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Synthesis and solution properties of a quaternary ammonium polyelectrolyte and its corresponding polyampholyte

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Abstract

The quaternary ammonium salt, *N*,*N*-diallyl-*N*-5-carbomethoxypentyl-*N*-methylammonium chloride (DACPMAC), on cyclopolymerization in aqueous solution using *tert*-butylhydroperoxide, afforded the polyelectrolyte poly(DACPMAC), having five-membered cyclic structure on the polymeric backbone, in excellent yield. The polyelectrolyte on acidic hydrolysis of the pendent ester groups gave the corresponding polyampholyte poly(DAMAH) having the equivalent of 6-(*N*,*N*-diallyl-*N*-methyl ammonio) hexanoate (DAMAH) as monomeric unit. The solution properties of these polymers as well as the polyelectrolyte, poly(DACMMAC), and its corresponding polyampholyte, poly(DAMAE), [having the monomeric unit equivalent of *N*,*N*-diallyl-*N*-carboethoxymethyl-*N*-methylammonium chloride (DACMMAC) and *N*,*N*-diallyl-*N*-methyl ammonio ethanoate (DAMAE)] are investigated by potentiometric and viscometric techniques. Basicity constants of the polyampholytes are found to be 'apparent' and as such follow the modified Henderson–Hasselbalch equation. While the protonation of the polyampholyte poly(DAMAH) becomes more and more difficult as the degree of protonation (α) of the whole macromolecule increases, the polyampholyte poly(DAMAE), exhibits the reverse trend i.e. the protonation process becomes easier and easier with increasing α.

Keywords: Polyelectrolyte; Polyampholyte; Poly(quaternary ammonium salt)

1. Introduction

Butler and coworkers [1] have polymerized a large number of diallyl quaternary ammonium salts **1** to yield linear water-soluble polymers **2** (Scheme 1). These cationic polyelectrolytes have found extensive industrial and commercial applications [2–5]. Polydiallyldimethylammonium chloride alone accounts for over 1000 patents and publications. There are a quite few reports [6–12] in the literature of polyampholytes (polyzwitterions) derived from zwitterionic monomers **1**. Recently, we have reported [13,14] a convenient synthetic route leading to polyampholyte (PA) **4** and poly(ampholyte–electrolyte) **5** by polymerizing nonzwitterionic monomers containing ester functionality and subsequent ester hydrolysis of the resultant polyelectrolytes (such as **3**) (Scheme 1). Polyampholytes have found applications in various fields. Polyampholytes can reduce the energy loss due to friction in turbulent flow [15], serve as biosensors, act as amphoteric buffers for electrophoresis [16] and used as a simple model [16–19] for understanding the complex behavior of proteins. While the polyelectrolytes are usually soluble in water, the overwhelming majority of the reported polyampholytes [7,20,21] are known to be insoluble in water. This solubility behavior is attributed [22,23] to the collapsed coil conformation of the polyampholytes as a result of inter- and intra-chain interactions leading to a three-dimensional ionic network. The presence of an inorganic salt (NaCl) neutralizes the ionically cross-linked network and causes the dissolution of the coiled polyampholyte. Unlike polyelectrolytes, the ampholytic polymers show 'anti-polyelectrolyte behavior' [22] and have greatly enhanced solubility and extensive chain expansion, hence higher viscosity, with increasing salt (NaCl) concentration.

The present paper describes the synthesis of a polyampholyte (PA) **11** via hydrolysis of the polyelectrolyte (PE) **10** which is prepared from the nonzwitterionic monomer **9** (Scheme 2). The study provided an opportunity to examine and compare the solution properties of a polyelectrolyte and its corresponding polyampholyte, having a similar degree of polymerisation. The presence of the pH triggerable carboxybetaine in polyampholytes **4** and **11**, which differ only in the length of their pendants, allowed us to investigate their pH responsive solution behaviors. To the best of our knowledge, basicity constant of the COO^- groups in these

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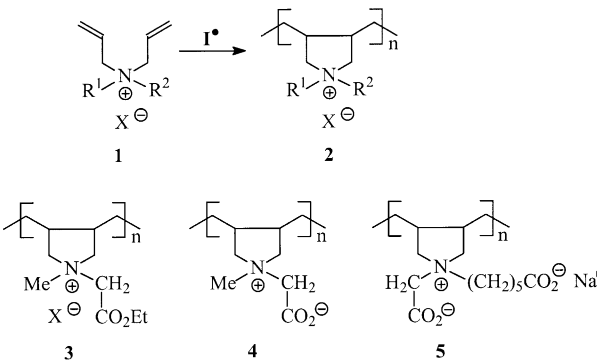


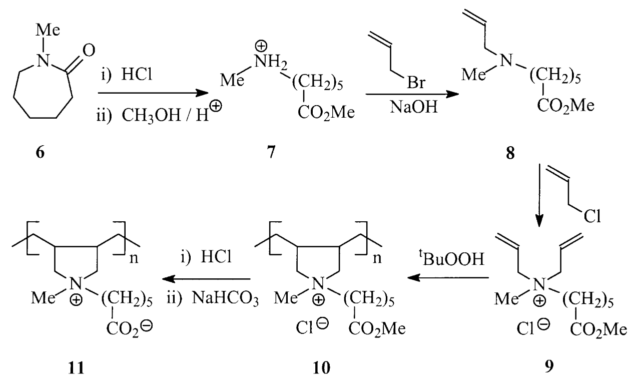
Scheme 1.

polyampholytes **4** and **11** is studied for the first time. It would indeed be of special interest to determine whether the basicity constant in these polyampholytes is real (i.e. independent of the degree of protonation, α) or apparent (i.e. dependent on the α).

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, $4\ \mathrm{cm}^{-1}$; 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 at all temperatures) using pure water (see Section 2.9) under N_2 in order to avoid CO_2 absorption which may affect the viscosity data.



Scheme 2.

2.2. Materials

Ammonium persulfate (APS) from BDH Chemical (Poole, UK), *t*-butylhydroperoxide (80% in ditertiarybutylperoxide) and *N*-methylcaprolactum (**6**) from Fluka Chemie AG (Buchs, Switzerland) were used as received. All glassware were cleaned using deionized water. A sample of PE **3** and its corresponding PA **4** were prepared as described [13].

2.3. Methyl 6-(N-methylamino)hexanoate hydrochloride (7)

Hydrochloride salt of 6-(*N*-methylamino)hexanoic acid was prepared using procedure as described [24]. Thus, *N*-methylcaprolactam (**6**) (63.6 g, 0.5 mol) was hydrolyzed under reflux in 15% HCl solution (300 cm^3) for 12 h. After removal of most of the water by distillation under reduced pressure, the residual viscous liquid was crystallized from cold acetone to give the hygroscopic amine salt in 87% yield. A solution of the amine salt (63.0 g, 0.347 mmol) in methanol (100 cm^3) containing HCl (4.4 g, 0.12 mol) was refluxed for 12 h. Excess methanol was removed by blowing a gentle stream of N_2 at 50°C. The residual viscous liquid was triturated with ether. The highly hygroscopic white crystalline solid of **7**, thus obtained, was filtered and washed with liberal excess of ether (yield: 61.2 g, 90%); mp (closed capillary) 96–98°C; $\nu_{\max}$ (KBr) 3398, 2942, 2766, 2478, 2430, 1732, 1666, 1596, 1466, 1316, 1248, 1192, 1078, 934, 884, 834, and 736 cm^{-1}; δ_H (CD_3OD) 1.42 (2H, quint, $J = 7.5$ Hz), 1.67 (2H, m), 2.36 (2H, t, $J = 7.4$ Hz), 2.69 (3H, s), 2.99 (2H, t, $J = 7.8$ Hz), 3.65 (3H, s).

2.4. Methyl 6-(N-allyl-N-methylamino)hexanoate (8)

To a magnetically stirred solution of the hydrochloride salt (**7**) (30.6 g, 0.157 mol) in methanol (50 cm^3) under N_2 was added, simultaneously, allyl bromide (19.0 g, 0.157 mol) from a dropping funnel and a methanolic solution (50 cm^3) of NaOH (9.45 g, 0.236 mol) from another dropping funnel over a period of 30 min. The reaction mixture was stirred at 40–45°C for an additional hour. After removal of most of the methanol by blowing a gentle stream of N_2, the residual reaction mixture was taken up in water (50 cm^3) and extracted with ether (50 cm^3). The aqueous layer, after addition of K_2CO_3 (~15 g), was further extracted with ether (2 × 50 cm^3). The combined organic layers was dried ($MgSO_4$), concentrated and the residual liquid upon distillation afforded **8** as a colorless liquid (19.0 g, 62%), bp$_{0.05\ \mathrm{mbarHg}}$ 80°C (Found: C, 66.2; H, 10.5; N, 6.85. $C_{11}H_{21}NO_2$ requires C, 66.29; H, 10.62; N, 7.03%); $\nu_{\max}$ (neat) 3076, 2940, 2860, 2786, 1740, 1650, 1440, 1356, 1200, 1170, 1078, 1022, 998, 920, and 852 cm^{-1}; δ_H ($CDCl_3$, TMS) 1.34 (2H, quint, $J = 8.0$ Hz), 1.49 (2H, quint, $J = 7.7$ Hz), 1.64 (2H, quint, $J = 7.7$ Hz), 2.20 (3H, s), 2.32 (4H, m), 2.98 (2H, d, $J = 6.6$ Hz), 3.67 (3H, s), 5.14 (2H, m), 5.85 (1H, m); δ_C ($CDCl_3$) 24.92, 27.08 (2C), 34.05, 42.09, 51.45, 57.12, 61.07, 117.32, 135.89, 174.17 (middle C 77.09, TMS 0.00).

2.5. *N,N-diallyl-N-5-carbomethoxypentyl-N-methylammonium chloride (DACPMAC) (**9**)*

A solution of **8** (16.0 g, 80.3 mmol) and allyl chloride (12.0 g, 157 mmol) in acetone (40 cm^3) was stirred in closed vessel at 70°C for 24 h. The light yellow solution was decolorized with charcoal and the filtered solution was concentrated and agitated with ether (100 cm^3). The upper ether layer was decanted. The lower layer containing the quaternary salt **9** was redissolved in acetone (10 cm^3) and agitated with ether (50 cm^3). The process was repeated four times. Finally, the thick viscous liquid was dried under vacuum at 65°C until constant weight (colorless viscous liquid, 20.3 g, 91%). There were minor impurities present as evident from the ^{1}H NMR spectrum and as such no elemental analysis of the monomer was performed. Since the hygroscopic salt was not a solid, it could not be purified by crystallization. ν_{max} (neat) 3376, 2950, 1730, 1640, 1436, 1366, 1196, 1100, 960, 862, and 738 cm^{-1}; δ_{H} (D_2O) 1.28 (2H, quint, $J = 7.5$ Hz), 1.58 (2H, quint, $J = 7.5$ Hz), 1.72 (2H, quint, $J = 8.2$ Hz), 2.34 (2H, t, $J = 7.5$ Hz), 2.90 (3H, s), 3.15 (2H, t, $J = 8.6$ Hz), 3.61 (3H, s), 3.82 (4H, d, $J = 7.4$ Hz), 5.63 (4H, m), 5.94 (2H, m), (HOD: δ4.65); δ_{C} (D_2O) 22.40, 24.94, 26.20, 34.56, 48.45, 53.39, 61.86, 64.81 (2C), 125.49 (2C), 129.92 (2C), and 178.26 (dioxan: δ_{C} 67.8).

2.6. *General procedure for the polymerization of **9** using tert-butylhydroperoxide*

A solution of the monomer **9** in deionized water (of appropriate concentration) in a 10 cm^3 round bottomed flask was purged with N_2, and after adding the required amount of *tert*-butylhydroperoxide (as listed in Table 1), the mixture was stirred in the closed flask at 50°C for 24 h and then for a further 24 h at 70°C. The reaction mixture became noticeably viscous and remained transparent throughout the process. The reaction mixture was cooled, transferred to a dialysis bag and dialyzed against deionized water for 12 h in order to remove 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 hygroscopic white polymer **10** was stored in a desiccator. Mp (closed capillary) 270–280°C with color darkening above 350°C and became black around 400°C (Found: C, 53.8; H, 9.85; N, 4.7. $C_{14}H_{26}NO_2Cl{\cdot}2H_2O$ requires C, 53.92; H, 9.70; N, 4.49%); ν_{max} (KBr) 3444, 2952, 1726, 1640, 1560, 1460, 1202 cm^{-1}.

2.7. *Polymerization of the monomer **9** using ammonium persulfate*

APS (39.7 mg) was added under N_2 to a solution at 80°C containing the monomer **9** (3.00 g) in water (1.285 g) (70:30 (w/w) monomer concentration) in a 10 cm^3 round bottomed flask and the solution in the closed flask was stirred at 90°C for 1.3 h. The ^{1}H NMR spectrum revealed the presence of about 18% polymer in the reaction mixture.

Table 1
Effect of concentration of monomer and initiator (polymerization reactions were carried out in aqueous medium at 50°C for 20 h followed by 70°C for 24 h) [tertiary butylhydroperoxide, (TBHP)] on polymerization of the monomer **9**

Entry No.	Monomer concentration (% w/w)[a]	TBHP (mg g^{-1} monomer)[a]	Yield[b] (%)	Intrinsic viscosity[c] (dl g^{-1})
1	65	3	41 (36)	0.265
2	65	5	51 (44)	0.234
3	65	10	83 (68)	0.242
4	65	12	92 (77)	0.297
5	65	15	95 (81)	0.290
6	70	5	86 (74)	0.325
7	70	12	85 (72)	0.282
8	70	15	95 (80)	0.440
9	80	15	97 (76)	0.402
10	85	10	18	–

[a] Polymerization reactions were carried out in aqueous medium at 50°C for 20 h followed by 70°C for 24 h.

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

[c] Viscosity of 1–0.125% polymer solution on 0.1N NaCl at 30°C was measured in Ubbelohde viscometer.

2.8. *Acidic hydrolysis of the PE **10***

A solution of the PE **10** (4.00 g) (entry 8, Table 1) in 6 N HCl (60 cm^3) was stirred in a closed flask at 50°C for 120 h (or until the hydrolysis of the ester group was complete as indicated by the absence of the methoxy proton signals in the ^{1}H NMR spectrum). The reaction mixture was then dialyzed against deionized water (to remove HCl). The aqueous polymer solution was basified with $NaHCO_3$ in the dialysis bag and dialyzed to remove excess $NaHCO_3$ and NaCl (monitored by $AgNO_3$ test) and 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 PA **11** was stored in a dessicator. Mp (Closed capillary) 250–265°C (seems to change to liquid and does not char up to 400°C). Yield 3.16 g (94.6%) (Found: C, 60.2; H, 10.6; N, 5.6. $C_{13}H_{23}NO_2{\cdot}2H_2O$ requires C, 59.74; H, 10.41; N, 5.36); ν_{max} (KBr) 3420, 2948, 1656, 1560, 1462, 1402, 1314, 1098, 1040 and 940 cm^{-1}.

2.9. *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 for titration in salt-free and salt (NaCl, 99.9% purity) solutions and for viscosity measurements. For each titration, 200 cm^3 of 0.1N NaCl solution containing a weighed amount (usually around 0.5 mmol) of the PA **4** or **11** in the zwitterionic form was used. The solution was titrated with 0.1015 M HCl delivered through a buret under N_2. After each addition of the titrant (in the range 0.10–0.25 cm^3) the solution was magnetically stirred briefly under N_2 and 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. At each point of the titrations the analytical concentration of the initial amount of the PA, $(Z^{\pm})_i$, and the added HCl (C_H^+) was calculated. $[H^+]$ at equilibrium was calculated from the pH value. The concentration of the protonated form at equilibrium, $[ZH^+]$, at each step was calculated using the equation [25]: $[ZH^+] = C_H^+ - [H^+] + [OH^-]$. The α values (i.e. the degree of protonation) were then calculated using the equation: $\alpha = [ZH^+]_{eq}/[Z^{\pm}]_i$. Using the equation for 'apparent basicity constants': $pH = \log K^0 + n \log[(1-\alpha)/\alpha]$, the linear regression fit of pH vs. $\log[(1-\alpha)/\alpha)]$ gave $\log K^0$ and n as the intercept and slope, respectively (see Section 3 for the detailed description of various terms in the equation). While the PA **11** was studied in the α-range of 0.10–0.80, the $\log K^0$ for the **4** was calculated usually for $\alpha < 0.5$. High concentration of C_H^+, required for larger values of α for the weaker base PA **4** was avoided since that could affect the total ionic strength of the solution and the liquid junction potential.

3. Results and discussion

N-methylcaprolactum (**6**) on acidic hydrolysis followed by esterification afforded the amine salt **7** in excellent yield. Allylation of **7** with allyl bromide gave the tertiary amine **8** which upon quaternization with allyl chloride yielded the hygroscopic monomer **9**. The monomer was found to be soluble in acetone, methanol and water. Absorption at 1730 cm^{-1} in the IR spectrum of **9** reveals the presence of ester group. The strong peak at 3376 cm^{-1} indicates the hygroscopic nature of the monomer. The monomer **8** was subjected to polymerization in water using APS as the initiator to obtain the polymer **10** in very low yield (18%). However, the polymerization reaction went smoothly using tertiary butylhydroperoxide as the initiator. The results of the polymerization under various conditions are given in Table 1. As is evident from the Table 1, the highest intrinsic viscosity was obtained for the polymerization under entry 8, with a monomer concentration of 70% (w/w) and 15 mg initiator/g of the monomer.

The PE **10** (entry 8, Table 1) was hydrolyzed under acidic conditions (6M HCl, 50°C), to give the PA **11** in excellent yield (95%). The hydrolysis was found to be almost complete (*vide infra*). While absorption at 1726 cm^{-1} in the IR spectrum of **10** reveals the presence of the ester group, the absorption around 1656 cm^{-1} indicates the presence of CO_2^- functionality in **11**. Strong OH absorption indicates the very hygroscopic nature of the polymers. ^1H and ^{13}C NMR spectra of the polymers (**10** and **11**) are displayed in Figs. 1 and 2, respectively. It is evident after comparing the proton spectra of the polymers that the CH_3–OC protons that appeared at δ 3.60 ppm for the polyelectrolyte **10**, is almost absent in the spectrum of the polyampholyte **11**, thus indicating the removal of the methyl group via hydrolysis. Similar observations are made from the ^{13}C NMR spectrum; the methyl carbon of the CH_3–OC (which appears at 53.07 ppm for the polymer **10**) was almost absent in the spectrum of the polymer **11**. The carbonyl carbons (not shown in the spectra) of the polymers **10** and **11** appear at 178.08 and 184.04 ppm, respectively.

Both the polymers were found to be soluble in a range of solvents (Table 2). While the overwhelming majority of reported polyampholytes [7,19,21] are known to be insoluble in water, the polyampholyte **11** was found to be soluble in water as well as in several protic solvents. Viscosity data for the poyelectrolyte **10** (entry 8, Table 1) and the corresponding polyampholyte **11** are shown in Fig. 3. In the absence of added salt (NaCl), the viscosity plot for **10** as well as **11** is typical for a electrolyte i.e. concave upwards. The addition of strong electrolytes, like sodium chloride, suppresses the ionization of the polyelectrolyte and polyampholyte and the viscosity behavior becomes normal. By increasing the ionic strength, while the viscosity of the polyelectrolyte **10** decreases, as expected, the viscosity of the polyampholyte **11** increases due to its 'antipolyelectrolyte' [4] behavior. The viscosity plot reveals that the polyampholyte **11** has lower reduced viscosities in salt-free water and in 0.1N NaCl and thus has a more compact conformation than that of the polyelectrolyte **10**. While the linear dependence of the reduced viscosity on the polymer concentration in salt-free water illustrated [13] the absence of polyelectrolyte behavior for the PA **4**, the reduced viscosity of PA **11** shows a marked increase upon dilution, a characteristic for polyelectrolytes. This implies the zwitterionic character of the PA **4** because of full deprotonation of the strongly acidic ammonioacetate moiety. The increased basicity of the ammoniohexanoate group leads to partial protonation of the carboxylate and converts the polybetaine **11** into a weak polycation whose relative concentration (vs. polybetaine) increases with dilution.

Extensive studies of basicity constants of polyamidoamines (**12a**) (Scheme 3) and related polymers have been carried out in aqueous solution [26]. The study helps to correlate basicity constants with conformation of the polymers. In polymeric amines, protonation of nitrogens at one part of the polymer chain may or may not affect the basicity of the nitrogens at the other parts. The small molecules (like triethylamine) shows 'sharp basicity constant' since basicity constant, K, remains constant throughout the titration with acid. ('Sharp' means that the basicity constant is independent of the degree of protonation, α of the whole macromolecule, and 'apparent' means that it is dependent.) The

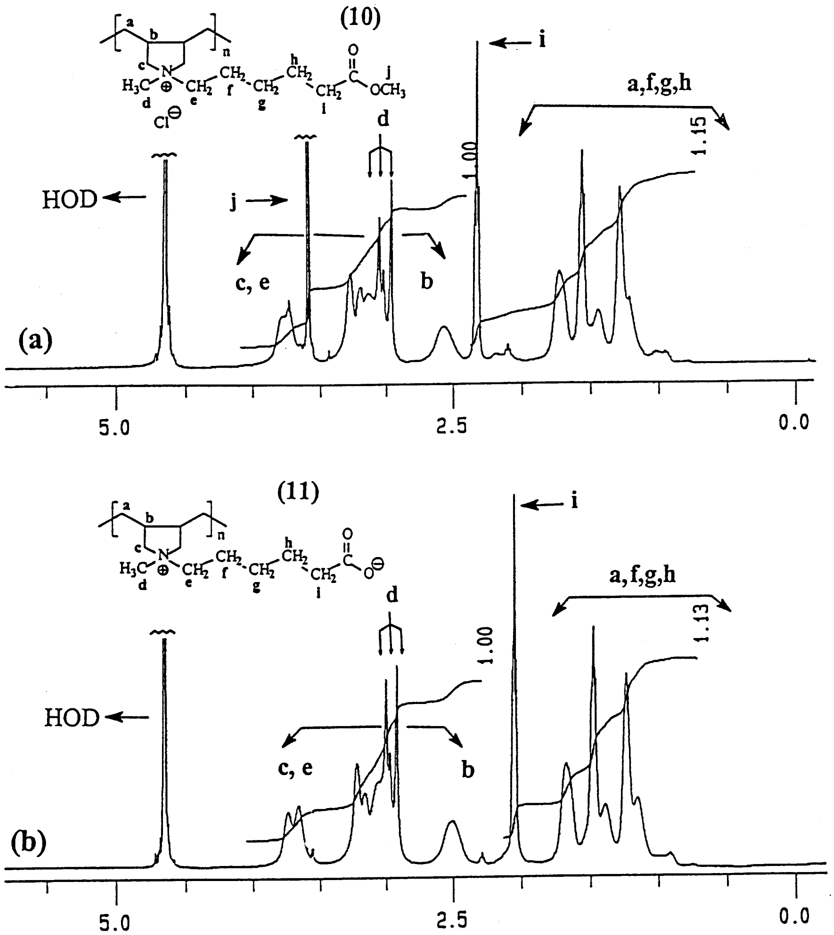


Fig. 1. ^{1}H NMR spectrum of (a) polyelectrolyte **10** and (b) polyampholyte **11** in D_2O.

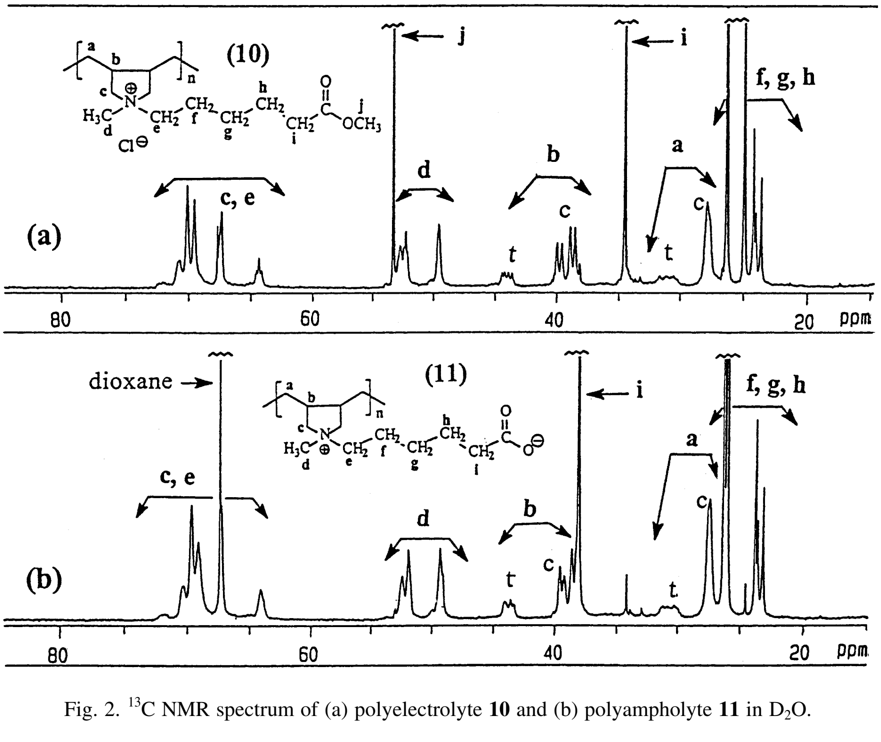


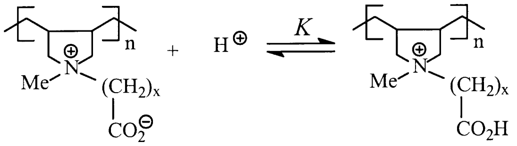
Fig. 2. ^{13}C NMR spectrum of (a) polyelectrolyte **10** and (b) polyampholyte **11** in D_2O.

Table 2
Solubility (2% (w/w) of polymer solution was made after heating the mixture at 70°C for 1 h and then bringing the temperature back to 23°C, (+) indicates soluble; (−) indicates insoluble) of polyelectrolyte **10** and polyampholyte **11**

	ϵ	PE **10**	PA **11**
Water	78.4	+	+
Methanol	32.3	+	−
Formic acid	58.5	+	+
Formamide	111.0	+	+
Ethylene glycol	37.3	+	−
Triethylene glycol	23.7	+	−
Acetic acid	6.15	+	+
Acetone	21	−	−

repeating units containing basic nitrogens shielded by diacryloylpiperazine groups in (**12a**) show sharp basicity constants (K) independent of the degree (α) of protonation of the polymer [27]. However, the presence of COO^- pendant groups in **12b** leads to loss of independence of the monomeric unit [28]. The apparent basicity constants of the polyamido polymers **12b** containing ω-aminoresidues vary with the degree of protonation (α) and this behavior, known as polyelectrolyte effect, depends on the length of the pendant chain. Polymer exhibiting a strong polyelectrolyte effect shows a large change in $\log K$ in going from uncharged to the charged state.

$\log K$ for the PA **4** and **11** are calculated at each pH value by the well-known Henderson–Hasselbalch equation as shown in Eq. (1)



$$Z^{\pm} + H^{+} \rightleftharpoons ZH^{+}$$
$$(1 - \alpha) \qquad (\alpha)$$

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

where degree of protonation (α) is the ratio $[ZH^+]_{eq}/(Z^{\pm}]_i$. The $(Z^{\pm}]_i$ is the initial analytical concentration of the monomeric units in the PA and $[ZH^+]_{eq}$ is the concentration of the protonated species at the equilibrium given by [25] $[ZH^+]_{eq} = C_H^+ - [H^+] + (OH^-]$ where C_H^+ is the concentration of the added HCl. The typical electrolytes having apparent basicity constant could be described by the Eq. (2) where $\log K^0 = \mathrm{pH}$ at $\alpha = 0.5$ and $n = 1$ in the case of sharp basicity constants. Inserting the value of pH from Eq. (2) into Eq. (1) leads to modified Henderson–Hasselbalch equation (Eq. (3)) [28,29] 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).

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

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

The basicity constants, $\log K^0$, relative to the protonation of the COO^- groups in **4** and **11** are reported in Table 3 together with the corresponding $n$values. The magnitude of the n reflects the polyelectrolye effect and can be regarded as an index of accessibility of the proton to the COO^- group during the protonation reaction. Both the polyampholytes show apparent basicity constants since the n values are not equal to 1.

The differences in $\log K^0$ of the PA **4** and PA **11** reflect the differences in inductive stabilization of the COO^- by the cationic charge on the pyrrolidinium moieties. The negative charge on the carboxylate groups in PA **4** is more dispersed, hence less hydrated, less basic and exhibit stronger Coulombic interactions (due to closer proximity) with the cationic charges on the polymer backbone. The apparent basicity constants ($\log K$) of the COO^- in PA **11** increases quite drastically in 0.1N NaCl in compare to salt-free water. The presence of strongly binding chloride ions is expected to screen and partially neutralize the positive charges on the rings and diminishes the through-space electrostatic attraction between the positive nitrogen and the negative carboxyl moiety. As a consequence the negative charge density increases thus making the carboxyl moiety in PA **11** more basic in 0.1N NaCl solution. One might argue that the simultaneous presence of the Na^+ may neutralize the negative charges on the pendants. However, the hydration shell of Na^+ is quite large and may not be able to approach the CO_2^- more closely to effectively neutralize the additional negative charge density gained in the absence of the through-space electrostatic attraction as discussed above [20]. The situation is different in case of the PA **4**; here the basicity constant increases, albeit slightly, in salt-free water solution, as occurs for small molecular weight carboxylate salts [32].

The n values for the protonation of the PA **4** in 0.1N NaCl and salt-free water were found to be 0.885 and 0.606, respectively. The n values less than 1, considered as diagonistic 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 ($\log K$) thus increases progressively. Increase in the degree of protonation leads to a decrease in the number of zwitterionic groups with a consequent increase in size of the macromolecular coil thus exposing the COO^- groups for easier access to protonation. While in salt-free water intrachain attraction leads to highly compact conformation, the polymer coil is less compact in 0.1N NaCl. The presence of the strongly binding chloride ions effectively neutralize the cationic charges on the polymeric backbone in PA **4**, and is

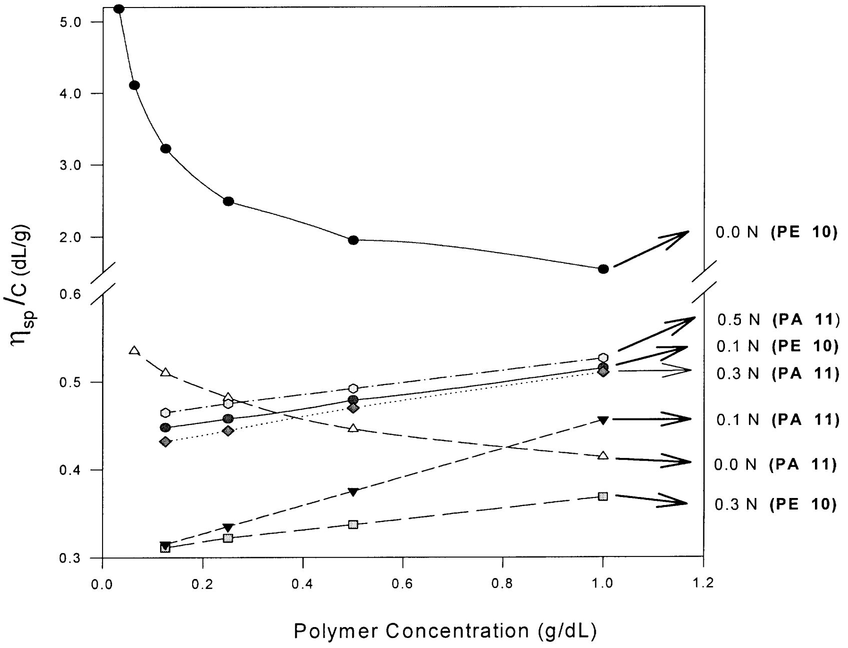
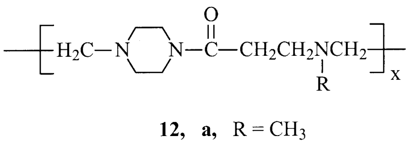


Fig. 3. Effect of added salt (NaCl) on the viscosity behavior of the polyelectrolyte **10** (entry 8, Table 1) and its corresponding polyampholyte **11** (obtained via hydrolysis of the sample from entry 8, Table 1) in water at 30°C using an Ubbelohde viscometer.

known to extend the polymer backbone due to increased repulsion between COO^- groups with increased negative charge density [13,20]. The more compact the polymer coil the smaller the value of n. This behavior seems to be general in all cases in which the basic COO^- group is in the α position to the nitrogen [29]. The basicity constant of the COO^- group increases, albeit slightly, in salt-free system [30,31]. In the presence of salt, the PA **4** behave as a weaker base ($\log K^0 = 2.30$ in salt solution; 2.49 in salt-free water) since its conjugate acid becomes stronger because the increased counter-ion density reduces the large chemical free energy of ionization of the acid in the salt solution. The n value for the protonation of the PA **11** in salt-free and 0.1N NaCl solution was found to be 1.17 and 1.21, respectively. The basicity constant thus decreases with the increasing degree of protonation as was observed in the case of the polymers **12b** ($x = 2$–5) [28].

Potentiometric titration curves for the PA **4** and **11**, both (a) in salt-free water and in (b) 0.1N NaCl solution, are depicted in Figs. 4 and 5. The titration curves for **4** are similar to that of a strong acid and, as expected, only a small influence of NaCl is observed. The potentiometric titration curves of **11** are reminiscent of that of a weak acid and shows an increase of ~1 pH unit on addition of NaCl. The plot of the apparent log K vs. α (degree of protonation) for the polymers PA **4** and PA **11** are depicted in Figs. 6 and 7. While we observed a regular increase in log K with an increasing degree of protonation of the polymer PA **4**, a gradual decrease in log K is observed in case of polymer PA **11**.

Calorimetric studies [33] on the protonation the polymers in the series (**12b**) indicate that the enthalpy changes (exothermic) are independent of α but the magnitude of the positive entropy changes (ΔS) increase for $x = 1$ and decreases for $x = 2$–5 as the α increases. Increasing ΔS with increasing α indicates larger and larger splitting of water molecules from the hydration shell of the polymer



12, a, R = CH_3
b, R = $(CH_2)_yCOO^-$

Scheme 3.

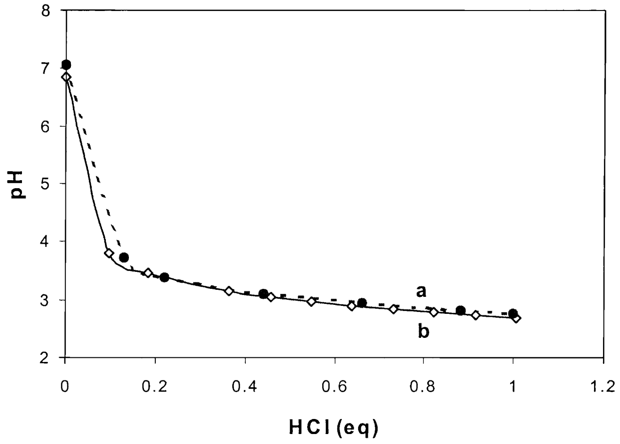


Fig. 4. Potentiometric titration curves for PA **4** (a) in salt-free water and (b) in 0.1N NaCl.

Table 3
Experimental details for protonation of polymers at 25°C in 0.1 M NaCl and salt-free water using 0.1015 M HCl

Run	$Z^{\pm}$ (mmol)	α-range	pH-range	Points[a]	log K^{0b}	n^{b}	R^{2c}
Polymer **11** in 0.1 M NaCl							
1	0.9312	0.11–0.82	5.52–3.65	25	4.38	1.22	0.9985
2	0.4132	0.12–0.75	5.40–3.77	20	4.34	1.22	0.9996
3	0.5012	0.11–0.77	5.46–3.73	23	4.37	1.20	0.9993
Average					4.36 (2)	1.21 (1)	
log $K^{d} = 4.36 + 0.21 \log[(1-\alpha)/\alpha]$							
Polymer **11** in salt-free water							
1	0.5127	0.18–0.70	4.37–3.31	22	3.54	1.18	0.9894
2	0.3726	0.17–0.72	4.45–3.15	15	3.51	1.16	0.9993
3	0.4523	0.12–0.68	4.50–3.12	18	3.52	1.16	0.9908
Average					3.52 (1)	1.17 (1)	
log $K^{d} = 3.52 + 0.17 \log[(1-\alpha)/\alpha]$							
Polymer **4** in 0.1 M NaCl							
1	0.5200	0.13–.38	3.06–2.52	18	2.30	0.882	0.9973
2	0.5550	0.15–0.42	2.96–2.42	30	2.28	0.872	0.9986
3	0.4018	0.14–0.44	3.01–2.37	15	2.32	0.902	0.9937
Average					2.30 (2)	0.885 (15)	
log $K^{d} = 2.30 - 0.015 \log K[(1-\alpha)/\alpha]$							
Polymer **4** in salt-free water							
1	0.3841	0.16–0.43	2.96–2.61	14	2.51	0.622	0.9948
2	0.4609	0.09–0.60	3.10–2.40	18	2.47	0.589	0.9893
3	0.4250	0.12–0.41	3.03–2.59	15	2.49	0.607	0.9994
Average					2.49 (2)	0.606 (17)	
log $K^{d} = 2.49 - 0.394 \log K[(1-\alpha)/\alpha]$							

[a] Number of data points from titration curve.
[b] Values in the parentheses are standard deviations in the last digit.
[c] R: correlation coefficient.
[d] $\log K = \log K^{0} + (n-1)\log[(1-\alpha)/\alpha]$.

12b ($x = 1$) having tightly compact conformation which uncoils during protonation. It could be assumed that the polyelectrolytic effect, i.e. variation of basicity constant with α in our study is also due only to entropy effects. The more compact conformation of the PA **4** which uncoils during protonation is entropically favored because of greater conformational freedom. The hydration shell of COO^{-} in each unit increases on protonation of the adjacent carboxyl group because of greater exposure to the solvent molecules. This makes the next protonation easier because of the entropically favored greater and greater liberation of

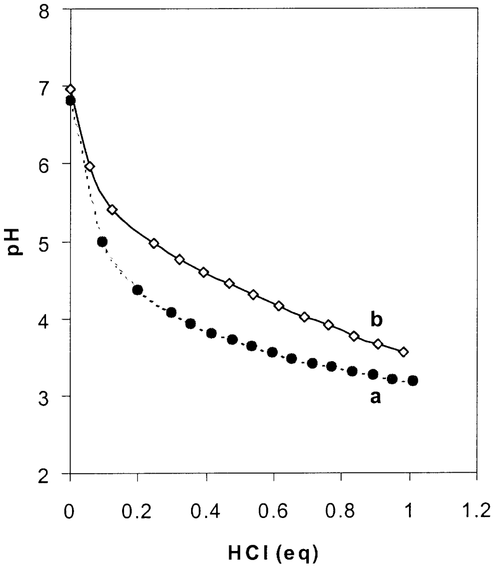


Fig. 5. Potentiometric titration curves for PA **11** (a) in salt-free water and (b) in 0.1N NaCl.

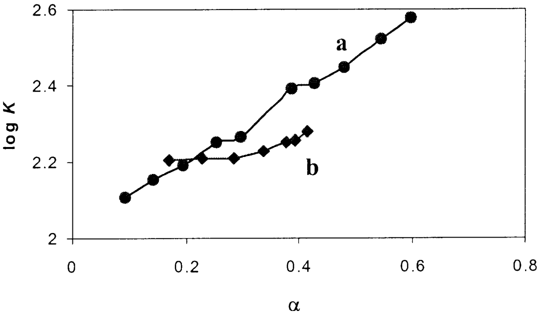


Fig. 6. Plot for the apparent log K vs. a for PA **4** (a) in salt-free water and (b) in 0.1N NaCl.

Table 4
Effect of NaCl and HCl on the viscosity of the polymers **3**, **4**, **10** and **11**

Entry No.	Polymer	NaCl (N)	HCl (equiv.)	Intrinsic viscosity[a] (dl g^{-1})
1PE **3**	0.1	0	0.481	
2	PA **4**	0.1	0	0.319
3	PA **4**	0.1	1	0.268
4	PA **4**	0	0	0.296
5	PA **4**	0	1	0.452
6	PE **10**[b]	0.1	0	0.297
7	PA **11**[c]	0.1	0	0.199
8	PA **11**[c]	0.1	1	0.221
9	PA **11**[c]	0	0	Concave
10	PA **11**[c]	0	1	Concave

[a] Viscosity of 1–0.125% polymer solution on 0.1N NaCl at 30°C was measured in Ubbelohde viscometer.

[b] Entry 4, Table 1.

[c] PA **11** obtained by hydrolysis of PE **10** from entry 4, Table 1.

Table 5
Degree of protonation (α) of the polymers in presence of 1 equiv. of HCl at 25°C

Polymer	NaCl (N)	Polymer concentration (M)	Polymer concentration (g dl^{-1})	α
PA **4**	0.1	0.00253	0.000429	0.243
PA **4**	0	0.00225	0.000380	0.225
PA **11**	0.1	0.00203	0.000529	0.844
PA **11**	0	0.00250	0.000653	0.75

water molecules. The magnitude of this effect is lesser in 0.1N NaCl because in salt solution the macromolecular chain of PA **4** is already expanded [13] and as a result the n value was found to be more than that in the salt-free solution.

The observations presented above are supported by the viscometric studies of the polyelectrolytes **3**, **10** and their corresponding polyampholytes **4** and **11** in 0.1N NaCl and salt-free solution in absence and presence of 1 equivalent HCl (Table 4 and Fig. 8). As is evident from the Table 4 both the PE **3** and PE **10** have higher intrinsic viscosities than their corresponding PA **4** and PA **11** (entries 1 vs. 2; 6 vs. 7) indicating that the polyampholytes have maintained their compact coil conformations in 0.1N NaCl, even though it is more compact for the PA **4**, as expected, in salt-free water solution (entries 2 vs. 4). It is interesting to note that while the intrinsic viscosities of the PA **4**, upon addition of 1 equivalent of HCl, decreases in 0.1N NaCl, it is considerably increased in salt-free water (entries 2 vs. 3; 4 vs. 5). This explain the considerable uncoiling of the zwitterionic species in salt-free water thus resulting in a very low value of n (0.606). In salt-free water, both in absence (entry 9) and presence (entry 10) of HCl, the PA **11** behave like polyelectrolytes having concave shaped viscosity graphs and hence

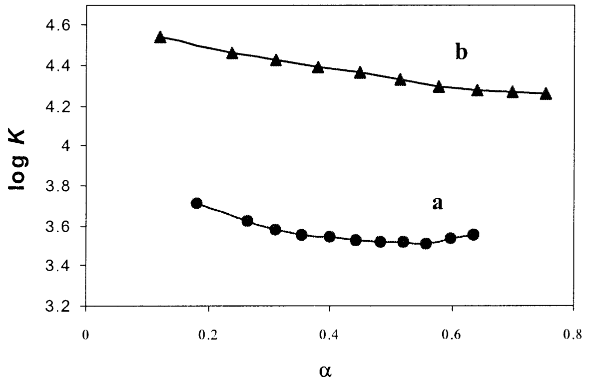


Fig. 7. Plot for the apparent log K vs. a for PA **11** (a) in salt-free water and (b) in 0.1N NaCl.

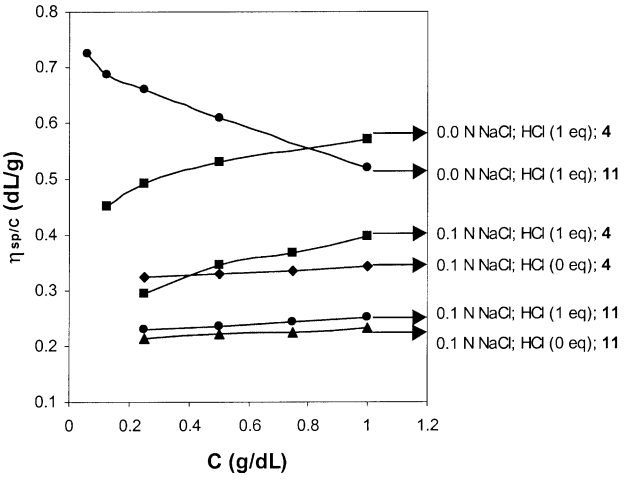


Fig. 8. Effect of added salt (0.1N NaCl) and HCl (1 equiv.) on the viscosity behavior of the polyelectrolyte **10** (entry 4, Table 1) and its corresponding polyampholyte **11** (obtained via hydrolysis of the sample from entry 4, Table 1) in water at 30°C using an Ubbelohde viscometer.

extended macromolecular backbone. The degree of protonation (α) and polymer concentration for some of the trials (used to construct the Table 3) in presence of 1 equiv. HCl are given in Table 5 which indicate the dominant form to be the polyampholyte and polyelectrolyte for the PA **4** and **11**, respectively.

4. Conclusion

The monomer **9** is prepared from inexpensive starting materials. The study has demonstrated a simple way to convert polyelectrolytes to polyampholyte and thus provides an opportunity for the direct comparison of the solution properties of a polyelectrolyte and polyampholyte having the same degree of polymerization. Both the polyampholytes **4** and **11** exhibited apparent basicity constants which increases and decreases, respectively, with the degree of protonation (α). The polyampholytes are soluble in salt-free as well as salt solutions. The corresponding polyelectrolytes PE **3** and **10** have higher [η] values in water. However, in salt solution, the polyampholyte exhibits higher viscosity with increasing salt (NaCl) concentration.

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