was dialyzed briefly (3 h) against deionized water to remove the unreacted monomer. To the polymer solution, taken in a flask, was added an equal volume of concentrated HCl solution. The solution was stirred in the closed flask at 50 °C for

Table 1
Effect of concentration of monomer and initiator on polymerization of the monomer **1a**

Entry no.	Monomer[a] conc (%, w/w)	Solvent	Initiator (mg/g monomer)[b,c]	Temp. (°C)	Time (h)	Yield[d] (%)
1	70	Water	A 20	70	15	Trace
2	50	DMSO	B 55	50	48	Trace
3	50	DMSO	C 65	58	20	11
4	75	Water	B 30	95	4	22
5	80	Water	B 55	95	4	45 (40)
6	80	Water	B 80	95	4	62 (51)
7	80	Water $(+H^{+})$[e]	B 80	95	4	27
8	80	Water $(+H^{+})$[e]	A 20	70	15	Trace

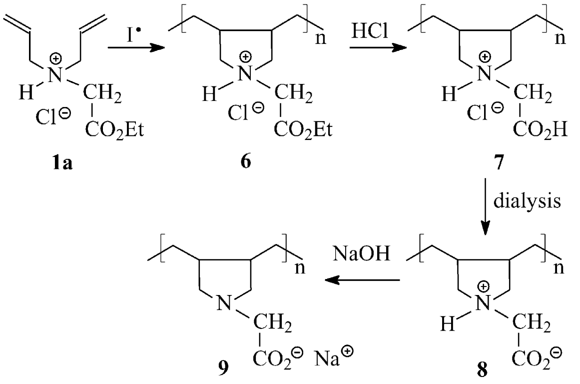
[a] In each experiment, 2.5 g of the monomer **1a** was used. The experiment as described in entry no. 6 was repeated using 18 g of the monomer.

[b] A, *t*-butylhydroperoxide; B, ammonium persulfate; C, azobisisobutyronitrile.

[c] Two-third of the inititor B is added in the beginning and the rest is added at the half time.

[d] Yield as determined by ^{1}H NMR analysis; isolated yields are written in parentheses.

[e] The reaction mixture contained 0.05 mmol of added HCl per mmol of the monomer **1a** to ascertain complete protonation of the monomer.



$$\underset{\mathbf{9}}{Z^-} + H^+ \overset{K_1}{\rightleftharpoons} \underset{\mathbf{8}}{ZH^\pm} \qquad \underset{\mathbf{8}}{ZH^\pm} + H^+ \overset{K_2}{\rightleftharpoons} \underset{\mathbf{7}}{ZH_2^+}$$

$$\log K_i = \mathrm{pH} - \log[(1-\alpha)/\alpha] \quad (1)$$

$$\mathrm{pH} = \log K_i^o + n \log[(1-\alpha)/\alpha] \quad (2)$$

$$\log K_i = \log K_i^o + (n-1) \log[(1-\alpha)/\alpha] \quad (3)$$

Scheme 2.

72 h (or until the hydrolysis of the ester group was complete as indicated by the absence of the ethoxy proton signals in the ^{1}H NMR spectrum). The reaction mixture was then dialyzed against deionized water (to remove HCl). The dialysis was continued against distilled deionized water for an additional 48 h after the negative test with $AgNO_3$ in order to ensure the complete removal of the small ions. The resulting solution was freeze-dried and subsequently dried to a constant weight at 70 °C under vacuum. The white zwitterionic PB **8** was stored in a dessicator. Yield 6.74 g (47.5% in two steps). The onset of thermal decomposition (closed capillary): the polymer did not melt, change color or char up to 400 °C. (Found: C, 56.01; H, 8.66; N, 8.13. $C_8H_{13}NO_2{\cdot}H_2O$ requires C, 55.47; H, 8.73; N, 8.09); υ_{max} (KBr) 3442, 2926, 2856, 1624, 1458, 1400, 1062 and 918 cm^{-1}.

2.5. Basification of the PB 8

To a solution of PB **8** (2.70 g, 15.6 mmol) in water (7 cm^3) was added a solution of NaOH (1.20 g, 30 mmol) in water (5 cm^3). The polymer APE **9** was precipitated into acetone, filtered and washed with liberal excess of acetone. The polymer was soaked in a mixture of 10% methanol in acetone for several hours and the supernatant liquid was decanted off. The process was repeated three times to ensure the removal of any excess NaOH in the polymer sample. The resulting solution was dried to a constant weight at 70 °C under vacuum to obtain the APE **9** as a white solid (2.73 g, 89.8%).

The onset of thermal decomposition (closed capillary): the color changed to dark yellow at 390 °C, but the polymer did not melt or char up to 400 °C. (Found: C, 48.85; H, 7.51; N, 6.92. $C_8H_{12}NO_2Na{\cdot}H_2O$ requires C, 49.23; H, 7.23; N, 7.18%); υ_{max} (KBr) 3424, 2924, 2860, 2790, 1590, 1408, 1318, 1162, 994, and 904 cm^{-1}.

2.6. Acidification of PB 8 with HCl

A sample of the polymer PB **8** (2.70 g, 15.6 mmol) was treated with 5 cm^3 of concentrated HCl solution. After removal of the water by a gentle stream of N_2, the residue was dried under vacuum at 50 °C. The polymer was then crushed into powder and redried to a constant weight at 50 °C under vacuum to obtain the CAS **7** (3.18 g, 97.3%) as a white polymer.

The onset of thermal decomposition (closed capillary): the color changed to brown at 375 °C, but the polymer did not melt or char up to 400 °C. (Found: C, 46.26; H, 7.87; N, 6.69. $C_8H_{14}NO_2Cl{\cdot}H_2O$ requires C, 45.83; H, 7.69; N, 6.68%); υ_{max} (KBr) 3434, 2928, 2664 (broad), 1738, 1636, 1420, 1204, 1072, and 900 cm^{-1}.

2.7. General procedure for the copolymerization of the monomer 1a with SO2

All the polymerizations were carried out using conditions as described in Table 2 and according to the procedure reported earlier [28]. The copolymer **2** from the entry 1 was converted to the CAS **3a** (91.5% yield) and the APE **5a** using procedures as described [28].

2.8. Potentiometric titrations

The potentiometric titrations were carried out at 25 °C. A gentle stream of N_2 was passed through distilled deionized water at 90 °C for 15 min in order to remove dissolved gases. This water was used in the titration in salt-free and salt (NaCl, 99.9% purity) solutions and for viscosity

Table 2
Effect of concentration of monomer and initiator on polymerization of the monomer **1a**/SO_2 copolymerization

Entry no.	Monomer **1a** (mmol)	SO_2 (mmol)	DMSO (g)	AIBN[a] (mg)	Temp. (°C)	Time (h)	Yield[b] (%)	$[\eta]$[c] (dl/g)
1	20	40	15	220	60	28	58	0.0773
2	20	20	12	220	60	18	78	0.217
3[d]	20	20	4	80	55	15	73	1.11

[a] Azobisisobutyronitrile.

[b] Based on 1/1 monomer complex of **1a**/SO_2.

[c] Viscosity of 1–0.125% polymer solution in 0.1N NaCl at 30 °C was measured with a Ubbelohde Viscometer ($K = 0.005718$).

[d] Taken from our previous work [28].

measurements. For each titration, 200 cm^3 of salt-free or 0.1N NaCl solution containing a weighed amount (usually around 0.26–0.47 mmol) of the APE **9** (or CAS **7**) was used. The solution was titrated at 25 °C with 0.1015 M HCl (or 0.1073 M NaOH) delivered by a buret under N_2. After each addition of the titrant (in the range 0.10–0.25 cm^3), the solution was stirred briefly, using a magnetic stir bar, under N_2. The pH of the solution was recorded using a Corning pH Meter 220. Under the conditions (containing large volume of 0.1N NaCl), the small amount of polymers or the small volume of the titrant used do not contribute much to the ionic strength, and as such the data were not corrected to zero ionic strength and activity coefficient corrections were not applied.

The protonation constant of the amine nitrogen, log K_1, is calculated at each pH value by the well-known Henderson–Hasselbalch Equation 1 (Scheme 2) where degree of protonation (α) is the ratio $[ZH^{\pm}]_{eq}/[Z]_0$. The $[Z]_0$ is the initial analytical concentration of the monomeric units in the APE **9** (or CAS **7**) and $[ZH^{\pm}]_{eq}$ is the concentration of the protonated species at the equilibrium given by $[ZH^{\pm}]_{eq} = C_H^+ - [H^+] + [OH^-]$, where C_H^+ is the concentration of the added HCl; $[H^+]$ and $[OH^-]$ at equilibrium were calculated from the pH value [30]. The typical electrolytes having apparent basicity constants could be described by Equation 2 (Scheme 2), where $\log K^0 = \mathrm{pH}$ at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. The linear regression fit of pH versus $\log[(1-\alpha)/\alpha]$ gave log K^0 and n as the intercept and slope, respectively. Simultaneous protonation of the two basic sites is least likely since the basicity constant for the COO^- group is less than that of the amine group by at least seven orders of magnitude. The second step protonation constant (log K_2) involving the COO^- is calculated by subtracting the equivalent volume from the total volume of the titrant. In this case, α represents the ratio $[ZH_2^+]_{eq}/[Z]_0$, whereby $[ZH_2^+]_{eq}$ equals $C_H^+ - [H^+] + [OH^-]$. For the titration of the CAS **7** with NaOH, the concentration of the protonated species is given by $[ZH_{i=1,2}]_{eq} = [Z]_0 - C_{OH}^- - [H^+] + [OH^-]$, where C_{OH}^- is the concentration of the added NaOH.

The experimental details of the potentiometric titrations are summarized in Table 3. Inserting the value of pH from Equation 2 to Equation 1 leads to modified Henderson–Hasselbalch Equation 3 [31,32] (Scheme 2) where ($n - 1$) gives a measure of the deviation of the studied polymers from the behavior of small molecules showing sharp basicity constants (for molecules having sharp basicity constants, n becomes 1).

2.9. Viscometric titration

The viscometric measurements were performed at 25 °C in the presence of various amounts of HCl and NaOH, but the concentration of the polymer was kept constant throughout. Two stock solutions of 0.02173 M (#A) and 2 × 0.02173 M (#B) polymer CAS **8** are prepared in 0.1N NaCl. The 0.02173 M stock solution (which is 0.448 g/dl) also contained 0.493 equivalent of HCl added from a 0.1015 M HCl solution. The reduced viscosity and pH of the 0.02173 M stock solution were measured. A known volume (usually about 1–2 ml), each of a 0.1073N NaOH solution and the stock solution #B was added to a known weight or volume (30 ml) of the stock solution #A in an Erlenmeyer flask. Equal volumes of NaOH solution and stock #B (having twice the molarity of the stock #A) are added to the stock #A in order to keep the concentration of the polymer same (i.e. 0.02173 M). However, the dilution changes the mole equivalent of the added HCl and its amount should be recalculated. The reduced viscosity and pH of the new solution A_1 were measured. The solution was then returned to the original Erlenmeyer flask and its weight was noted. Again, an equal volume of #B and 0.1073N NaOH were added to the known weight of the A_1. The pH and viscosity of the new solution A_2 were measured. Each time, the viscometer is cleaned and dried. Similar dilutions were done to obtain pH and reduced viscosity values of the 0.02173 M polymer solution in the presence of different amounts of added HCl and NaOH, the range of which is shown in Fig. 6. Pure CO_2-free water was used throughout, and the solutions were used immediately after preparation. A gentle stream of N_2 was passed over the open arms of the viscometer in order to prevent carbon dioxide absorption. The percentage of different ionic species in the solutions was calculated using Equation 2 (Scheme 2).

3. Results and discussion

3.1. Synthesis of the homopolymers

It has been found [15,29] that quaternary ammonium salts having pendant ester functionality do not give polymers in appreciable yields. Our earlier attempts [29] to homocyclopolymerize the monomer **1b** in DMSO failed to give the corresponding CPE. However, the monomer **1a** did undergo cyclopolymerization in aqueous solution in the presence of excessive amount of the initiators to give the CPE **6** (Scheme 2). The results of the polymerization under various conditions are given in Table 1. As is evident from the table, TBHP in water (entry 1) and APS in DMSO (entry 2) failed to give the polymer **6**. In order to ensure complete protonation of the monomer, the pH of the medium was adjusted to below 4 (entries 7 and 8), yet no polymer was obtained using TBHP, while the initiator APS gave the polymer in 27% yield only. A reasonable yield of the polymer was obtained with a 80 wt% monomer in water (entry 6) using APS as the initiator. The ^{1}H NMR spectra revealed significant (~50%) hydrolysis of the ester groups during polymerization and isolation of the polymer by dialysis. The hygroscopic white polymer was thus found to be a mixture of **6**, **7** and **8** and as such viscosity data of these mixtures were not measured. Upon hydrolysis in 6 M HCl, the polymer

Table 3
Experimental details for the protonation of the polymers APE **9** (Z^-) and PB **8** ($ZH^{\pm}$) at 25 °C in salt-free water and 0.1 M NaCl

Run	$ZH_2^{\pm}$ or Z^- (mmol)	C_T[a] (mol/dm^3)	α-Range	pH-range	Points[b]	log K_i^0[c]	N_i[c]	R^2[d]
Polymers in salt-free water								
1	0.4717 (ZH_2^+)	−0.1073	0.88–0.53	7.97–?10.74	16	10.80	3.16	0.9963
2	0.3945 (ZH_2^+)	−0.1073	0.85? − 0.48	8.42–11.02	20	10.74	3.12	0.9964
3	0.3253 (ZH_2^+)	−0.1073	0.82–?0.46	8.42?–10.89	22	10.59	3.17	0.9965
4	0.3739 (Z^-)	0.1015	0.46–?0.65	10.93?–9.81	15	10.67	3.22	0.9980
Average						10.70 (6)	3.17 (4)	
log K_1[e] = 10.70 + 2.17 log[(1 − α)/α]. For the reaction $Z^- + H^+ \rightleftharpoons ZH^{\pm}$								
1	0.3945 (ZH_2^+)[f]	−0.1073	0.49–0.11	2.36–3.06	34	2.41	0.74	0.9938
2	0.2576 (Z^-)	0.1015	0.11–0.57	3.28–2.56	17	2.60	0.68	0.9906
3	0.3453 (Z^-)	0.1015	0.14–0.62	3.20–2.47	18	2.58	0.72	0.9845
4	0.3739 (Z^-)	0.1015	0.09–0.39	3.20–2.62	25	2.48	0.73	0.9915
Average						2.52 (9)	0.72 (3)	
log K_2[e] = 2.52 − 0.28 log[(1 − α)/α]. For the reaction $ZH^{\pm} + H^+ \rightleftharpoons ZH_2^+$								
Polymers in 0.1 M NaCl								
1	0.4731 (ZH_2^+)	−0.1073	0.78–0.27	8.87–10.92	23	9.99	2.04	0.9947
2	0.3987 (ZH_2^+)	−0.1073	0.82–0.20	8.60–11.17	27	9.95	1.93	0.9958
3	0.3065 (ZH_2^+)	−0.1073	0.86–0.21	8.11–11.01	22	9.87	2.02	0.9946
4	0.3611 (Z^-)	0.1015	0.25–0.69	10.65–8.98	15	9.75	1.94	0.9906
5	0.2626 (Z^-)	0.1015	0.27–0.68	10.55–9.10	17	9.79	1.88	0.9877
Average						9.87 (10)	1.96 (7)	
log K_1[e] = 9.87 + 0.96 log[(1 − α)/α]. For the reaction $Z^- + H^+ \rightleftharpoons ZH^{\pm}$								
1	0.3987 (ZH_2^+)[f]	−0.1073	0.55–0.09	2.55–3.31	20	2.59	0.692	0.9915
2	0.3065 (ZH_2^+)[f]	−0.1073	0.58–0.09	2.64–3.43	18	2.70	0.698	0.9938
3	0.3611 (Z^-)	0.1015	0.11–0.44	3.36–2.68	26	2.61	0.807	0.9962
4	0.2626 (Z^-)	0.1015	0.15–0.52	3.30–2.75	17	2.74	0.718	0.9913
Average						2.66 (7)	0.73 (5)	
log K_2[e] = 2.66 − 0.27 log[(1 − α)/α]. For the reaction $ZH^{\pm} + H^+ \rightleftharpoons ZH_2^+$								

[a] Titrant concentration (negative and positive values indicate titrations with NaOH and HCl, respectively).
[b] Number of data points from titration curve.
[c] Values in the parentheses are standard deviations in the last digit.
[d] R, correlation coefficient.
[e] $\log K_i = \log K_i^0 + (n-1)\,log[(1-\alpha)/\alpha]$.
[f] Titration was carried out in the presence of 1.015 mmol of added HCl to attain the required values of the α.

mixture from entry 6 was converted to the cationic amine salt (CAS) **7** which underwent almost complete equilibration to PB **8** during prolonged dialysis. PB **8**, in addition of excess HCl and NaOH, was converted to the CAS **7** and APE **9**, respectively (Section 2). It is to be noted that the CAS **7** or the APE **9** cannot be purified by dialysis since they invariably equilibrate to the PB **8**.

3.2. Synthesis of low molecular weight copolymers, and solubility of the homo- and co-polymers

While PB **8** and APE **9** were found to be readily soluble in water but insoluble in methanol, CAS **7** was found to be soluble in both the solvents. This is in stark contrast to our earlier findings [28,29] on the solubility behavior of the corresponding SO_2 copolymers **3**–**5**. While the APE **5a** and **b** were soluble in water, the CAS **3a** and PB **4a** were found to be practically insoluble in every common solvent including methanol and water in the presence or absence of common salts (e.g. KCl). The PB **4b** or a polymer containing varying proportion of PB **4b** and CAS **3b** were found to be partially soluble in salt-free water. A mixture having an approximate composition of 3:1 for the PB **4b** and CAS **3b** has almost zero solubility, and as the proportion of the CAS **3b** increases the solubility also increases. However, in 0.1N NaCl, the PB **4b** was found to be soluble, and a mixture having an approximate composition of 1:1 of CAS **3b** and PB **4b** had the least solubility. Such a difference in the solubility behavior was thought partly to be the result of the higher molecular weight of the SO_2 copolymers. The copolymers **5a** and **b** used for the studies [28,29] had the intrinsic viscosity values of 1.50 and 0.614 dl/g in 0.1N NaCl at 30 °C, respectively, whereas the homopolymer **9** used in this work has much lower viscosity values (vide infra). In order to find out the effect of molecular weight on the solubility behavior, we synthesized low molecular weight copolymer **2** as described in Table 2 (entry 1). Manipulating the ratio of the comonomer SO_2, we were able to get the polymer **2a** and its corresponding APE **5a** of low molecular weight as indicated by their very low intrinsic viscosity values of 0.0773, and 0.184 dl/g, respectively, in 0.1N NaCl at 30 °C. The ^1H and ^{13}C NMR spectra of these low molecular weight polymers (**2a** and **5a**, Scheme 1) (entries 1 and 2, Table 2) matched with that of the polymer (entry 3) reported in our earlier work [28]. The elemental analyses of the copolymers indicated that the monomers **1a** and SO_2 were incorporated in a 1:1 ratio, regardless of the molar ratio of the starting monomers. It has been unequivocally confirmed by several groups [16,33] that the cyclocopolymerization of diallyl quaternary ammonium salts with SO_2 leads to the formation of alternating cyclocopolymer having symmetric five-membered pyrrolidine ring structure in the polymer backbone. Our ^{13}C NMR spectral data [28] were consistent with the five-membered ring structure, and ruled out the presence of six-membered piperidinium rings in the polymer backbone.

The CAS **3a** and PB **4a** derived from hydrolysis of the low molecular weight polymer **2a** (entry 1, Table 2) were found to be insoluble in water, thus implying the dependence of solubility on structural matter rather than on the molecular weight. End group analysis by ^1H NMR spectroscopy enabled us to estimate the molecular weight of the polymer (entry 1, Table 2). The spectra (both ^1H and ^{13}C) revealed the absence of any alkene proton or carbon, thus suggesting that the chain termination is a degradative chain transfer process [34] involving transfer of an allylic hydrogen from the monomer to a chain radical. The signal of the $(CH_3)_2C(CN)$ moiety (originating from the AIBN initiator) attached to the chain end is displayed as a singlet at δ 1.31 ppm and was free of any overlapping signal. Careful integration of the peak indicated the number average degree of polymerization to be about 52.

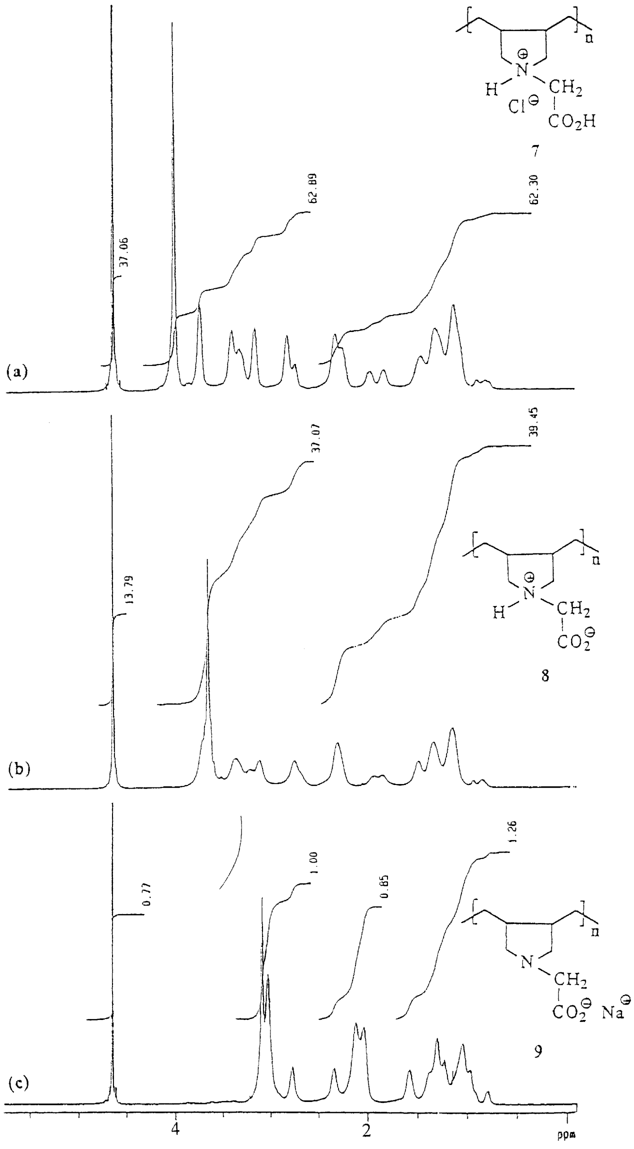


Fig. 1. ^1H NMR spectrum of (a) CAS **7**, (b) PB **8**, and (c) APE **9** in D_2O.

3.3. Infrared spectra

The IR spectra of the homopolymers **6–9** indicate the presence of the CO_2 unit into the polymer. Absorption at 1738 cm^{-1} was attributed to C=O stretch of COOH in the CAS **7**. While the symmetric stretching of COO^- in the dipolar form of PB **8** and anionic form of APE **9** appeared at 1400 and 1408 cm^{-1}, respectively, their corresponding anti-symmetric stretching appeared at 1624 and 1590 cm^{-1}. The absorption peaks are in agreement with those observed for simple amino acids [35].

3.4. NMR spectra

^1H and ^{13}C NMR spectra of the polymers **7–9** are displayed in Figs. 1 and 2, respectively. Carbonyl carbon resonances for **7**, **8** and **9**, observed at δ 169.18, 171.60 and 178.59 ppm, respectively, are not shown in Fig. 2. The absence of any residual alkene proton or carbon signal in the homopolymer spectra also suggested the degradative chain transfer process [34] for the termination reaction. The absence of the ester alkyl group (OCH_2CH_3) is evident, thus indicating its complete removal by hydrolysis. The assignments of the ^{13}C peaks are based on earlier works [7,15,36–38] on quaternary ammonium salt monomers which undergo cyclopolymerization to afford kinetically favorable five-membered ring rather than the thermodynamically favorable six-membered one. The use of the amine salt monomer in this work, however, does not change the preference; the spectral data are in agreement with the presence of five-membered pyrrolidine ring structure in the polymer backbone of the newly synthesized polymers **7–9**. The substituents at the C-b of the polymers **7** and **8** can either be in the symmetrical *cis* (**A** and **B**) or unsymmetrical *trans* (**C**) dispositions (Scheme 3). The presence of the two major *cis* forms **A** and **B** in unequal proportions, with *trans*- or *cis*-oriented $N{-}CH_2CO$ group, respectively, leads to the

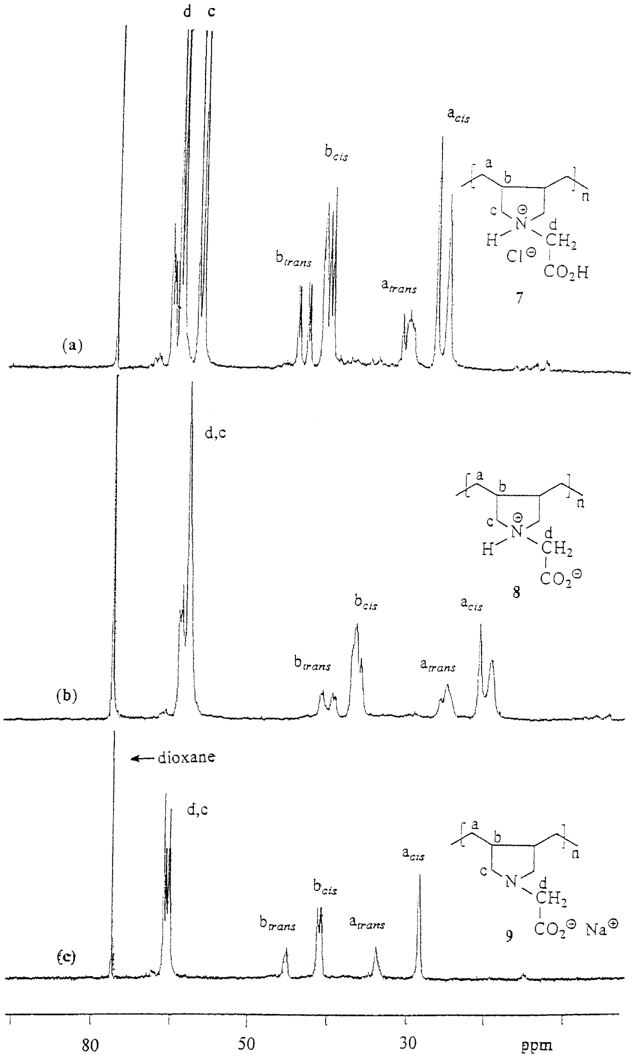
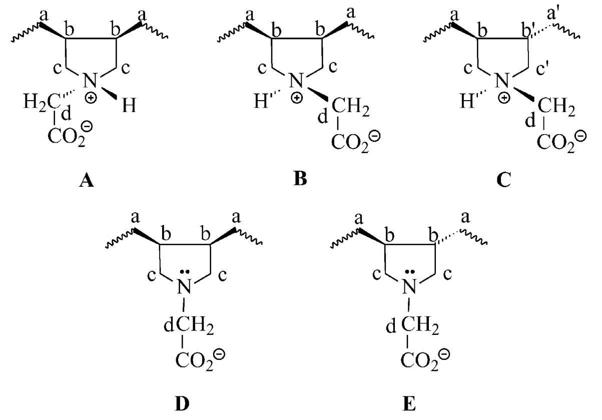


Fig. 2. ^1H decoupled ^{13}C NMR spectrum of (a) CAS 7, (b) PB 8 and (c) APE 9 in D_2O.



Scheme 3.

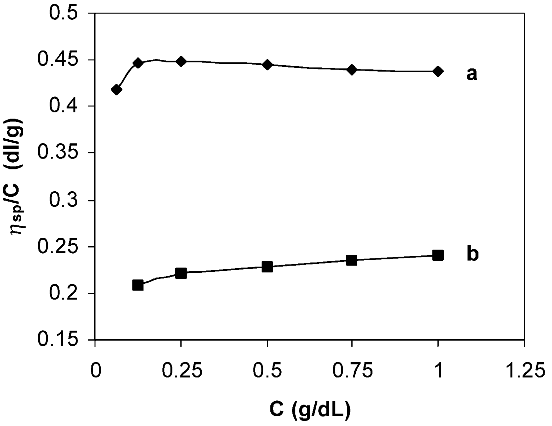


Fig. 3. The viscosity behavior of the APE **9** (obtained via hydrolysis of the CPE **6** from entry 6, Table 1) in (a) salt-free water and (b) 0.1N NaCl at 30 °C using an Ubbelohde Viscometer.

unequal splitting of the signals (e.g. a_{cis}, Fig. 2(a) and (b)). The C-b signals of the polymers **7** and **8** show two weak lines of equal intensity for the minor *trans* **C** (e.g. b_{trans}, Fig. 2(a) and (b)). However, it is interesting to note that the polymer **9** having trivalent nitrogen undergoes fast nitrogen lone pair inversion in the NMR time scale, and as such the N–CH_2CO group looses stereochemical integrity, and the splitting of the carbon signals in the *cis* (**D**) or *trans* (**E**) forms is not observed (Fig. 2(c), Scheme 3). The occurrence of further small splitting of equal intensity for some of the carbon signals (e.g. b_{trans} in **7** and **8** and b_{cis} in **9**, Fig. 2) may be ascribed to tacticity effects arising from the different configurations of the adjacent rings: the adjacent rings can add in two ways (*R* or *S*) with equal probabilities.

Integration of the relevant peaks in the ^{13}C spectrum yields the *cis*/*trans* ratio of the ring substituents to be 76/24 which is similar to that observed for the copolymers **2**–**5** and related homopolymers derived from the corresponding quaternary ammonium salts [15,16]. The appearance of N–CH_2CO_2 protons of the polymers **7**–**9** at δ 4.02, 3.66, and 3.09 ppm as broad singlets, respectively, indicates the progressive decrease in the electronegativity of the nitrogens due to the depletion of the positive charges. Both APE **9** and the CAS **7**, on dialysis, equilibrate to the PB **8** as indicated by the shift of the proton signals toward that of the PB, and the extent of the shift depends on the duration of the dialysis. The polymers were very stable and did not show any appreciable decomposition up to 400 °C.

3.5. Viscosity measurements

The simple conversion of the CPE **6** to ionic polymers **7**–**9** and their complete solubility in the acidic and basic media provided us an opportunity for the direct comparison of the solution properties of a cationic, anionic and zwitterionic polymer having the same degree of polymerization. Viscosity data for APE **9** (entry 6, Table 1) and its corresponding PB **8** and CAS **7** are presented in Figs. 3 and 4, respectively. In the absence of added salt (NaCl), the plot for APE **9** (Fig. 3(a)) is typical for polyelectrolyte, i.e. concave upwards in

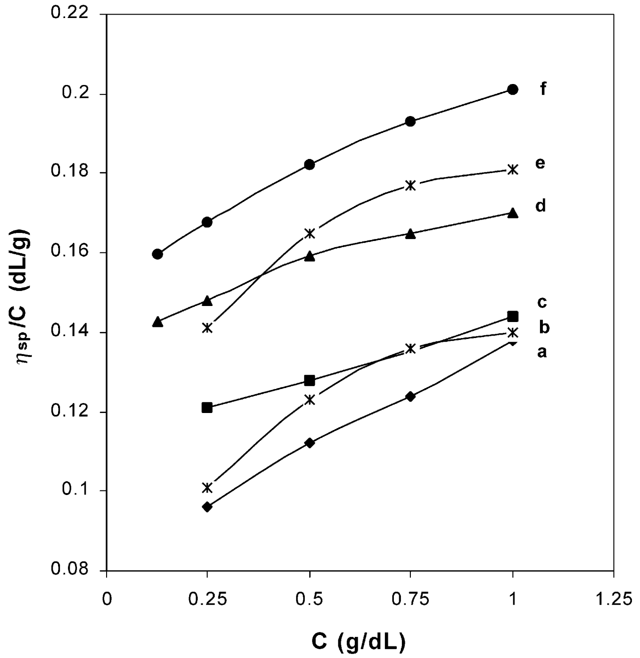


Fig. 4. The viscosity behavior of the PB **8** (obtained via hydrolysis of the CPE **6** from entry 6, Table 1) in (a) salt-free water, (c) 0.1N NaCl, (d) 0.3N NaCl, (f) 0.5N NaCl and of CAS **7** in (e) salt-free water and (b) 0.1N NaCl at 30 °C using an Ubbelohde Viscometer.

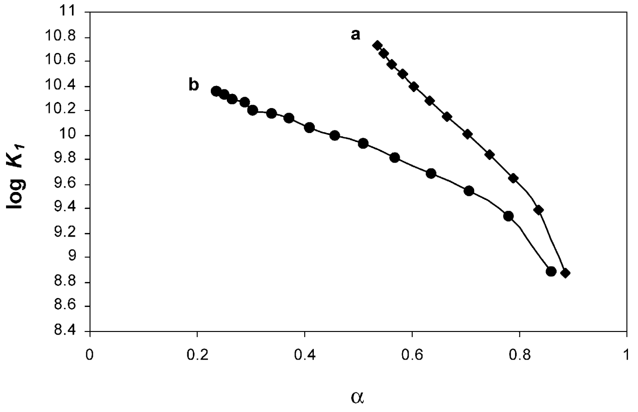


Fig. 5. Plot for the apparent log K_1versus α for APE **9** in (a) salt-free water and (b) 0.1N NaCl.

the concentrated solution; however, at higher dilution, the reduced viscosity tends to fall off due to the formation of the zwitterionic species **8** by partial protonation of APE **9**; the relative concentration of PB **8** is expected to increase with dilution. As expected, the viscosity values for the APE **9** decrease in the presence of added salt NaCl (Fig. 3(b)). The CAS **7** and PB **8** were found to have lower viscosity values as shown in Fig. 4. An increase in the intrinsic viscosity of the PB **8** with increasing NaCl concentration is a demonstration of the 'anti-polyelectrolyte' behavior of the PB. While the PB remains virtually electroneutral, the CAS **7** is a CPE, and like the APE **9**, its reduced viscosity values falls off rapidly in the higher dilution range due to the increasing equilibration to the PB **8**.

3.6. Basicity constants

In order to gain further information on the conformational transitions, we have determined the basicity constants, K_i^0, and the corresponding n_i values relative to the protonation of the tertiary amine and carboxylate in the polymer APE **9** in salt-free water and 0.1N NaCl solution. Basicity constants and the corresponding n_i values as well as the experimental details of the potentiometric titrations are given in Table 3.

The basicity constants of this polymer are found to be 'apparent' [31,32,39,40] since the n values are not equal to 1, and as such they vary with the degree of protonation (α). This behavior, i.e. the variation of K with α, is known as polyelectrolyte effect; polymer exhibiting a strong polyelectrolyte effect shows a large change in $\log K$ in going from one end to the other end of the titration. The magnitude of the n reflects the polyelectrolyte effect, and can be regarded as an index of accessibility of the proton to the amine nitrogen during the protonation reaction.

The basicity constant ($\log K_1^0$) of the amine group is higher by almost an unit in salt-free water when compare to 0.1N NaCl (Fig. 5 and Table 3). The n_1 values for the protonation of the amine nitrogen of APE **9** in salt-free water and 0.1N NaCl were found to be 3.17 and 1.96, respectively (Table 3). The n_1 values greater than 1 indicate that the approach of the incoming protons to the amine nitrogen groups becomes more and more difficult as the degree of protonation (α) of the whole macromolecule increases. The basicity constant ($\log K$) thus decreases progressively due to a decrease in the electrostatic field force as a result of decreasing overall negative charge density in the macromolecule (Fig. 5).

Several studies [41] indicated that the protonation of polymers is dictated by entropy effects involving release of water molecules from the hydration shell of the repeating unit that is being protonated. The exothermic enthalpy changes (ΔH^0) remain constant with the degree of protonation, α, and the ΔG^0 becomes less or more negative depending on whether the next repeating unit being protonated releases less or more water molecules, respectively, from its hydration shell than that of the unit protonated in the previous step. The polymer **9** in salt-free water is highly extended as indicated by higher viscosity values (Fig. 3(a)) and as such more hydrated (more water molecules in each hydration shell) than in salt solution (0.1N NaCl) (Fig. 3(b)) where the polymer chain adapts a compact conformation due to screening of the negative charges by the sodium ions. While each protonation of the amine nitrogen in APE **9** leading to zwitterions causes only a smaller contraction of the already compact polymer coil in 0.1N NaCl (Fig. 3(b) changes toward Fig. 4(c)), a larger contraction of the polymer coil happens in salt-free water (Fig. 3(a) changes toward Fig. 4(a)). The contraction of the macromolar chain leads to the lesser hydration of the repeating unit;

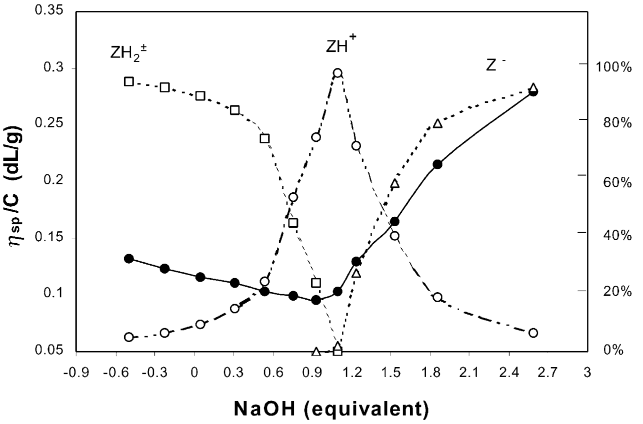
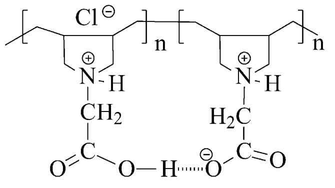


Fig. 6. Reduced viscosity (η_{sp}/C) of a 0.02173 M (i.e. 0.448 g/dl) solution of polymer CAS **7** in 0.1N NaCl (●) versus equivalent of added NaOH at 25 °C. Negative (−) values indicate the equivalent of added HCl. Distribution curves (dashed lines) of the various ionized species calculated from the basicity constants log K_1 and log K_2 in 0.1N NaCl at 25 °C.

thus with progressive protonation, the number of water molecules released from the hydration shell of the repeating unit being protonated becomes greater in salt-free water than in 0.1N NaCl. This is reflected by the higher n_1 value (3.17), greater basicity constant (log K_1: 10.70), and greater changes in the basicity constant in salt-free water (Fig. 5(a)) than in the 0.1N NaCl where the basicity constant and the n_1 values are found to be 9.87 and 1.96, respectively.

The n_2 values for the protonation of the COO^- in PB **8** in salt-free water and 0.1N NaCl were found to be 0.72 and 0.73, respectively. The n values less than 1, considered as diagnostic of a compact conformation, thus indicate that the approach of the incoming protons to the COO^- groups becomes easier and easier as the degree of protonation (α) of the whole macromolecule increases. The basicity constant (log K_2) thus increases progressively. Increase in the degree of protonation leads to a decrease in the number of zwitterionic groups with a consequent increase in the size of the macromolecular coil thus exposing the COO^- groups for easier access to protonation. With each protonation of the COO^-, the overall positive charges on the macromolecular chain, hence the number of water molecules to be released in the next protonation from the hydration shell of each unit, increases. This behavior seems to be general in all cases in which the basic COO^- group is in the α position to the nitrogen [32,42]. The basicity constants and the n_2 values for the protonation of the COO^- group are found to be similar in the salt-free and 0.1N NaCl solution (log $K_1^0 = 2.52$ in salt-free water; 2.66 in salt solution). The viscosity data support these findings since the PB has very similar viscosity values in the salt-free and 0.1N NaCl solutions (Fig. 4(a) and (c)).

3.7. Viscometric titrations



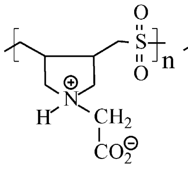
Scheme 4.

A viscometric titration of a 0.02173 M (0.448 g/dl) solution of the polymer CAS **7** containing 0.493 mole equiv. of HCl (i.e. for each mole of the repeating unit, 0.493 mole of HCl added) in 0.1 M NaCl solution at 25 °C is reported in Fig. 6. The figure also includes the distribution curves of the different ionized species ZH_2^+ (CAS **7**), $ZH^{\pm}$ (PB **8**) and Z^- (APE **9**) calculated from the basicity constants (vide supra) and pH values. The titration was performed by adding a certain volume of a sodium hydroxide solution stepwise along with an equal volume of a 2×0.02173 M solution of the polymer CAS **7**. This was done to keep the polymer concentration constant throughout the titration. Reduced viscosity decreases continuously until a critical minimum value is reached after an addition of about one equivalent of NaOH. At this point the concentration of the zwitterionic species, $ZH^{\pm}$, reaches the maximum percentage point and the polymer remains as a compact coil due to the internal neutralization of charges. A steep increase in the viscosity values is observed on further addition of the NaOH solution which changes the polymer to the APE **9**, thereby provoking a continuous extension of the macroion. On the acidic side of the titration, the chain extension, hence increment in the reduced viscosity values, are not so significant thus indicating the compact conformation of the polymer. The intrachain hydrogen bonding, as shown in Scheme 4, may result in a locally ordered structure which helps to reduce the hydrodynamic volume of the polymer thus giving lower viscosity values. Another point to be made is that in NaCl solution, while the chloride ions with smaller hydration shell may effectively neutralize cationic charges in the polymer backbone, the cation Na^+ with larger hydration shell, may not be able to approach close enough to neutralize the anionic charges on the carboxylate group. As a consequence, the polymer chains remain compact in the acidic side, but extensive chain expansion results in the anionic form. The observations presented earlier are supported by the viscometric studies (vide supra).

3.8. Polymer structure versus solubility

Solubility behavior and basicity constant of several PBs at 25 °C in salt-free and 0.1N NaCl solution are listed in Table 4. It is evident from the table that the presence of zwitterionic moiety does not invariably lead to insolubility in salt-free water. While all the listed homopolymers are soluble in salt as well as salt-free solutions, the corresponding copolymers with SO_2 are

Table 4
Solubility behavior and basicity constant of several PBs at 25 °C in salt-free and 0.1N NaCl solution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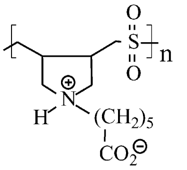
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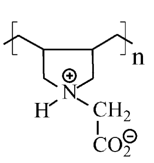
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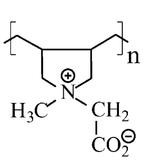
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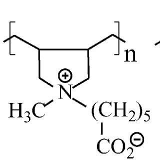
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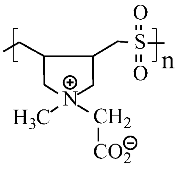
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Polybetaine	Salt-free water		0.1N NaCl		Solubility in	
	$\log K_i^0$	n_i	$\log K_i^0$	n_i	Salt-free water	0.1N NaCl
4a	8.73	1.81	7.88	1.16	Insoluble	Insoluble
4b	8.88	1.61	8.04	1.32	Insoluble	Soluble
8	10.70 $i = 1$	3.17	9.87	1.96	Soluble	Soluble
	2.52 $i = 2$	0.72	2.66	0.73		
10	2.49	0.61	2.30	0.89	Soluble	Soluble
11	3.52	1.17	4.36	1.21	Soluble	Soluble
12	–		–		Insoluble	Soluble

found to be insoluble. The presence of SO_2 seems to be a requirement for the insolubility of this type of cyclopolymers, however, at this stage, we are unable to offer any rationale behind this.

4. Conclusions

Following our continued interest in the establishment of correlations between chemical structure and physicochemical properties in pH-responsive polymers, we have synthesized and studied a new polymer containing pH-triggerable amine and carboxylate functionalities. The work has also demonstrated a simple way to convert a CPE into a PB and APE and thus has provided the opportunity to compare the solution properties of the different type of ionic polymers having identical degree of polymerization. Conformational behavior of the polymers is strongly influenced by the nature and the net charge on the macromolecular chain.

Acknowledgements

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