

Synthesis and Comparative Solution Properties of a Cationic Polyelectrolyte and Its Corresponding Polyzwitterion from 1,1-Diallyl-4-methoxycarbonylpiperidinium Chloride

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ABSTRACT: The quaternary ammonium monomer 1,1-diallyl-4-methoxycarbonylpiperidinium chloride was synthesized in good yield. On polymerization in water using *t*-butylhydroperoxide as initiator, a cationic polyelectrolyte (CPE) with a five-membered cyclic structure on the polymeric backbone was obtained. On acid hydrolysis, followed by basification, the CPE gave the corresponding polybetaine (PB). The solution properties of these polymers were investigated by potentiometric and viscometric techniques. The PB demonstrated "antipolyelectrolyte" behavior. The basicity constant of the carboxylate function-

ality in the polyzwitterionic polymers was 'apparent' in a 0.1 N NaCl solution and followed the modified Henderson-Hasselbalch equation. It was found that as the degree of protonation (α) of the whole macromolecule increases, the protonation of the amine nitrogen becomes increasingly more difficult. Unlike other polyzwitterions/polybetaines, the PB was soluble in salt-free water. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1477–1485, 2011

Key words: polyelectrolyte; polybetaine; ionic polymer; viscosity; water-soluble polymers

INTRODUCTION

Polybetaines (polyzwitterions) are an important class of macromolecules containing cationic and anionic groups embedded in the same monomer units,^{1–3} while the polyampholytes possess charged groups of different signs on different monomer units. In addition to common betaines like sulfo-, carbo-, and phospho-betaines, a few researchers have reported dicyanoethenolates also as betaines.⁴ There has been a tremendous interest to obtain polybetaines with advanced polymer architectures that mimic the functions of biopolymers and biomembranes with respect to their responsiveness to pH, temperature, or ionic strength change among other environmental stimuli. As such, polybetaines have found applications in various fields^{5,6} including their use as a simple model^{7,8} for understanding the complex behavior of proteins, and in bioseparations,² and DNA assay.⁹ Polybetaines, unlike polyelectrolytes, exhibit "antipolyelectrolyte" behavior,^{10–18} i.e., increase in viscosity and solubility in the presence of added electrolytes (e.g., NaCl) due to the neutralization of the physical attraction between the equivalent anions

and cations in the same monomer unit in a collapsed coil conformation.

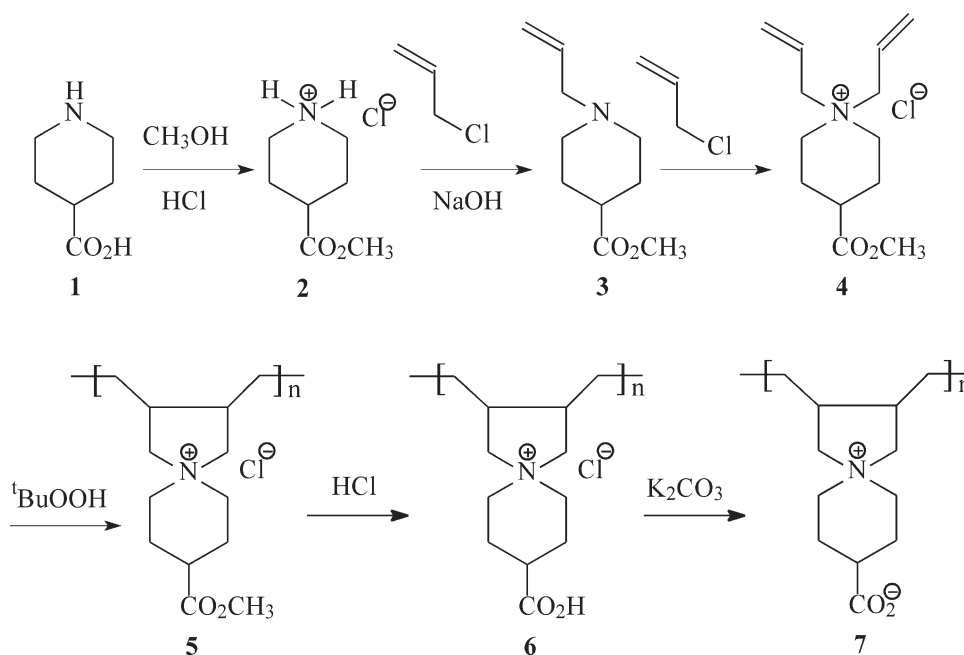
The synthesis of polybetaines has been the subject of several reviews.^{3,19–21} Polybetaines are obtained by two processes; (i) the polymerization of zwitterionic monomers and (ii) zwitterionic functionalization of precursor polymers.^{1,2,22–25} This article reports the synthesis and comparative solution properties of a cationic polyelectrolyte (CPE) **5** and its corresponding polybetaine (PB) **7** derived from cyclopolymerization of 1,1-diallyl-4-methoxycarbonylpiperidinium chloride (**4**); a quaternary ammonium salt having a pendant ester functionality (Scheme 1). The hydrolysis of the ester pendants would change the cationic motifs in CPE **5** to pH-responsive zwitterionic motifs in PB **7**. The study has scientific significance in that, to the best of our knowledge, the placement of a zwitterionic motif in a six-member ring has not been previously reported. This study also provides an opportunity to compare the solution properties of CPE **5** with its corresponding pH-responsive PB **7** having an identical degree of polymerization.

EXPERIMENTAL

Materials

Piperidine-4-carboxylic acid ($\geq 97\%$), allyl chloride ($\geq 96\%$), and *t*-butylhydroperoxide (TBHP) (80% in

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Scheme 1 Synthesis and cyclopolymerization of the monomer 4.

di-*t*-butylhydroperoxide) were obtained from Fluka Chemie AG (Buchs, Switzerland), and were used as received. All glassware was cleaned using deionized water. For dialysis, Spectra/Por membrane with a molecular weight cut-off (MWCO) of 6000–8000 was purchased from Spectrum Laboratories, Inc., (Rancho Dominguez, CA, USA).

Physical methods

Melting points were recorded in a calibrated Electrothermal IA9100 Digital Melting Point Apparatus using a heating rate of 1°C/min in the vicinity of the melting point. 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. ¹H-NMR and ¹³C-NMR spectra of the polymers were measured on a JEOL LA 500 MHz spectrometer. Dioxane was used as internal standard in recording ¹³C-NMR spectra when D₂O was the solvent. Viscosity measurements were made by an Ubbelohde viscometer (having a viscometer constant of 0.005718 cSt/s at all temperatures) using CO₂-free water. A gentle stream of N₂ was passed through distilled deionized water at 90°C for 15 min to remove dissolved gases. This water was used to prepare solutions for the potentiometric titrations and viscosity measurements. For the salt solutions, 99.9% pure NaCl was used.

4-Methoxycarbonylpiperidinium chloride (2)

Moisture-free gaseous HCl (7 g, ~ 0.5 equivalent) was absorbed into a magnetically stirred solution of

piperidine-4-carboxylic acid (**1**) (50.6 g, 392 mmol) in 200 cm³ methanol at 20°C. An additional volume of methanolic HCl (100 cm³ containing 7 g HCl) was added, and the mixture was refluxed for 3 h. This was followed by using a gentle stream of N₂ at 50°C until the volume of the solution was halved. Ether was then added to obtain 4-methoxycarbonylpiperidinium chloride (**2**) as colorless needles (66 g, 94%). δ_H (D₂O): 1.75 (2 H, m, *J* 6.9 Hz), 2.05 (2 H, d, *J* 14.7 Hz), 2.66 (1 H, q, *J* 7.2 Hz), 2.95 (2 H, t, *J* 12.5 Hz), 3.30 (2 H, d, *J* 13.2), 3.60 (3 H, s, *J* 16.0 Hz).

1-Allyl-4-methoxycarbonylpiperidine (3)

Whilst a solution of the hydrochloride salt **2** (58.0 g, 321 mmol) in methanol (100 cm³) in an atmosphere of N₂ was stirred and kept cold using an ice-salt bath, an equivalent amount of sodium hydroxide (12.8 g, 321 mmol) was added. The temperature of the mixture was allowed to rise to 20°C, then allyl chloride (6.14 g, 80 mmol ~ 0.25 equivalent) were added portionwise over 15 min. A further 0.75 equivalents of allyl chloride (18.4 g, 241 mmol) was also added in small portions of 2 cm³ (in 3–5 min) followed by adding approximately the corresponding amount of NaOH/methanol from a stock solution of methanol (70 cm³) containing NaOH (12.8 g, 321 mmol). These additions were carried out over a period of 40 min, and stirring was continued for 20 h. After the elapsed time, the product mixture was diluted with an aqueous solution of 25% K₂CO₃ (150 cm³), and extracted with dichloromethane (5 × 120 cm³). The combined organic layers was dried using Na₂SO₄, concentrated, and the residual liquid was purified by

TABLE I
Cyclopolymerization of the Monomer 4^a

Entry No.	Monomer conc. (%w/w)	Initiator ^b	% Conversion by ¹ H-NMR ^b	Isolated yields	Intrinsic viscosity ^c (dL/g)
1	65	4.2	64	48	0.260
2	70	7.0	92	63	0.435
3	70	1.0	49	34	0.439
4	70	4.2	86	70	0.467
5	75	4.4	93	74	0.446
6	75	4.0	91	76	0.491
7	75	3.2	90	72	0.495

^a Polymerization reactions were carried out in water in the presence of *t*-BuOOH at 60°C for 24 h followed by an additional 24 h at 75°C.

^b Initiator (*t*-BuOOH) taken as mg/gram monomer.

^c Obtained by extrapolation of the linear parts of the curves usually in the range 0.25–0.0625 g/dL polymer solution in 0.1 N NaCl at 30°C measured with an Ubbelohde viscometer ($K = 0.005718$).

chromatography over silica gel using ether/methanol yielding **3**, (37 g, 63%) which was further purified by distillation (bp_{0.2mbar} 68°C). (Found: C, 65.4; H, 9.3; N, 7.6. C₁₀H₁₇NO₂ requires C, 65.54; H, 9.35; N, 7.64%); v_{\max} (neat) 3616, 3462, 3076, 2949, 2791, 1735, 1642, 1445, 1375, 1642, 1445, 1375, 1325, 1285, 1170, 1047, 1013, 920, 856, and 791 cm⁻¹; δ_{H} (CDCl₃): 1.77 (2 H, dq, *J* 4.0, 11.6 Hz), 1.90 (2 H, dt, *J* 4.0, 11.6 Hz), 2.01 (2 H, t, *J* 6.5), 2.30 (1 H, tt, *J* 4.5, 11.6 Hz), 2.87 (2 H, m), 2.98 (2 H, apparent d, *J* 7.1 Hz), 3.68 (3 H, s), 5.16 (2 H, m), 5.87 (1 H, m); δ_{C} (CDCl₃): 28.06, 40.79, 51.47, 52.69, 61.85, 117.75, 134.96, and 175.33.

1,1-Diallyl-4-methoxycarbonylpiperidinium chloride (**4**)

A mixture of 1-allyl-4-carbomethoxypiperidine (**3**) (13.0 g, 70.8 mmol) and allyl chloride (11.3 g, 148 mmol) in acetone (16 cm³) was stirred at 55°C in a closed vessel for 92 h. The reaction mixture was cooled, stirred with ether (40 cm³), allowed to settle, and the supernatant ether layer was removed by decantation. The insoluble salt was washed with ether and crystallized from acetone/methanol (~2%) at the low temperature of a freezer. It gave the monomer **4** as hygroscopic colorless crystals (15 g, 82%), mp 140–141°C. (Found: C, 59.8; H, 8.7; N, 5.2. C₁₃H₂₂ClNO₂ requires C, 60.11; H, 8.54; N, 5.39%); v_{\max} (KBr): 3435, 3058, 2962, 2884, 1727, 1640, 1442, 1306, 1216, 978, 868, 829, 776, 665, and 643 cm⁻¹; δ_{H} (D₂O): 2.05 (4 H, m, *J* 6.1 Hz), 2.73 (1 H, m), 3.24 (2 H, m), 3.44 (2 H, apparent d, *J* 13.1 Hz), 3.64 (3 H, s), 3.81 (2 H, d, *J* 7.6 Hz), 3.88 (2 H, d, *J* 7.3 Hz), 5.59 (2 H, d, *J* 8.2 Hz), 5.63 (2 H, d, *J* 10.4 Hz), 5.92 (2 H, m, *J* 6.26 Hz); δ_{C} (D₂O): 22.32, 38.08, 53.62, 57.44, 58.61, 124.55, 129.89, and 176.53. Because of its hygroscopic nature, the quaternary ammonium salt was stored inside a desiccator.

General procedure for the polymerization reactions

All the polymerizations were carried out under the conditions described in Table I. A solution of monomer **4** in deionized water was purged with N₂. After adding the required amount of the initiator *t*-butylhydroperoxide (as listed in Table I), the mixture was magnetically stirred in the stoppered flask at 60°C for 24 h and then at 75°C for a further 24 h. The ¹H-NMR spectra of the crude reaction mixture revealed the composition of the polymer **5** and unreacted monomer **4**. The reaction mixture was dissolved in a minimum amount of methanol and precipitated in acetone (3 times). The polymer was then dried to a constant weight at 60°C under vacuum. The hygroscopic white polymer **5** was stored in a desiccator. The onset of thermal decomposition (closed capillary): the color changed to tan at 290°C with some phase changes; and the color turned to dark brown at 365°C with more darkening on further heating at 390°C and slight charring at 395°C. (Found: C, 59.7; H, 8.7; N, 5.3. C₁₃H₂₂ClNO₂ requires C, 60.11; H, 8.54; N, 5.39%); v_{\max} (KBr): 3447, 2952, 1727, 1637, 1457, 1384, 1297, 1212, 1141, 1044, 934, 904, and 530 cm⁻¹.

Acidic hydrolysis of the polymer **5** to polybetaine **7**

A solution of the CPE **5** (3.66 g, 14 mmol, Entry 7, Table I) in 6 M HCl (40 cm³) was stirred at 50°C for 96 h (or until hydrolysis of the ester group was complete as indicated by the absence of the methoxy proton signals in the ¹H-NMR spectrum). The cationic acid salt **6** was then dialyzed against deionized water to remove HCl. The solution in the dialysis tube was then basified with K₂CO₃ (1.2 g, 8.7 mmol). Dialysis against deionized water was resumed to remove excess K₂CO₃, KHCO₃, and KCl (monitored by AgNO₃ test). The resulting solution of polybetaine **7**

was then freeze dried and subsequently dried under vacuum to a constant weight (2.4 g, 82%) at 65°C. The onset of thermal decomposition (closed capillary): the color started to become brownish at 255°C with slight and slow darkening on further heating up to 400°C where color became darker with no sign of charring. (Found: C, 68.5; H, 9.3; N, 6.5. $C_{12}H_{19}NO_2$ requires C, 68.87; H, 9.15; N, 6.69%); ν_{\max} (KBr): 3441, 2924, 1660, 1574, 1394, 1060, 936, and 704 cm^{-1} .

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 for the removal of dissolved gases. This water was used for titration in salt-free and salt (NaCl, 99.9% purity) solutions and for viscosity measurements. For each titration, 200 cm^3 of a salt-free or 0.1 N NaCl solution containing a weighed amount (usually ca. 0.40–0.63 mmol) of the polybetaine **7** was used. The solution was titrated at 25°C with 0.09950 M HCl delivered by a buret under N_2 gas. After each addition of the titrant (0.25 cm^3), the solution was stirred briefly with a magnetic stir bar under N_2 . The pH of the solution was recorded with a Corning 220 pH meter. Under these conditions (including a large volume of 0.1 N NaCl), the contributions of the small amount of polymers or the small volume of the titrant used to ionic strength is negligible, and as such, the data were not corrected to zero ionic strength and the activity coefficient corrections were not applied.

RESULTS AND DISCUSSION

Synthesis of monomer, polymers, and physical characterization

Carbomethoxypiperidinium chloride (**2**), obtained via esterification of the corresponding carboxylic acid **1**, was allylated to give **3**, which on further allylation gave the quaternary ammonium salt **4** in excellent yield (Scheme 1). Polymerization reactions of the monomer **4** were carried out in deionized water using *t*-butylhydroperoxide as the initiator. The results of the polymerization under various conditions and the intrinsic viscosities of the resultant polymers are given in Table I. It has been reported^{16,24} that quaternary ammonium salts with pendent ester functionality do not usually give polymers in appreciable yields; however, the current monomer **4** gave polymer **5** in very good yields. The resulting quaternary ammonium polymers were found to be soluble in methanol and were precipitated in acetone. As is evident from Table I, the higher yields and intrinsic viscosities were obtained for the polymerization reactions with a monomer

concentration of 75% (w/w). However, no clear trend was observed for the variation of the viscosity values with the initiator concentration.

The CPE **5**, containing ester pendants gave, on acid hydrolysis, the cationic acid salt (CAS) **6** in almost quantitative yield (Scheme 1). The hydrolysis of the ester group was complete as indicated by the absence of 1H and ^{13}C signals of the methoxy group in the NMR spectrum (Fig. 1). Subsequent basification of **6** with potassium carbonate led to polybetaine (PB) **7** containing charge centers of opposite signs in the same repeat unit. Unlike normal polyzwitterions which are soluble in brine only, both CAS **6** and polyzwitterions **7** were found to be soluble in salt-free water as well. The solubility of the PB **7** in salt-free water is rather unusual. Simply being a polyzwitterion is not enough to dictate solubility behavior; molar mass, the strength of the Coulombic attractions between the zwitterionic dipoles among other factors need to be considered.¹³

Earlier literature documented and provided a rationale for the solubility of quite a few polyzwitterions. Thus, the solubility behavior of the polybetaines **8–11** (Scheme 2) has been reported²⁶ to depend on the number of methylene units between the opposite charges. Carbobetaines having carboxyl pK_a values ≤ 2.0 are found to be insoluble in salt-free water and soluble in salt solutions. The apparent pK_a values of 2.0, 3.5, and 4.0 for polymers **8**, **10**, and **12**, respectively, reflect the effect of increasing distance between the charges. Polymer **8**, thus, has the most dispersed, hence least hydrated, negative charge in the carboxylate groups and as such is expected to exhibit the strongest Coulombic interactions between the opposite charges among these polymers.²⁷ While polymer **8** is reported to be insoluble in salt-free water, polymers **9–12** are soluble. Sterically crowded cationic charges in polymer **9**, owing to the presence of a methyl side group, are unable to manifest effective intra- or intermolecular Coulombic interactions thereby leading to its solubility in salt-free water. Similar screening of positive charges by the presence of methyl side groups or crowded environments in some sulphobetaines has led to their solubility in salt-free water as the steric encumbrance minimizes the intramolecular contacts between the opposite charges.^{10,12} Polymers **12a**, **12b**, and **13**, with carboxyl pK_a values of 2.52, 2.49, and 3.52, respectively, were reported to be soluble in salt-free water.^{16,18,25}

PB **7**, with carboxyl pK_a values >2 (2.93 in salt-free water; and 3.45 in 0.1 N NaCl solution) is expected to be soluble in water in line with the earlier findings. Sterically crowded cationic charges in polymer PB **7**, owing to the presence of the quaternary nitrogen in a spiro-position, may also find it difficult to manifest effective intra- or intermolecular Coulombic interactions thereby leading to its solubility in salt-free water.

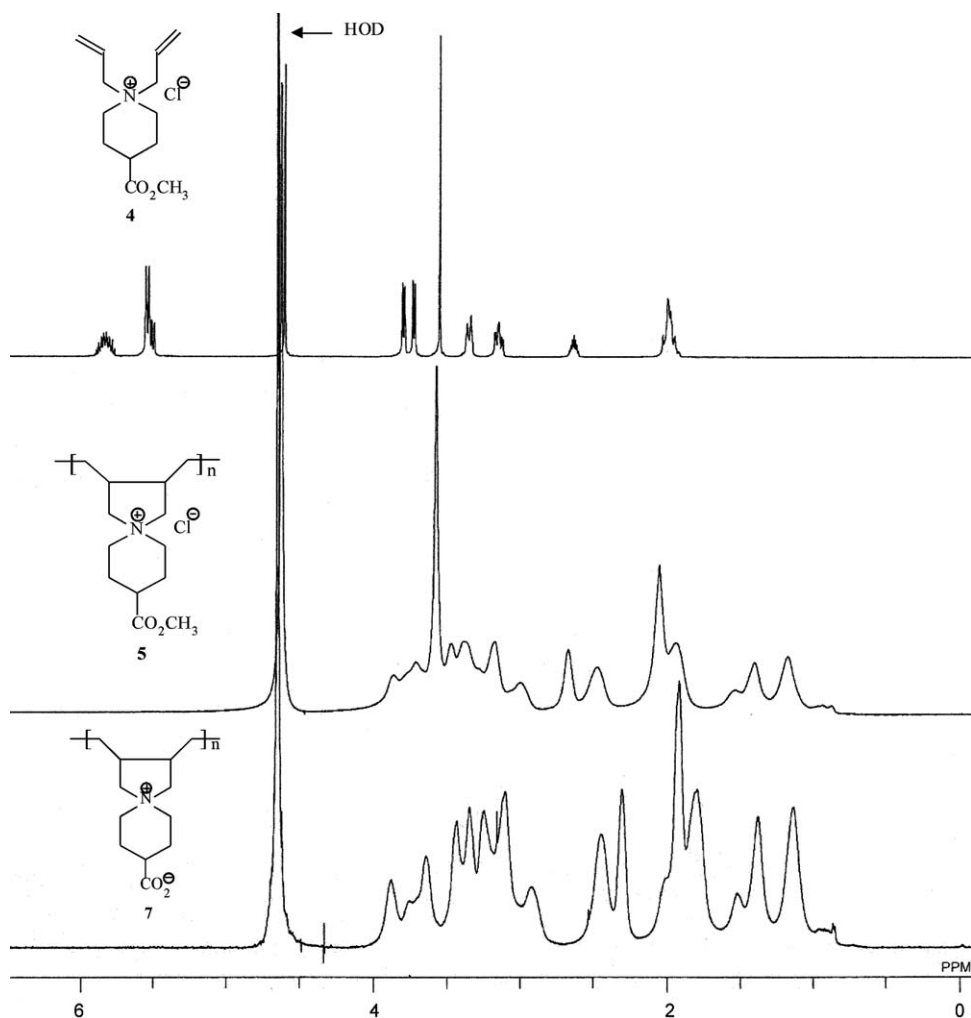
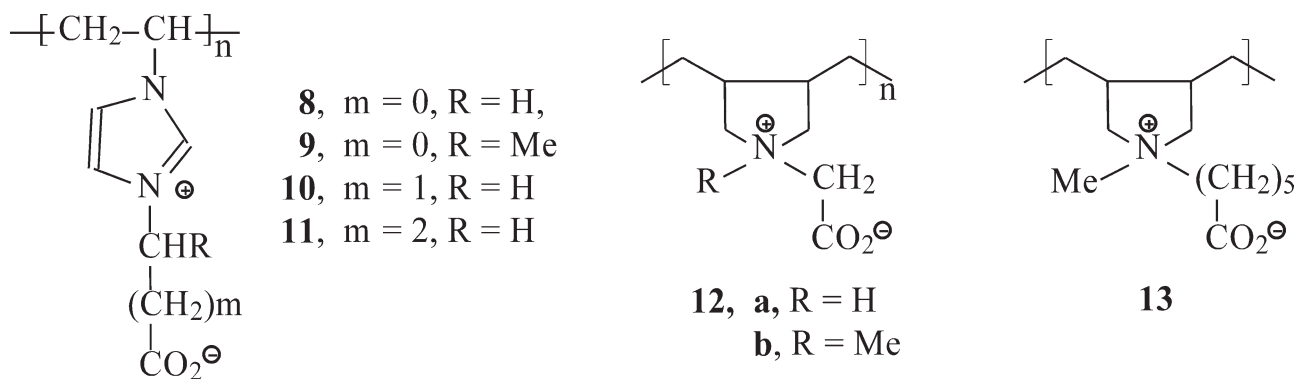


Figure 1 ^1H -NMR spectrum of 4, 5, and 7 in D_2O .

While CPE 5 showed a change of phase around 290°C and decomposed at $\sim 365^\circ\text{C}$, PB 7 did not even melt at 400°C . While the absorption at 1727 cm^{-1} in the IR spectrum of 5 revealed the presence of ester functionality, the absorptions at 1660 cm^{-1} (antisymmetric stretching) and 1574 cm^{-1} (symmetric stretching) were attributed to the carboxylate group in PB 7.

^1H signals at δ 5.59, 5.63, and 5.92 ppm (Fig. 1) and ^{13}C signals at δ 124.48 and 129.93 ppm (Fig. 2) of the vinyl group in 4 were absent in the spectra of CPE 5 or PB 7; thereby indicating the complete absence of a residual double bond. Note that the carbonyl resonance appearing at δ 176.59 ppm in the spectrum of 5 is shifted downfield to δ 181.98 ppm in the spectrum of 7.



Scheme 2 Structures of polybetaines.

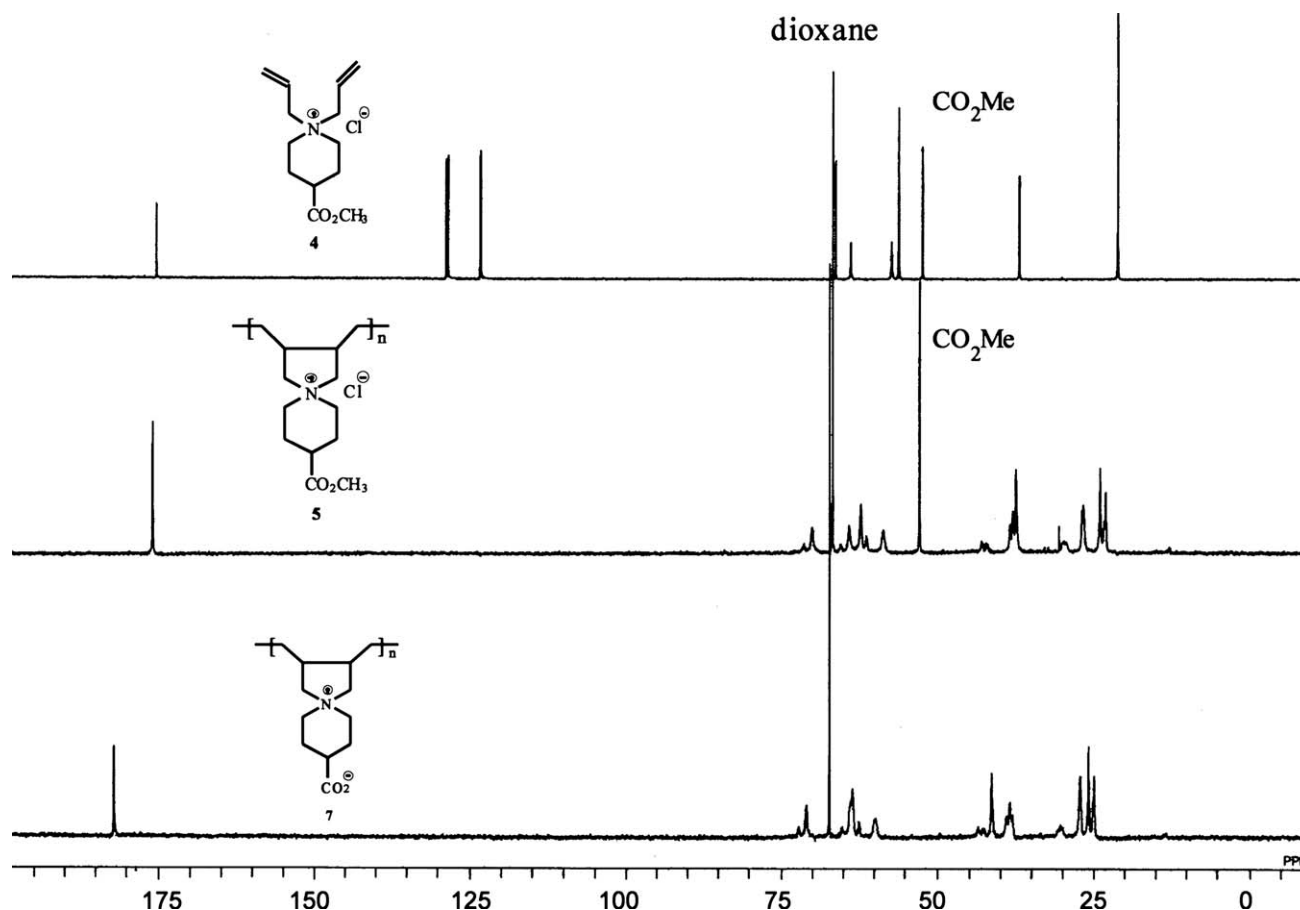


Figure 2 ^1H decoupled ^{13}C -NMR spectrum of 4, 5, and 7 in D_2O .

Viscosities of the polymers

The simple conversion of CPE 5 to PB 7 provided an opportunity for the direct comparison of the solution properties of polymers having the same degree of polymerization. The viscosity curves for CPE 5 are presented in Figure 3. In the absence of added salt (NaCl), the plot for 5 is typical for a polyelectrolyte, i.e., concave upwards. The addition of strong elec-

trolyte like sodium chloride suppresses the ionization of the polyelectrolyte 5, due to the common ion effect, and the viscosity becomes normal. The viscosity curve for polybetaine 7, on the other hand, is a straight line, and the viscosity is enhanced with the addition of sodium chloride (Fig. 4). The addition of salt causes the polybetaine to achieve more expanded

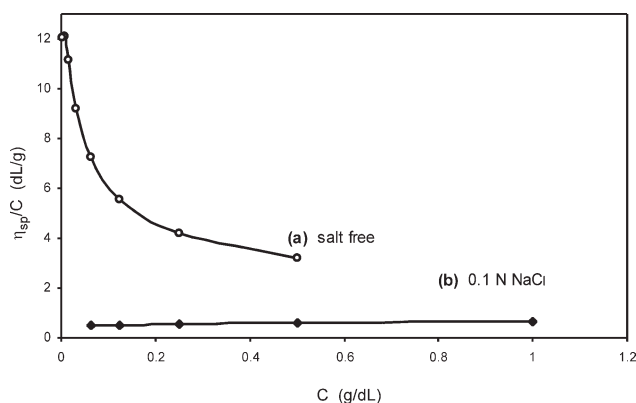


Figure 3 Viscosity behavior of polyelectrolyte 5 (Entry 7, Table I) (a) in salt-free water and (b) in 0.1 N NaCl at 30°C using an Ubbelohde viscometer.

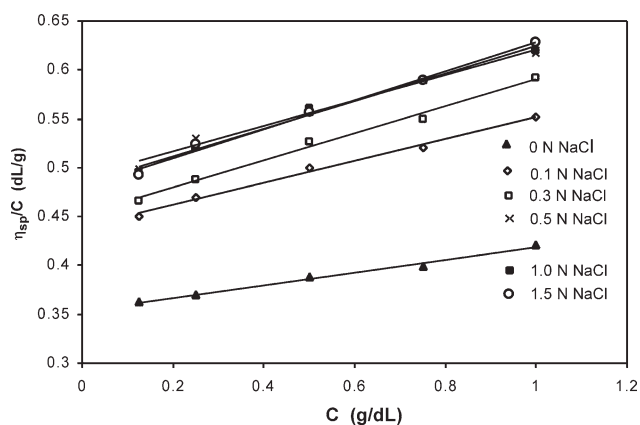


Figure 4 Viscosity behavior of PB 7 (obtained by hydrolyzing sample from Entry 7, Table I) in salt-free water and various concentration of NaCl at 30°C using an Ubbelohde viscometer.

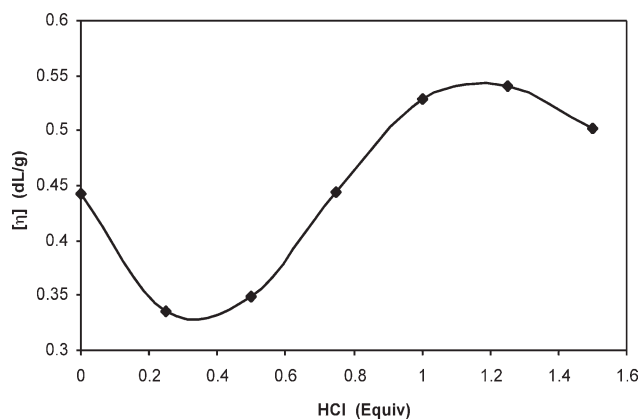


Figure 5 The effect of HCl (x equivalent) on the viscosity behavior of PB 7 in 0.1 N NaCl at 30°C.

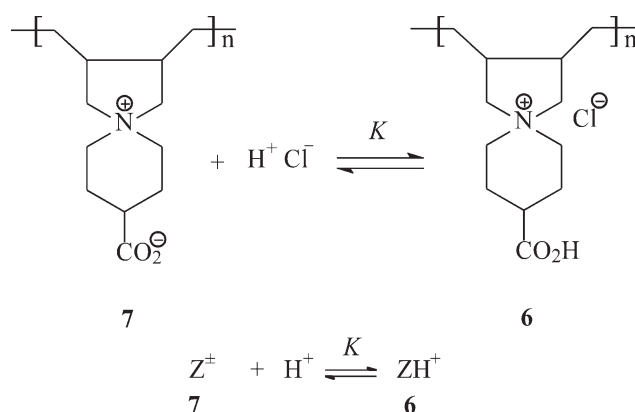
conformation,¹¹ to relieve the repulsion between pendant carboxylate anions. It seems apparent that, while the cationic charge on the polymer chain could be effectively neutralized by strongly binding chloride anions, the anionic carboxylate pendant is not shielded to that extent by the fairly large hydration shell of the Na⁺ cation. The overall effect of the addition of NaCl is to make the polymer more expanded and hence to increase the intrinsic viscosity of the polybetaine solution. An increase in the intrinsic viscosity of the polybetaine with increasing salt concentration is characterized as “anti-polyelectrolyte” behavior.¹³ Note that CPE 5 has an intrinsic viscosity $[\eta]$ of 0.495 g/dL in 0.1 N NaCl (Entry 7, Table I), that is slightly higher than that of the corresponding PB 7 which has the values of 0.354 and 0.443 dL/g at 30°C in salt-free water and in a 0.1 N NaCl solution, respectively. Note that the viscosity increase is halted when the salinity is equal to and higher than 0.5 N NaCl. This could be attributed to the binding ability of the added salt to the zwitterionic dipoles; after a certain concentration of NaCl is added there would be no more potential binding sites available, and as such the viscosity remains constant at concentrations above 0.5 N NaCl.

Figure 5 shows the effect of HCl (x equivalent) on the viscosity behavior of polybetaine 7 in a 0.1 N NaCl solution at 30°C. The intrinsic viscosities $[\eta]$ upon addition of 0, 0.25, 0.50, 0.75, and 1 equivalent of HCl were found to be 0.443, 0.336, 0.350, 0.443, and 0.529 dL/g, respectively. The addition of HCl did not change the viscosity values considerably; the maximum viscosity value was achieved upon addition of 1 equivalent of HCl. The increase in the viscosity could be attributed to the absence of any appreciable number of zwitterionic motifs in the polymer chain as a result of protonation of the anionic motifs in the presence of 1 equivalent of HCl. The absence of zwitterions is expected to expand the coil thus resulting in an increase in viscosity. Note

that further increase of the amount of HCl to 1.25 equivalents, did not increase the viscosity appreciably; while it decreased slightly in the presence of 1.5 equivalents of HCl as a result of screening of the positive charges by the additional Cl⁻ ions.

Basicity constants

To gain further information on the conformational transitions, the basicity constants, K^0 , and the corresponding n values relative to the protonation of the CO₂⁻ functionality in PB 7 in salt-free water and 0.1 N NaCl solution were determined. The experimental details of the potentiometric titrations, calculated basicity constants and the corresponding n values are reported in Table II. The protonation constant of the carboxylate group, $\log K$, was calculated at each pH value by the well-known Henderson-Hasselbalch equation [eq. (1)] (Scheme 3), where the degree of protonation (α) is the ratio $[ZH^+]_{eq}/[Z^\pm]_0$. The $[Z^\pm]_0$ is the initial analytical concentration of the monomeric units in the PB 7, and $[ZH^+]_{eq}$ is the concentration of the protonated species at the equilibrium given by $[ZH^+]_{eq} = C_{H^+} - [H^+] + [OH^-]$, where C_{H^+} is the concentration of the added HCl; $[H^+]$ and $[OH^-]$ at equilibrium were calculated from the pH value.²⁸ The typical electrolytes having apparent basicity constants could be described by eq. (2), where $\log K^0$ is the pH at $\alpha = 0.5$, and $n = 1$ in the case of sharp basicity constants. The linear least squares fit of pH versus $\log [(1-\alpha)/\alpha]$ gave $\log K^0$ and n as the intercept and slope, respectively. Inserting the value of pH from eq. (2) into eq. (1) leads to modified Henderson-Hasselbalch equation [eq. (3)],^{29,30} where $n - 1$ is a measure of the deviation of the studied polymers from the behavior of small molecules



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

$$\text{pH} = \log K^0 + n \log [(1 - \alpha)/\alpha] \quad (2)$$

$$\log K = \log K^0 + (n - 1) \log [(1 - \alpha)/\alpha] \quad (3)$$

Scheme 3 Protonation of polybetaine 7.

TABLE II
Experimental Details for Protonation of Polymbetaine 7 at 25°C in Salt-Free Water and 0.1 N NaCl Using 0.09950 M HCl

Run No.	Z [±] (mmol)	α-range	pH-range	Points ^a	Log K ^{0b}	n ^b	R ^c
Polybetaine 7 in salt-free water							
1	0.4088	0.12–0.57	3.91–2.87	18	3.04	0.987	0.9880
2	0.5135	0.10–0.54	3.96–2.81	22	2.88	1.17	0.9960
3	0.6302	0.09–0.56	4.00–2.78	25	2.87	1.08	0.9923
Average		Log K ^d = 2.93 + 0.08 log [(1–α)/α]			2.93 (10)	1.08 (9)	
Polybetaine 7 in 0.1 N NaCl							
1	0.3945	0.09–0.60	4.83–3.04	29	3.38	1.50	0.9937
2	0.5049	0.09–0.75	4.85–2.93	24	3.52	1.30	0.9983
3	0.6087	0.09–0.75	4.90–2.86	29	3.46	1.32	0.9988
Average		Log K ^d = 3.45 + 0.37 log [(1–α)/α]			3.45 (7)	1.37 (11)	

^a Number of data points from titration curve.

^b R = correlation coefficient.

^c Values in the parentheses are standard deviations in the last digit(s).

^d log K = log K⁰ + (n–1) log [(1–α)/α].

showing sharp basicity constants (for molecules having sharp basicity constants, *n* becomes 1). The basicity constant of this polymer was found to be almost 'real' in salt-free water but 'apparent'^{29–33} in 0.1 N NaCl as the *n* values were determined to be 1.08 and 1.37, respectively. In 0.1 N NaCl, the basicity constant decreased with the degree of protonation (α) owing to a decrease in the overall negative charge density and in turn in the electrostatic field force in the macromolecule (Fig. 6). The magnitude of *n* reflects the polyelectrolyte effect and can be regarded as an index of the accessibility of the proton to CO₂[–] during the protonation reaction. The basicity constant (log K⁰) of the CO₂[–] in PB 7 was found to be 2.93 and 3.45 in salt-free water and in a 0.1 N NaCl solution, respectively (Fig. 6 and Table II). The *n* values greater than 1 indicate that the approach of the incoming protons to the amine nitrogen groups became more difficult as the degree of protonation (α) increased.

It is to be noted that in 0.1 N NaCl the 'apparentness' of the basicity constant of PB 7 increases as indicated by an increased 'n' value of 1.37. Several

studies³² have indicated that the entropy effects, involving release of water molecules from the hydration shell of the repeating unit that is being protonated, dictate the protonation of polymers. The PB 7 in salt-free water is less extended as indicated by lower viscosity values (Fig. 4) and as such less hydrated (less water molecules in each hydration shell) than in salt solution (0.1 N NaCl), where the polymer chain adopts a more extended conformation because of antipolyelectrolyte effects. The more exposed CO₂[–] in the presence of NaCl, generates a higher negative electrostatic field force than the more zwitterionic force in salt-free water. This leads to an increase in the protonation constant of the PB 7 in 0.1 N NaCl than in salt-free water. Thus with progressive protonation, the number of water molecules released from the hydration shell of the repeating unit being protonated becomes greater in 0.1 N NaCl than in salt-free water. This results in a more favorable entropy of protonation in 0.1 N NaCl. This is reflected by the higher *n* value (1.37), greater basicity constant (log K⁰ at α = 0.5 : 3.45), and greater changes in the basicity constant in 0.1 N NaCl (Fig. 6) than in the salt-free water where the basicity constant and the *n* values are found to be 2.93 and 1.08, respectively.

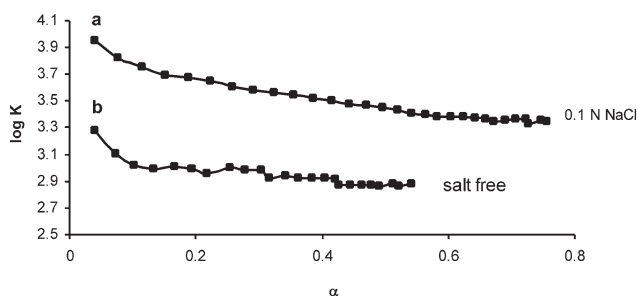


Figure 6 Plot of the apparent log *K* versus α for PB 7 (a) in salt-free water and (b) in 0.1 N NaCl at 25°C.

CONCLUSIONS

Readily available piperidine-4-carboxylic acid facilitated synthesis of monomer 4 which has an ester functionality. The study demonstrates a simple method to convert CPE 5 into PB 7 by hydrolysis of the pendant ester groups. This CPE-to-PB transformation provides an opportunity to compare the solution properties of these two types of polymers

having an identical degree of polymerization. The pH-triggerable carboxylate functionalities in PB 7 has allowed us to study its basicity constant which is found to be real in salt-free water and 'apparent' in a 0.1 N NaCl solution. Contrary to usual poly-zwitterions, PB 7 having carboxyl pK_a values above 2 (2.93 in salt-free water; and 3.45 in 0.1 N NaCl) was found to be soluble in salt-free water. CPE 5 was found to have a higher intrinsic viscosity than its corresponding PB 7 in 0.1 N NaCl. The polybetaine showed an "anti-polyelectrolyte" behavior, i.e., an increase in the intrinsic viscosity with increasing salt (NaCl) concentration. The intrinsic viscosity $[\eta]$ of the polybetaine was found to vary with the concentration of added HCl, attaining its maximum value in the presence of 1 equivalent of HCl.

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