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Synthesis and solution properties of a quaternary ammonium polyampholyte

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Abstract

The quaternary ammonium salt, *N*,*N*-diallyl-*N*-carboethoxymethyl-*N*-methylammonium chloride (**7**), has been synthesised in excellent yield. The monomer (**7**), on polymerisation in water solution using ammonium persulfate as an initiator, afforded the polyelectrolyte **8**. The polyelectrolyte (**8**), on acidic hydrolysis, gave the polyampholyte **9** in excellent yield. The solution properties of these polymers are discussed in detail. The polyampholyte **9** showed 'antipolyelectrolyte' behaviour. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyampholyte; Poly(quaternary ammonium salts); Polybetaine

1. Introduction

Butler and coworkers [1] have polymerised various diallyl quaternary ammonium salts (**1**) to yield linear water-soluble polymers with little or no unsaturation. The polymerisation proceeds via an intra-, inter-molecular chain propagation (termed cyclopolymerisation) through the five-membered [2,3] cyclic structure (**2**), to yield linear water-soluble polymers (**3**) (Scheme 1). These polyquaternary ammonium salts are one of the most significant polymers among the cationic polyelectrolytes and have found extensive industrial and commercial applications [4,5]. Polydiallyldimethylammonium chloride alone accounts for over 200 patents and publications.

One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the large decrease in the viscosity of their aqueous solutions in the presence of added salt (NaCl, etc.) [6]. However zwitterionic (ampholytic) polymers show 'antipolyelectrolyte behaviour' [7] and have low or no solubility in water but greatly enhanced solubility and extensive chain expansion, hence viscosification, upon increasing salt concentration. There are only a few reports in the literature of polyampholytes derived from zwitterionic *N*,*N*-diallyl quaternary ammonium monomers. The polymerisation of the sulfobetaine monomer (**4**) led to zwitterionic polysoaps [8]. Even though the synthesis of polyampholyte from the monomer (**5**) is mentioned [9], its solution properties are not reported. Disadvantages in the reported synthesis include relatively low yield obtained in the monomer and polymer synthesis [9] and the use of sultones, which are carcinogenic compounds [10]. Alternating ampholytic copolymers of maleic acid with allylamine, diallylamine, methyldiallylamine and diallyl quaternary ammonium salt were synthesised by free radical polymerisation [11].

The present paper reports the synthesis of a polyampholyte (polybetaine) (**9**) from a nonzwitterionic monomer (**7**), which is readily synthesised from inexpensive starting materials (Scheme 2). The study would indeed provide an interesting opportunity to examine the solution properties of the polyelectrolyte (**8**) and its hydrolysed product, the polyampholyte (**9**), with both having similar average molar masses.

2. Experimental

2.1. Physical methods

All MPs are uncorrected. Elemental analyses were carried out using a Carlo–Erba elemental analyser, Model 1102. I.r. spectra were recorded on a Perkin Elmer PC 16 *FT* i.r. and are reported in wave numbers (cm^{-1}). ^1H and ^{13}C n.m.r. spectra of the polymers were measured in D_2O using DSS or dioxane as an internal standard, on a JEOL LA 500 spectrometer. Viscosity measurements were made by Ubbelohde viscometer ($K = 0.005989$).

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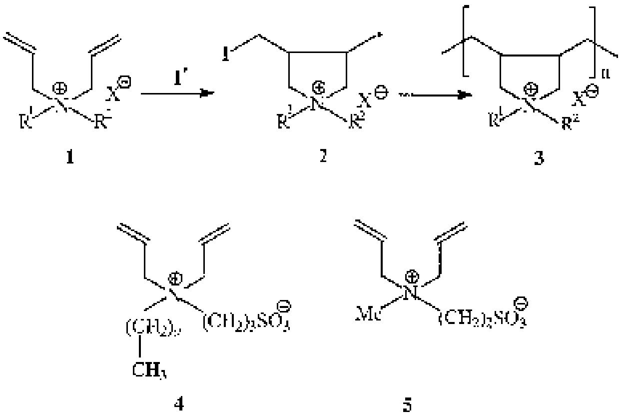


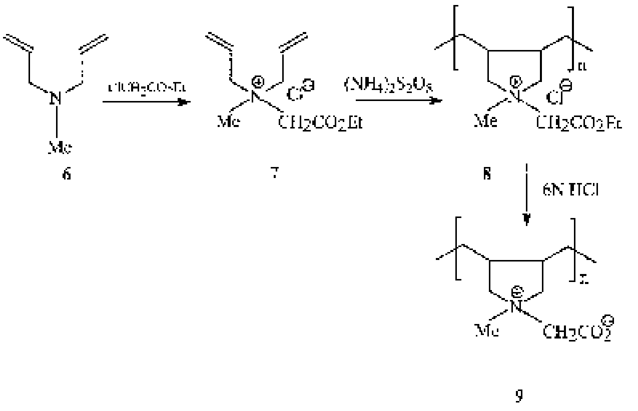
Scheme 1.

2.2. Materials

Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK) and *t*-butylhydroperoxide (80% in ditertiarybutylperoxide) from Fluka Chemie AG (Buchs, Switzerland) were used as received. *m*-Chloroperbenzoic acid of 99% purity and H_2O_2 (30%) were used. *N*,*N*-diallyl-*N*-methylamine (**6**) was synthesised as described [12]. All glassware were cleaned using deionised water. Deionised water was used in polymerisation reactions under a nitrogen atmosphere. Solvent dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at BP 64°C–65°C (4 mmHg).

2.3. *N,N-diallyl-N-carboethoxymethyl-N-methylammonium chloride (*7*)*

A solution of *N*,*N*-diallyl-*N*-methylamine (**6**) (55.5 g, 0.50 mol) and ethyl chloroacetate (100 g, 0.82 mol) was stirred at 20°C. After 24 h, the reaction mixture contained two layers which on further stirring over 24 h became one layer. The ^1H n.m.r. spectrum revealed the absence of any unreacted amine. The reaction mixture (viscous liquid) was agitated with ether ($3 \times 100\ cm^3$) and each time the upper ether layer was decanted off. This was done in order to remove excess ethyl chloroacetate. Finally, the thick liquid was slurried in methanol ($30\ cm^3$) and poured over magnetically stirred ether ($150\ cm^3$). The upper layer was decanted off. The thick viscous colourless liquid was dried under vacuum at 50°C until it reached a constant weight (111 g, 95%). When kept in the refrigerator, the viscous liquid was crystallised as colourless crystals, MP 55°C–59°C (closed capillary). (Found: C, 56.3; H, 8.7; N, 5.9; $C_{11}H_{20}NO_2Cl$ requires C, 56.52; H, 8.63; N, 5.99%); υ_{max} (KBr) 3442, 2984, 2940, 1748, 1638, 1472, 1422, 1386, 1306, 1226, 1126, 1028, 954, 924 and 860 cm^{-1}; δ_H (CD_3OD, TMS, 200 MHz) 1.30 (3 H, *t*, *J* 7.0 Hz), 3.27 (3 H, *s*), 4.32 (8 H, *m*), 5.77 (4 H, *m*), 6.14 (2 H, *m*); $\delta_C(D_2O)$ 14.5, 49.8, 59.7, 64.8, 66.4, 125.1, 131.2, 166.5 (dioxane 67.8 standard). Because of its hygroscopic nature, the quaternary ammonium salt was stored inside a desiccator.



Scheme 2.

2.4. *Attempted polymerisation of* **7**, *using tert-butylhydroperoxide*

A solution containing 70% monomer by mass was prepared by adding the monomer (4.049 g) and deionised water (1.735 g) in a 10 cm^3 round bottomed flask. To the reaction mixture, under N_2, was added eight drops (40 mg) of tert-butylhydroperoxide and the contents in the closed flask was stirred at 50°C for 24 h and 70°C for 24 h. Viscosity of the mixture did not change and there seemed to be no polymerisation. The ^1H n.m.r. spectrum revealed the absence of any polymer. Upon pouring the reaction mixture onto acetone, no white precipitate was obtained, indicating the absence of any polymer.

The above reaction was repeated under similar conditions using different initiators [benzoyl peroxide (55 mg), hydrogen peroxide (30%, 80 mg), *m*-chloroperbenzoic acid (50 mg)]. However no polymerisation product was obtained.

2.5. *General procedure for the polymerisation of* **7** *using ammonium persulfate*

Into a 10 cm^3 round bottom flask containing a magnetic stirrer, 5.0 g of the monomer (**7**) was placed. The appropriate concentration of the monomer was achieved by adding deionised water. The flask was purged with N_2 and heated to 75°C and briefly opened under N_2 to add the initiator ammonium persulfate. The mixture was stirred and heated at 90°C for 1 h. 5–10 min after the addition of the initiator, the solution became viscous. At the end, the transparent viscous liquid was poured onto acetone ($25\ cm^3$). The acetone was decanted off. The polymer (sticky semisolid) was dissolved in methanol ($5\ cm^3$) and coprecipitated in acetone ($25\ cm^3$). The process was repeated three times. The white polymer was dried under vacuum at 60°C until it reached a constant weight. Because of its hygroscopic nature, the polymer (**8**) was stored inside a desiccator. The MP (closed capillary) was 355°C–370°C (colour turned to faint yellow toward the end). (Found: C, 56.1; H, 8.8; N, 5.85. $C_{11}H_{20}NO_2Cl$ requires C, 56.52; H, 8.63; N, 5.99%); υ_{max} (KBr) 3454, 2980, 2940, 1748, 1636, 1468, 1420, 1386, 1226, 1118, 1028, 924 and 860 cm^{-1}.

2.6. Acidic hydrolysis of the polymer (**8**)

A solution of the polymer (**8**) (10 g) (entry three, Table 1) in water (80 cm^3) and concentrated hydrochloric acid (80 cm^3) was stirred in a closed flask at 40°C for 96 h (or until the hydrolysis of the ester group was completed, as indicated by disappearance of ethyl proton signals in the n.m.r. spectrum). The aqueous solution was then dialysed against deionised water (to remove HCl) and basified with excess $NaHCO_3$, before being dialysed again, against deionised water to remove excess $NaHCO_3$ (checked by $AgNO_3$ test). The polymer solution was then freeze-dried and finally the flaky white polymer was dried at 60°C under vacuum until a constant weight was obtained. Yield: 6.1 g (84%); MP (closed capillary): did not melt, even at 400°C. At 300°C onwards, the colour changed to yellowish brown. (Found: C, 63.4; H, 9.15; N, 8.1. $C_9H_{15}NO_2$ requires C, 63.87; H, 8.93; N, 8.28%); υ_{max} (KBr) 3442, 2924, 1628, 1460, 1402, 1332, 1226, 1002, 900 cm^{-1}.

2.7. Solubility measurements

Solubility of the polyelectrolyte (**8**) and polyampholyte (**9**) in organic solvents at room temperature was established for the 1% wt/wt solution after preheating at 70°C for 1 h.

3. Results and discussion

N,*N*-diallyl-*N*-methylamine (**6**), on treatment with ethyl chloroacetate at room temperature, afforded the quaternary ammonium salt (**7**) in almost quantitative yield. It is a crystalline solid and found to be very hygroscopic. The monomer is soluble in methanol, acetone and water. The i.r. spectra revealed the absorption at 1744 cm^{-1}, indicating the presence of ester functionality. A strong peak at 3442 cm^{-1} indicates OH absorption, owing to the hygroscopic nature of the monomer.

The monomer (**7**) was subjected to polymerisation in water (monomer concentraion 70% w/w), using tertiary butyl hydroperoxide as an initiator at 75°C, using the procedure as described by Butler [13], for the polymerisation of diallyldimethylammonium chloride. However, we were unable to get even a trace of polymer using the above procedure. The above reaction was repeated under similar conditions using different initiators such as benzoyl peroxide, hydrogen peroxide, metachloroperbenzoic acid without any success. It is to be noted that N^+-CH_2-CO protons in monomer **7** being adjacent to two electronegative centers are very acidic. At this stage, we are unable to offer an explanation for the inability of these compounds to initiate the polymerisation process. However, the polymerisation reaction went smoothly using ammonium persulfate as an initiator. The results of the polymerisation under various conditions are given in Table 1. As is evident from Table 1, the highest yield and intrinsic viscosity are obtained for the polymerisation reaction under entry three, with a monomer concentration of 70% (w/w). The effects of concentration of the initiator are represented by entries two, three and four. The results reveal that 15 mg of initiator (APS) per gram of monomer gives the polymer with the highest intrinsic viscosity. Entries eight and nine display the effects of solvent on the polymerisation reaction. Using DMSO as solvent, the viscosity or the yield of the polymer were not improved.

The polymer (**8**) (entry three, Table 1) was hydrolysed under acidic condition (6 N HCl, 40°C), to give the hydrolysed polyzwitterion (**9**) in excellent yield (84%). The hydrolysis was found to be almost complete (vide infra). The hydrochloric acid in the reaction mixture was removed by dialysing against deionised water, followed by basification ($NaHCO_3$) and dialysis against distilled water (see under experimental section). The polymer was recovered by freeze-drying.

Table 1
Effect of solvent and concentration of monomer and initiator [ammonium persulfate, (APS)] on polymerisation[a]

Entry number	Monomer concentration (%W/W)	APS mg g^{-1} monomer	Solvent	Temperature (°C)	Yield (%)	Intrinsic[b] viscosity (dl g^{-1})
1	60	15	A	90	35	0.216
2	70	10	A	90	65	0.451
3	70	15	A	90	78	0.555
4	70	20	A	90	63	0.330
5	80	15	A	90	50	0.409
6	90	15	A	90	38	0.416
7	100	15	A	90	~0	—
8	36	15	B	50	38	0.291
9	36	20	B	50	30	0.374

[a] Polymerization time: in solvent A (H_2O) 1 h; in B (DMSO) 20 h.
[b] Viscosity of 1.0%–0.0625% polymer solution in 0.1 N NaCl at 30°C was measured in Ubbelohde Viscometer ($K = 0.005989$).

While the polyelectrolyte (**8**) melted in the range of 355°C–370°C, the polyampholyte (**9**) did not melt, even at 400°C. The differential thermal analysis and thermal gravimetric analysis of the polyelectrolyte (**8**) and polyampholyte (**9**) are shown in Fig. 1. Absorption at 1784 cm^{-1} in the i.r. spectra of **8** reveals the presence of an ester group. Strong absorption at 3454 cm^{-1} indicates the hygroscopic nature of the polymer. The absorption around 1628 cm^{-1} indicates the presence of CO_2^- functionality in **9**. ^{1}H and ^{13}C n.m.r. spectra were measured in D_2O at 500 MHz and

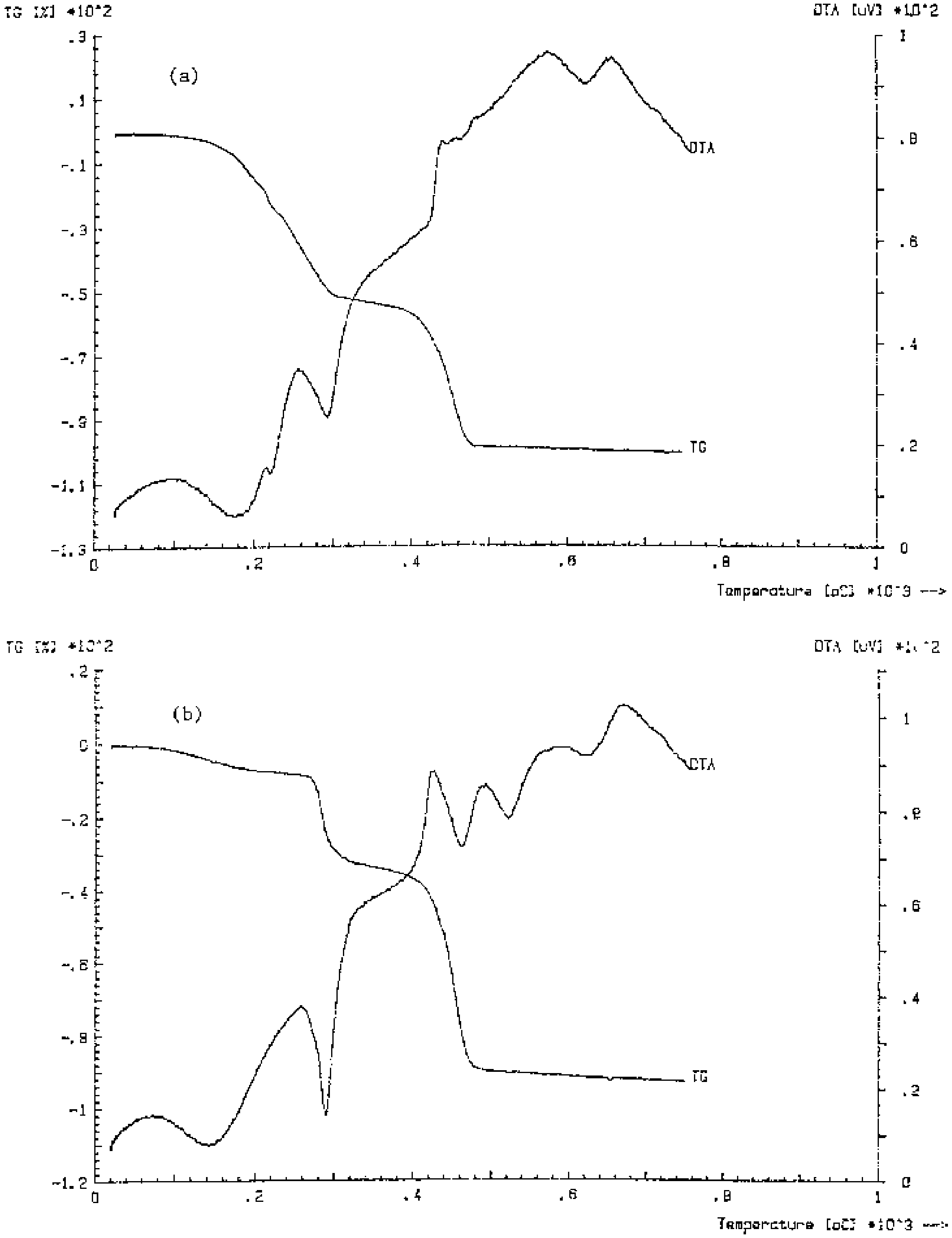


Fig. 1. Differential thermal and thermogravimetric analysis of (a) polyelectrolyte (**8**) (sample: entry three, Table 1) and (b) polyampholyte (**9**) with a scanning rate of 10°C per minute.

125.65 MHz, respectively, on a JEOL LA 500 spectrometer. *p*-dioxane ($\delta_c = 67.4$ ppm) and DSS were used as internal standards for the ^{1}H and ^{13}C spectra of the polymers (**8** and **9**) and are displayed in Figs 2 and 3, respectively. It is evident after comparing the ^{1}H spectra of the polymers (Fig. 2) that the CH_3-C-O protons which appeared at δ 1.25 ppm for the polyelectrolyte (**8**) is not present in the spectrum of the polybetaine (**9**), thus indicating the removal of the CH_3CH_2- group after hydrolysis. A similar observation is made from the ^{13}C n.m.r. spectra; the carbons of the ethyl group (Fig. 3) disappeared in the spectrum of the polyampholyte, thus ensuring the complete hydrolysis of the ester groups. Carbonyl resonances, observed around 166 ppm, are not shown in the figure. The assignment of the ^{13}C peaks are based on earlier works [2,3.14,15]. C-2 signals of the polymers show eight well-resolved lines; four weak lines for the *trans* and the other four for the *cis*. The large, unequal splitting of the *cis* can be assigned to the differences in the configuration at N^+, and the small splitting of equal intensity can be attributed to the different configurations of the adjacent rings, as these can add in two ways (R or S) with equal probabilities. Integration of the relevant peaks in the ^{13}C n.m.r. spectra yields the percentage of *trans* to be about 20% in these polymers.

The pH of 1% solution of the polyelectrolyte (**8**) and polyampholyte (**9**) was found to be 2.71 and 8.17, respectively. The solubility behaviour of the polymers is shown in Table 2. The polyelectrolyte (**8**) was found to be very soluble in water and methanol but insoluble in acetone. While the overwhelming majority of reported polyampholytes [9,16,17] are known to be insoluble in water, the polyampholyte (**9**) was found to be soluble in water as well as in most of the protic solvents. Viscosity data for the polymer (**8**) (entry three, Table 1) and polyampholytes (**9**) are presented in Fig. 4. In the absence of added salt (NaCl) the plot for **8** is typical for a polyelectrolyte i.e. concave upwards; the plot for the polyampholyte (**9**), on the other hand, is a straight-line curve, just like the behaviour observed for a normal polymer. The addition of strong electrolyte-like sodium chloride suppresses the ionisation of the polyelectrolyte (**8**) and the viscosity behaviour becomes normal, as can be seen in Fig. 4. By increasing the ionic strength, the

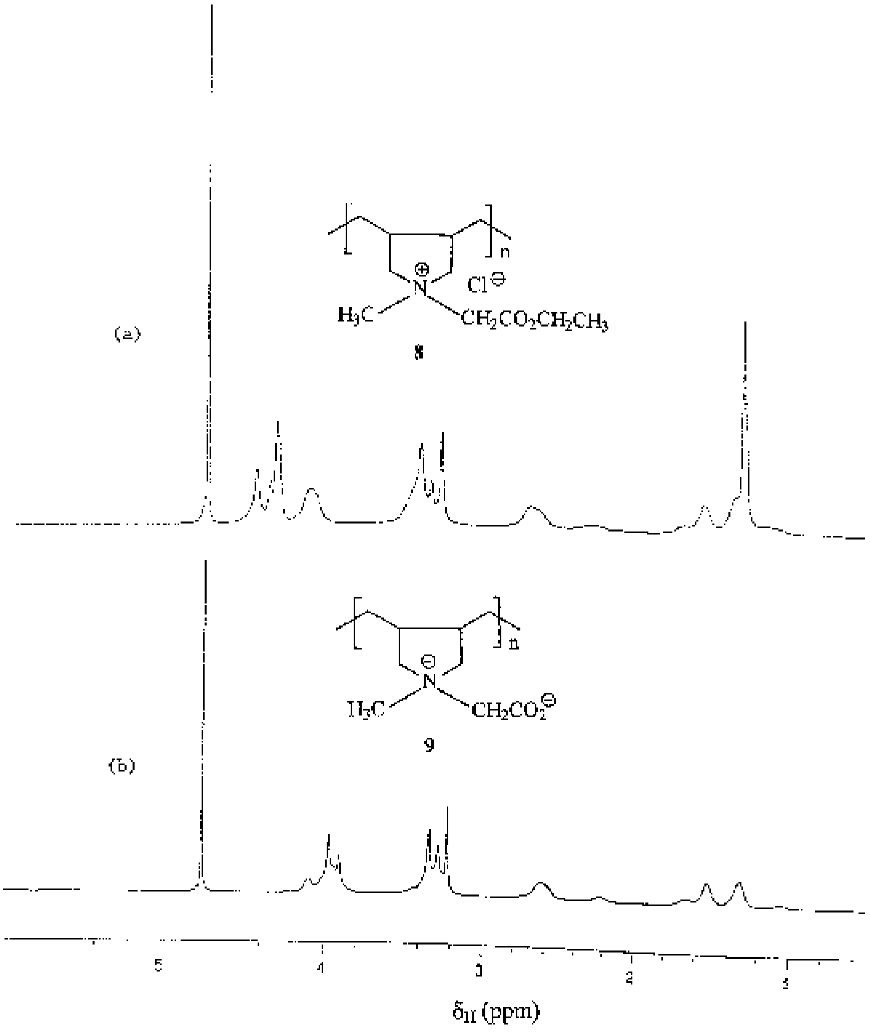


Fig. 2. ^{1}H n.m.r. spectrum in D_2O of: (a) polyelectrolyte (**8**); and (b) polyampholyte (**9**).

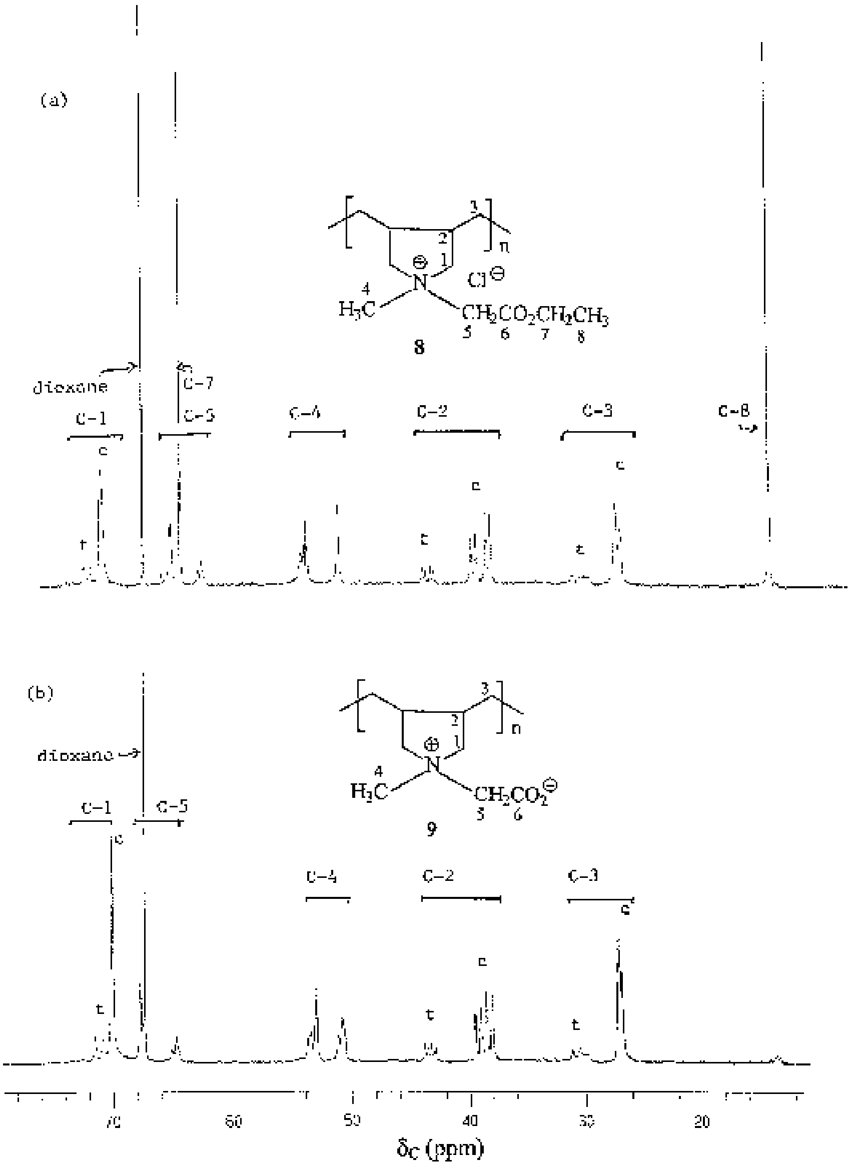


Fig. 3. ^{13}C n.m.r. spectrum in D_2O of: (a) polyelectrolyte (**8**); and (b) polyampholyte (**9**).

Table 2
Solubility[a,b] of homopolymer (**8**) and corresponding polyampholyte(**9**)

	ε	Polymer (**8**)	Polymer (**9**)
Water	78.4	+	+
Methanol	32.3	+	+
Formic acid	58.5	+	+
Formamide[c]	111.0	+	+
Ethylene glycol	37.3	+	+
Triethylene glycol	23.7	+	±
Acetic acid	6.15	+	−

[a] 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.

[b] ‘+’ indicates soluble; ‘−’ indicates insoluble; ‘±’ indicates partially soluble.

[c] Intrinsic viscosity in DMF at 30°C was determined to be 0.494 dl g^{-1}.

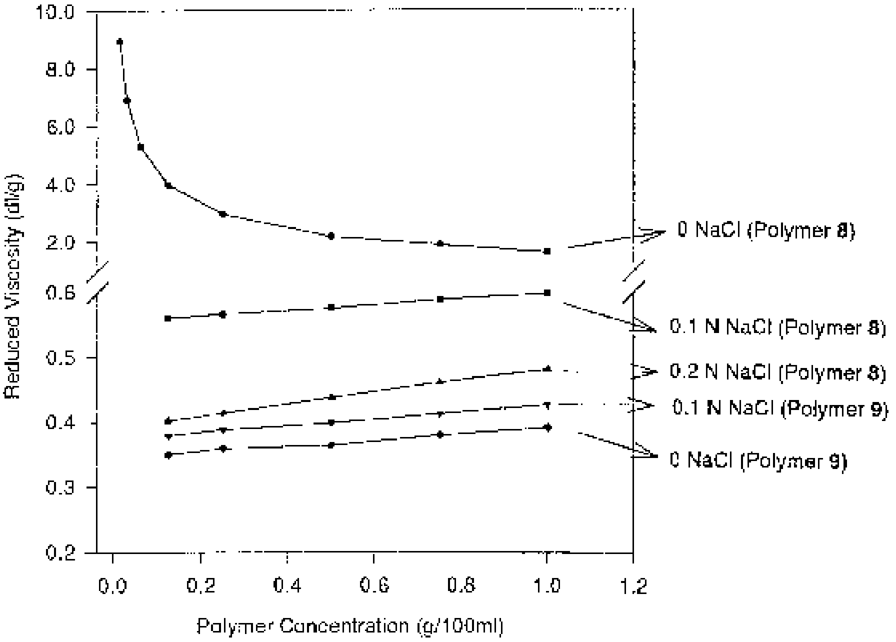


Fig. 4. Viscosity behaviour of polyelectrolyte (**8**) and polyampholyte (**9**) in water at 30°C at different NaCl concentrations, using an Ubbelohde viscometer ($K = 0.005989$).

viscosity decreases due to the screening of the charges on the macromolecular chain, thus leading to a decreased macromolecular expansion. As is evident, the intrinsic viscosity in 0.1 N and 0.2 N NaCl solution of the polymer (**8**) becomes 0.559 and 0.390 dl g^{-1}, respectively. For the polyampholyte (**9**), however, an increasing concentration of NaCl increases the intrinsic viscosity of the polyampholyte (Table 3). In Figs 4 and 5, the effects of NaCl concentration on the intrinsic viscosity is illustrated. It is possible to consider Fig. 5 to be composed of two straight lines. The first line with the higher slope may be attributed to the site binding [16,17] of the chloride ion by the quaternary ammonium centre. This line reflects the relatively rapid change in the intrinsic viscosity as the chloride ion concentration is increased. The second line, characterised by a slower rate of change of intrinsic viscosity, may be due to atmospheric binding of the Cl^- by the polyampholyte. At lower concentrations of added salt, the site binding of anions predominates and as the salt concentration is increased, more and more of the potential binding sites are occupied until, finally, there would be no more sites available for further site binding. In the second stage, the atmospheric binding

Table 3
Intrinsic viscosity of polyampholyte (**9**) in aqueous solution containing different concentrations of added salt, NaCl

Polymer	[NaCl] (N)	Intrinsic viscosity[a] (dl g^{-1})
9[b]	0	0.345
9	0.1	0.373
9	0.5	0.413
9	1.0	0.447
9	1.5	0.465
9	2.0	0.478
8[c]	0	—[d]
8	0.1	0.556
8	0.2	0.390

[a] Viscosity of 1.0%–0.0625% polymer solution at 30°C was measured in Ubbelohde Viscometer ($K = 0.005989$).

[b] Obtained by hydrolysis of the homopolymer from entry number three of Table 1.

[c] Homopolymer of entry three from Table 1.

[d] Concave upward (see Fig. 4).

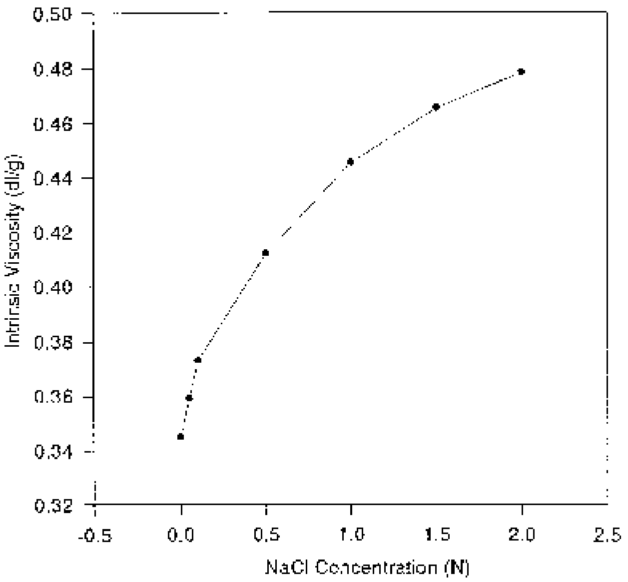


Fig. 5. Effect of NaCl concentration on the intrinsic viscosity of polyampholyte (**9**) in water at 30°C, using an Ubbelohde viscometer ($K = 0.005989$).

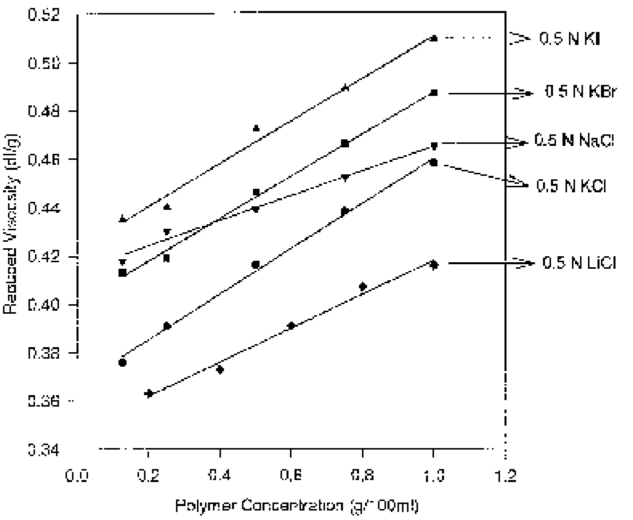


Fig. 6. Effect of added salt (0.5 N) on the viscosity behaviour of polyampholyte (**9**) in water at 30°C, using an Ubbelohde viscometer.

Table 4
Effect of anion and cation on the viscosity behaviour of polyampholyte (**9**)

Solvent (0.5 M)	Intrinsic viscosity (dl g^{-1})
KCl	0.368
KBr	0.400
KI	0.423
NaCl	0.412
NH_4Cl	0.397
LiCl	0.346
$CaCl_2$	0.391

tends to predominate and the increase in viscosity begins to lessen. The presence of an inorganic salt (NaCl) disrupts the intrachain interaction of the quaternary ammonium and carboxylate groups, thus causes the tightly coiled polyampholyte to behave as a flexible coil. The addition of salt causes the polyampholyte to achieve a more rod-like conformation [16] in order to relieve the repulsion between pendant carboxylate anions. It seems apparent that while the cationic charge on the polymer chain could be effectively neutralised by strongly binding chloride anions, the anionic pendant group is not shielded to that extent by the cation, Na^+. The hydration shell for a positively charged ion (e.g. Na^+) in water is generally fairly large, hence the distance of closest approach is not sufficient to effectively neutralise the charge on the pendant carboxylate anions. The overall effect of the addition of NaCl is to make the polymer more rod-like, and hence to increase the intrinsic viscosity of the polyampholyte solution. This type of behaviour has been characterised as ‘anti-polyelectrolyte’ [7].

The reduced viscosities of the polyampholyte in aqueous solution containing various added salts were studied and are illustrated in Fig. 6 and Table 4. It is observed that for the common cation potassium (K^+), the intrinsic viscosity increases as the anion is changed from Cl^- to Br^- to I^-. Iodide, having the smallest charge to radius ratio, is more polarisable, hence it can approach closely to the cationic centre in the chain, thus effectively neutralising the charge. One important feature of this investigation is that divalent cations, Ca^{2+}, which are known to precipitate anionic polyelectrolytes from aqueous solution even at low concentrations, did not precipitate the polyampholyte (**9**).

4. Conclusion

The monomer (**7**) is prepared from inexpensive starting materials and in almost quantitative yield. Efforts are underway to improve the viscometric behaviour of the polymers by using other initiators. This study has demonstrated the simple way to convert a polyelectrolyte into a polyampholyte and thus, has provided the opportunity to compare the solution properties of a polyelectrolyte and a polyampholyte having almost identical average molar masses.

Acknowledgements

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References

[1] Butler GB. Acc Chem Res 1982;15:370.
[2] Johns SR, Willing RI, Middleton S, Ong AK. J Macromol Sci Chem A 1976;10:875.
[3] Lancaster JE, Baccei L, Panzer HPJ. Polym Sci Polym Lett Edn 1976;14:549.
[4] Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA, 1983:581–10111, 581–5022L, 581–1012D.
[5] Ottenbrite RM, Ryan WS Jr.. Ind Engng Chem Prod Res Develop 1980;19:528.
[6] Armstrong RW, Strauss UP. In: Encyclopedia of polymer science and technology, vol. 10. New York: Interscience, 1969:781.
[7] Schultz DN, Peiffer DG, Agarwal PK, Larabee J, Kaladas JJ, Soni L, Handwerker H, Gardner RT. Polymer 1986;27:1734.
[8] Anton P, Laschewsky A. Makromol Chem 1993;194:601.
[9] Wielema TA, Engberts JBFN. Eur Polym J 1987;23:947.
[10] Fischer GW, Jentzch R, Kasanzewa V, Riemer F. J Prakt Chem 1975;317:943.
[11] Hahn M, Kotz J, Linow KJ, Philipp B. Acta Polym 1989;40:36.
[12] Harada S, Arai K. Makromol Chem 1967;107:78.
[13] Butler GB. US Patent No. 3288770, 1966.
[14] Ali SA, Wazeer MIM, Ahmed SZ. J Appl Poly Sci 1998;0:0. (in press).
[15] Ali SA, Ahmed SZ, Wazeer MIM, Hamad EZ. Polymer 1997;38:3385.
[16] Salamone JC, Volksen W, Olson AP, Israel SC. Polymer 1978;19:1157.
[17] Monroy Soto VM, Galin JC. Polymer 1984;25:254.