ELSEVIER

Polymer 40 (1999) 6849–6857

polymer

Synthesis and solution properties of a betaine-sulfur dioxide polyampholyte

S.A. Ali*, A. Rasheed

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Received 8 October 1998; received in revised form 23 December 1998; accepted 23 December 1998

Abstract

The copolymer **7** of quaternary ammonium salt, *N*,*N*-diallyl-*N*-carboethoxymethyl-*N*-methylammonium chloride (**5**) and sulfur dioxide were synthesized in excellent yield. The polyelectrolyte **7** on acidic hydrolysis gave the polyampholyte **8** readily in excellent yield. The solution properties of these polymers are discussed in detail. The polyampholyte **8** was found to be insoluble in water but dissolved readily in the presence of low molecular weight common salts. The polyampholyte shows "anti-polyelectrolyte" behavior; the viscosity of the polyampholyte increases by increasing the ionic strength of its aqueous solutions. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: Polyampholyte; Poly(quaternary ammonium salts); Polybetaine

1. Introduction

Butler et al. [1] have polymerized various diallyl quaternary ammonium salts (**1**) to yield linear water-soluble polymers. The polymerization proceeds via an intra-, inter-molecular chain propagation (termed cyclopolymerization) through five-membered [2,3] cyclic structure to yield linear water-soluble polymers **2** (Scheme 1). These polyquaternary ammonium salts have found extensive industrial and commercial applications [4,5]. Polydiallyldimethylammonium chloride alone accounts for over 200 patents and publications. The copolymers of quaternary ammonium salt and sulfur dioxide are reported to produce particularly good flocculants. Polysulfones are used as adhesives, thickeners and paints [5].

One of the major drawbacks of the use of high molecular weight polyelectrolytes in enhanced oil recovery (EOR) is the drastic decrease in the viscosity of their aqueous solutions in the presence of added salt (NaCl etc.) [6]. Moreover, the presence of divalent cations (Ca^{2+} etc.) tends to precipitate out anionic polyelectrolytes. However zwitterionic (ampholytic) polymers show "anti-polyelectrolyte behavior" [7] and have low or no solubility in water but greatly enhanced solubility and extensive chain expansion, hence higher viscosity, with increasing salt concentration. There are only a few literature reports [8,9] of polyampholytes derived from zwitterionic *N*,*N*-diallyl quaternary ammonium monomers **3** and **4**. Even though the synthesis of polyampholytes from the monomer **3** is mentioned [9], its solution properties are not reported. Disadvantages in the reported synthesis include a relatively low yield obtained in the monomer and polymer syntheses [9] and the use of sulfones which are carcinogenic compounds [10]. Alternating ampholytic copolymers of maleic acid with allylamine, diallylamine, methyldiallylamine and diallyl quaternary ammonium salt were synthesized by free radical polymerization [11]. Recently [12], the polyampholyte (**6**) with moderate limiting viscosity numbers was prepared by the hydrolysis of the corresponding polyelectrolyte derived from the monomer **5**. To our knowledge, the polyampholyte derived from the copolymer of diallyammonium salt of the type **5** and sulfur dioxide was not reported to date.

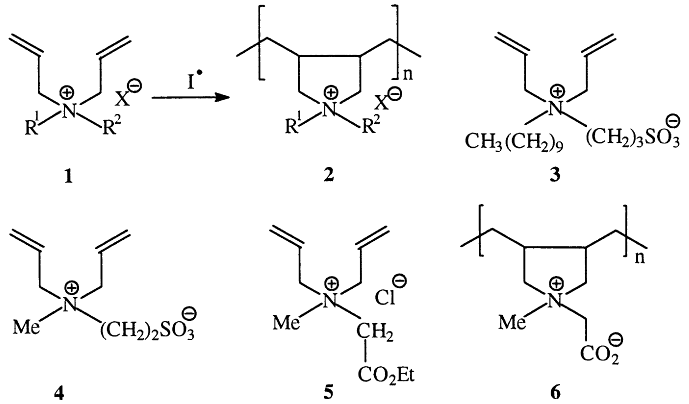
The present paper describes the synthesis of a polyampholyte (polybetaine) from a copolymer of sulfur dioxide and nonzwitterionic monomer **5** which is readily synthesized [12] from inexpensive starting materials (Scheme 2). The study provided an interesting opportunity to examine the solution properties of the polyelectrolyte **7** and its hydrolyzed product, the polyampholyte **8**, having a similar average molar mass.

---

* Corresponding author. Tel.: + 966-3-860-3083; fax: + 966-3-860-3586.

E-mail address: shaikh@kfupm.edu.sa (S.A. Ali)

PII: S0032-3861(99)00010-5



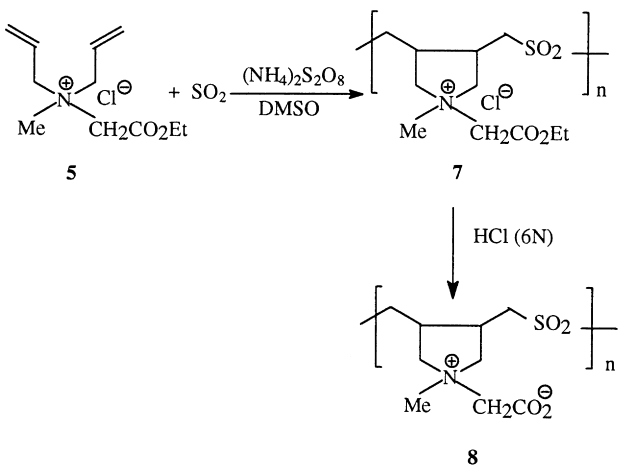
Scheme 1.

2. Experimental

2.1. Physical methods

All m.p.s are uncorrected. 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 a Ubbelohde viscometer (K 0.005989).

The equipment used for thermal analysis was a Simultaneous Thermal Analyzer (STA 429) manufactured by Netzsch, Germany. The polymer sample to be tested (usually 30 mg) was placed in an alumina crucible. The aluminum oxide (Al_2O_3, 100 mg), was placed in an identical alumina crucible as a reference sample. Using the sample carrier system, which has two sets of 10% Pt–Pt/Rh thermocouples, the sample carrier was placed in the middle of the vertical furnace, which was programmed and controlled by a microprocessor temperature controller. The temperature was raised to a uniform rate of 10°C/min. The analyses were performed over a temperature range of 20–1000°C in a dynamic atmosphere of N_2 flowing at a rate of 100 ml/min.



Scheme 2.

2.2. Materials

Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK) was used as received. The monomer **5** was synthesized as described earlier [12]. All glassware were cleaned using deionized water. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a b.p. of 64–65°C (4 mmHg).

2.3. General procedure for the copolymerization of the monomer (5) with SO_2

A stock solution of SO_2 in DMSO was prepared by absorbing a known amount of SO_2 in a known quantity of DMSO. In one such case, 0.274 g of the stock solution was found to contain 1.00 mmol of SO_2. To a dry flask (25 ml) containing the monomer **5** (10.0 g, 42.8 mmol), the required amount of SO_2 was added from the DMSO-SO_2 stock solution. Sometimes fresh DMSO was added for dilution. The mixture in the closed vessel was briefly heated at 50°C with stirring to achieve a homogeneous solution. The required amount of APS (as listed in Table 1) was added and the closed flask was magnetically stirred at 50°C for 12 h. The reaction mixture became viscous within 10–20 min after addition of the initiator and the magnetic stirring was stopped after 1 h. The reaction mixture remained transparent throughout the polymerization process. The mixture was dissolved in methanol (20 ml) and precipitated in acetone (150 ml). This process was repeated three times. The resulting hygroscopic white polymer **7** was dried to a constant weight at 50°C under vacuum. The onset of thermal decomposition (Closed Capillary) 240–250°C (decomposed, turned brown). (Found: C, 44.0; H, 6.8; N, 4.55; S, 10.5. $C_{11}H_{20}NO_4ClS$ requires C, 44.36; H, 6.77; N, 4.70; S,

Table 1
Effect of concentration of monomers, initiator and temperature on M/SO_2 copolymerization

Entry no.	Monomer (mmol)	SO_2 (mmol)	DMSO (g)	APS (mg)	Time (h)	Temperature (°C)	Yield[a] (%)	Intrinsic viscosity[b] (dl/g)
1	50	50	10.5	85	15	35	43	1.90
2	50	50	10.5	85	15	40	77	1.83
3	50	50	10.5	85	10	45	77	1.48
4	50	50	10.5	85	3	50	82	0.836
5	50	50	10.5	170	3	50	87	0.604
6	50	25	10.5	85	3	50	109	1.03

[a] Based on a 1:1 monomer composition of M/SO_2.

[b] Viscosity of 1–0.03125% polymer solution in 0.1 N NaCl at 30°C was measured in a Ubbelohde Viscometer ($K = 0.005989$).

10.77%); υ_{max} (KBr) 3430, 2984, 2940, 1748, 1638, 1472, 1422, 1386, 1306, 1226, 1126, 1028, 954, 924 and 860 cm^{-1}.

*2.4. Acidic hydrolysis of the polyelectrolyte **7***

A solution of copolymer **7** (10.0 g) in 5.5 M HCl (200 ml) was stirred at 40°C for 96 h (or until the hydrolysis was complete as indicated by ^1H NMR spectrum). During hydrolysis, the homogeneous solution became heterogeneous at the end of the second day as a result of the precipitation of the hydrolyzed polymer. The reaction solution was then cooled to room temperature and the aqueous layer was decanted, leaving the polymer in the flask. The polymer was washed with distilled water (2 × 30 ml). Then 50 ml of water was added to the polymer, which was

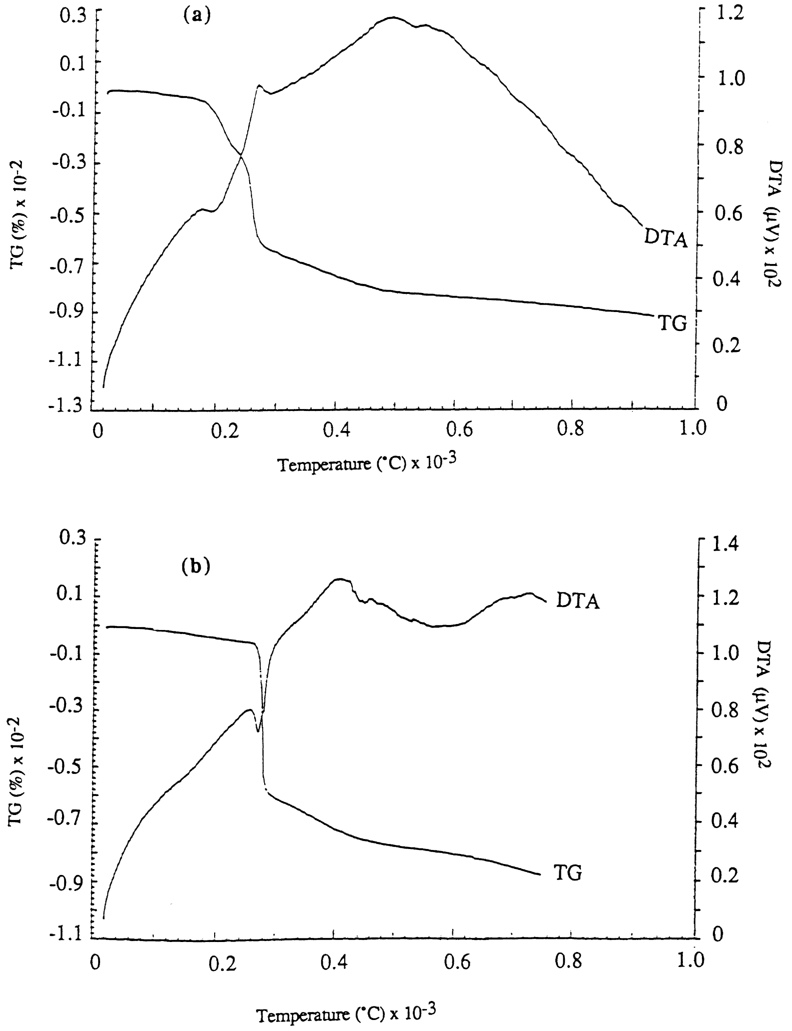


Fig. 1. Thermogravimetric analyses of (a) polyelectrolyte **7** and (b) polyampholyte **8** with a scanning rate of 10°C/min.

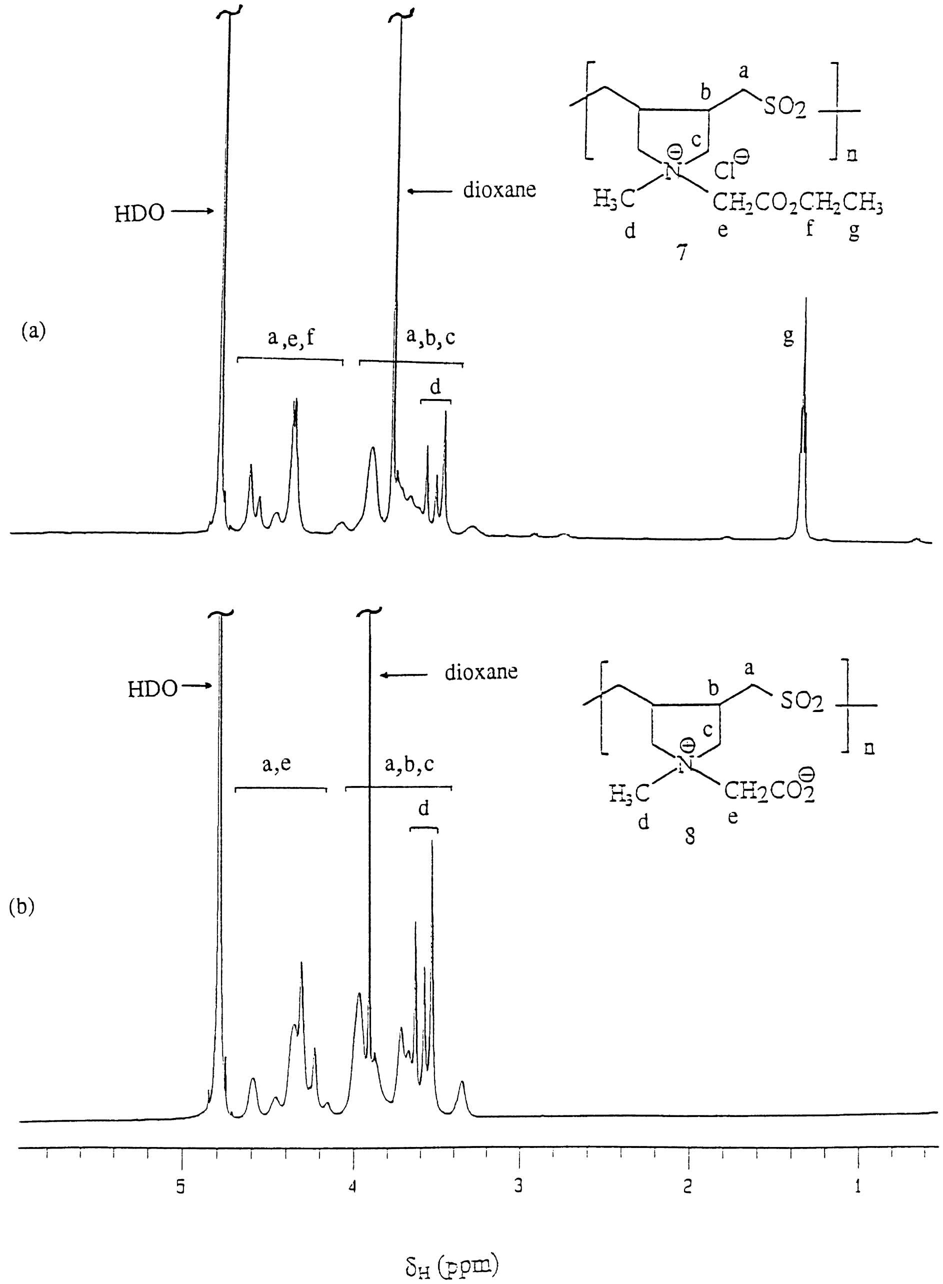


Fig. 2. ^{1}H NMR spectrum in D_2O of (a) polyelectrolyte **7** (b) polyampholyte **8**.

neutralized by addition of $NaHCO_3$. This caused dissolution of the polymer. After the polymer was completely dissolved, the aqueous solution was dialyzed against deionized water to remove excess $NaHCO_3$ ($AgNO_3$ test). During dialysis the polymer kept depositing on the walls of the dialysis bag. At the end, the polymer was collected and soaked in acetone and kept overnight. The white polymer **8** was dried at 50°C under vacuum until a constant weight was obtained. The polyampholyte was stored inside a desiccator. Yield: 6.7 g (85.5%). The onset of thermal decomposition (Closed Capillary) 270–280°C (turned dark brown) (Found: C, 46.0; H, 6.6; N, 5.85; S, 13.5. $C_9H_{15}NO_4S$ requires C, 46.33; H, 6.48; N, 6.00; S, 13.74%); υ_{max} (KBr) 3422, 2972, 2926, 1628, 1458, 1394, 1300, 1126 and 906 cm^{-1}.

2.5. Solubility measurements and cloud point titrations in aqueous salt solution

Solubility of the polyelectrolyte **7** and polyampholyte **8** in organic solvents at room temperature was established for 2% (w/w) solutions, after preheating at 70°C for 1 h.

The critical (minimum) salt concentration (CSC) required to promote a water solubility at 23°C was measured by titration of 1% (w/w) polymer solution at a sufficiently high salt concentration with deionized water. The accuracy

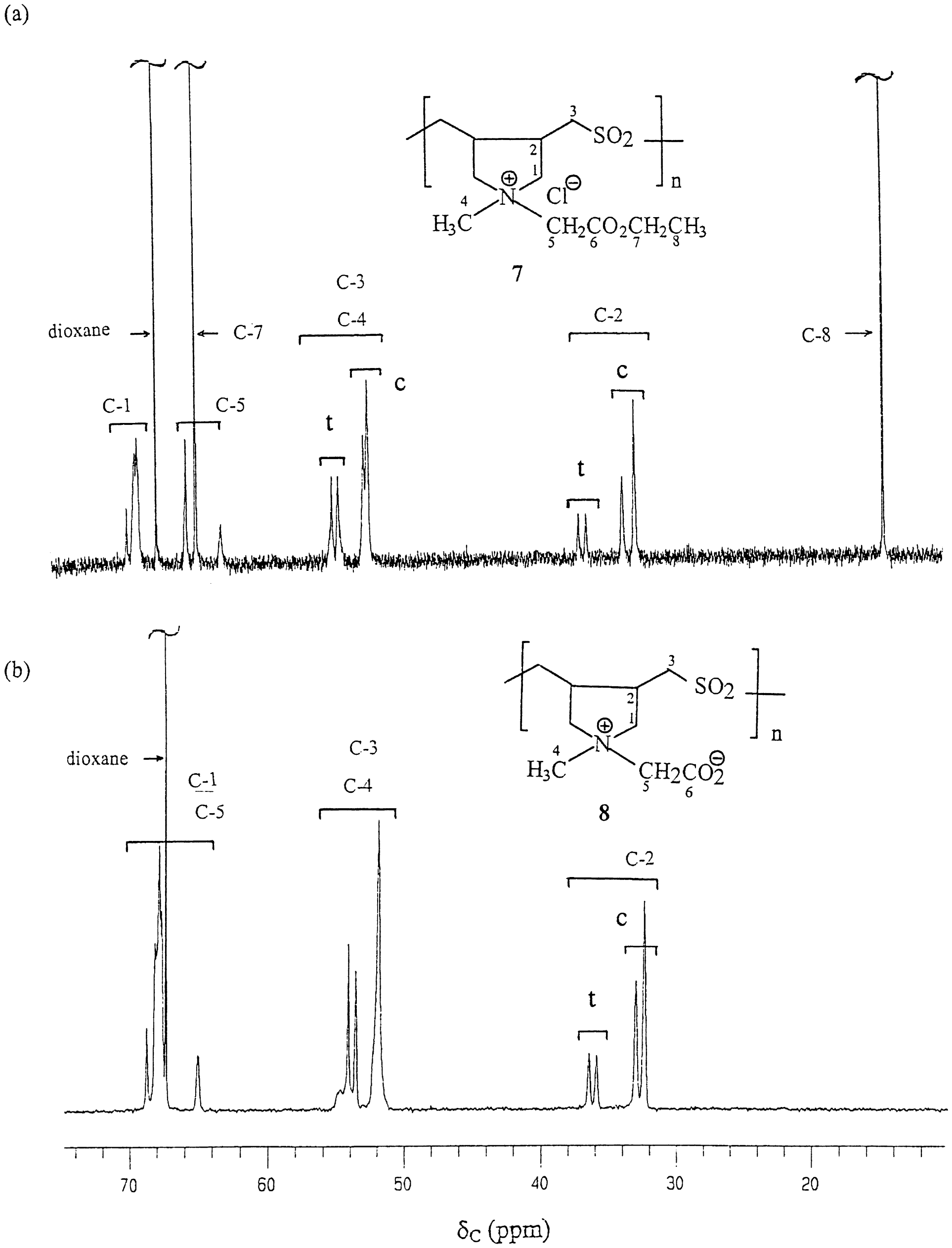


Fig. 3. ^{13}C NMR spectrum in D_2O of (a) polyelectrolyte **7** (b) polyampholyte **8**.

of the CSC values, obtained by visual determination of the first cloud point, was approximately ±1–2%.

3. Results and discussion

The results of the copolymerization are shown in Table 1. As is evident from the Table, for a 1:1 mole ratio of the monomer **5** and SO_2, the isolated yield of the copolymer **7** is maximum (82%) at 50°C and minimum (43%) at 35°C (entries 1–4, Table 1). However, the opposite is true for the intrinsic viscosity in 0.1 N NaCl solution. The maximum intrinsic viscosity of 1.90 dl/g was obtained at 35°C. The viscosity decreases with increasing temperature of the copolymerization and at 50°C it became 0.836 dl/g. The intrinsic viscosity of 1.90 dl/g is indeed very high for polyelectrolytes and thus indicates its very high molar mass. Polymerization carried out at 50°C (entries 4 and 5) using different initiator concentrations indicates that increasing the initiator concentration decreases the viscosity. For a polymerization using a 2:1 mole ratio of monomer and SO_2 gave the highest intrinsic viscosity value of 1.03 dl/g for the three polymerization reactions run at 50°C. The yield of 109% (entry 6) based on a 1:1 monomer complex, M/SO_2, presumably indicates that the alternating copolymer may contain some homopolymer blocks because the

Table 2
Solubility[a,b] of copolymer **7** and the corresponding polyampholyte **8**

	ϵ	Polymer **7**	Polymer **8**
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° for 1 h and then bringing the temperature back to 23°C.

[b] (+) indicates soluble; (−) indicates insoluble; (±); indicates partially soluble.

[c] Intrinsic viscosity in formamide at 30°C was determined to be 0.859 dl/g.

monomer **5** was used in excess. The polyelectrolyte **7** from entry 2 (Table 1) was hydrolyzed under acidic conditions to give the polyampholyte **8** in an excellent yield (86%). The detailed procedure for the isolation of the polyzwitterion **8** was given in Section 2. The elemental analysis of the hygroscopic polymers **7** and **8** indicates the presence of the monomer and SO_2 in an approximately 1:1 ratio, hence suggesting the formation of alternating copolymer. The onset of thermal decomposition of the polymers **7** and **8** was found to be 240–250 and 270–280°C, respectively, and in each case the polymers turned brown. The thermogravimetric analyses of the polymers are shown in Fig. 1. The IR spectra of the copolymer **7** indicates the presence of SO_2 into the polymeric backbone. The two strong bands at 1306 and 1126 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit. The strong absorption at 1748 cm^{-1} indicates the presence of an ester functionality. The hygroscopic nature of the polymer is revealed by the presence of a strong band at around 3450 cm^{-1}. The IR spectrum of the polyampholyte **8** indicates the absence of absorption as a result of the ester functionality. The absorption at 1628 cm^{-1} was attributed to the carboxylate group. The strong bands at 1300 and 1126 cm^{-1} were assigned to the asymmetric and symmetric vibrations of the SO_2 residues.

^1H and ^{13}C NMR spectra were measured in D_2O at 500 and 125.65 MHz, respectively, on a JEOL LA 500 spectrometer. *p*-Dioxane ($\delta_c = 67.4$ ppm) was used as internal standard for ^1H and ^{13}C spectra of the polymers (**7** and **8**) and are displayed in Figs. 2 and 3, respectively. It is evident after comparing the ^1H spectra of the polymers (Fig. 2) that the CH_3–C–O protons which appeared at δ 1.25 ppm for the polyelectrolyte **7** are not present in the spectrum of the polybetaine **8**, thus indicating the complete removal of the CH_3CH_2– group via hydrolysis. Similar observations are made in the ^{13}C NMR spectrum; the carbons of the ethyl group (Fig. 3) disappeared in the spectrum of the polyampholyte thus indicating the complete hydrolysis of the ester groups. Carbonyl resonances, observed around 166 ppm, are not shown in this figure. The assignment of the ^{13}C peaks are based on earlier work [2,3,13,14]. C-2 signals of the polymers show four well-resolved lines; two weak lines of equal intensity for the *trans* and the other two for the *cis* disposed substituents at 3, 3′. The unequal splitting of the *cis* form can be attributed to the difference in the configuration at N^+;—the *cis* substituents at 3, 3′ being *cis* or *trans* to the N–CH_3 in unequal proportions. Integration of the relevant peaks in the ^{13}C NMR spectra suggests the percentage of the *trans* form is about 20% in these polymers.

Table 3
CSC for aqueous solutions of polyampholyte **8** at 23°C

Salt	CSC (M)
LiCl	0.992
NaCl	0.069
KCl	0.070
KBr	0.014
KI	0.0026
NH_4Cl	0.073
$CaCl_2$	0.306
$(C_3H_7)_4NBr$	0.012

The pHs of a 1% aqueous solution of the polyelectrolyte **7** and polyampholyte **8** in 0.1 N NaCl were found to be 2.62 and 7.22, respectively. The solubility behavior of the polymers is shown in Table 2. The polyelectrolyte **7** was found to be very soluble in protic solvents except acetic acid. Like the overwhelming majority of the reported [9,15,16] polyampholytes, polyampholyte **8** was found to be insoluble in water, as well as in most of the protic solvents. As anticipated for zwitterionic polymers, polyampholyte **8** dissolved readily in aqueous solutions of salts including divalent cations such as Ca^{2+}, which are known to precipitate out polyelectrolytes. Such behavior was interpreted [7,17] in terms of collapsed coils in water as a result of inter- and intra-chain interactions leading to a 3-dimensional ionic network (or ionic crosslink). For the solubilization of polyampholyte **8** in an aqueous salt solution, the low molecular weight anions and cations of the added electrolyte enter and partially neutralize a portion of the ionic network of the polymer. The elastic forces, which oppose continued swelling, are gradually decreased and finally the swelled gel is ruptured and dissolved.

The CSC required to promote water solubility at 23°C was measured by titration of a 1% (w/w) solution of a sufficiently high concentration with deionized water. The accuracy of the CSC values, obtained by visual determination of the first cloud point, was approximately ±1–2%. The respective influence of the nature of the cation and anion on the CSC values are shown in Table 3. For a common anion, Cl^-, the CSC values for the Na^+, K^+, and NH_4^+ salts remain in a narrow range of 0.069–0.073 M. However, for the chloride salts of Li^+ and Ca^{2+}, the CSC values (0.992 and 0.306 M, respectively) are found to be considerably large. Differences of this magnitude were not observed for the reported polysulfobetaines [7,17]. The sequence of

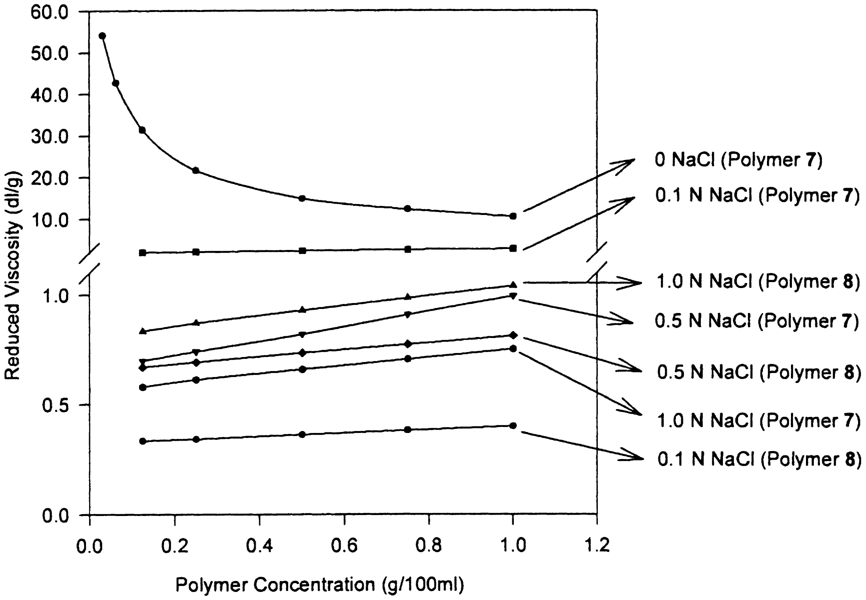


Fig. 4. Viscosity behavior of polyelectrolyte **7** and polyampholyte **8** in water at 30°C at different NaCl concentrations using a Ubbelohde viscometer ($K = 0.005989$).

increasing solubility power (decreasing order of CSC values) was found to be

$Li^+ \ll Ca^{2+} \ll NH_4^+ < K^+ \leq Na^+$.

The hydration shell of the Li^+ and Ca^{2+} cations in water is generally fairly large as a result of their large charge/radius ratio and presumably cannot approach close enough to neutralize the charge on the carboxylate group effectively. For a common cation, K^+, the CSC values are very sensitive to the nature of the anions. The sequence of increasing solubilizing power is found to be

$Cl^- < Br^- \ll I^-$.

Thus the concentration of KCl required to promote water solubility is found to be 27 times more than that of KI. The iodide anion is the most polarizable (soft), hence it is particularly effective in neutralizing ionic crosslinks, increasing the solubility of the polyampholyte. For a common bromide anion, the K^+ and $(^nC_3H_7)_4N^+$ salts are found to have a similar solubilizing power.

Viscosity data for polymer **7** (entry 2, Table 1) and its

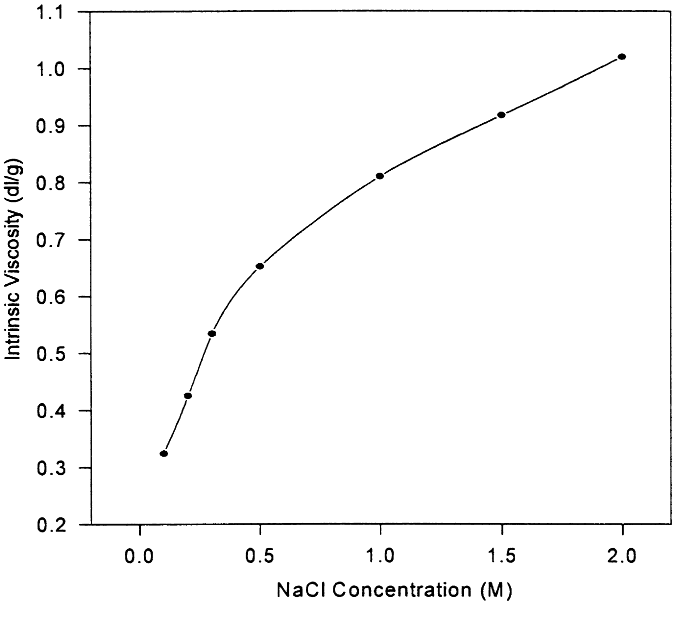


Fig. 5. Effect of NaCl concentration on the intrinsic viscosity of the polyampholyte **8** in water at 30°C using a Ubbelohde viscometer ($K = 0.005989$).

Table 4
Effect of NaCl concentration on the intrinsic viscosity and Huggin's constant k' of polyampholyte **8**

NaCl concentration (M)	Intrinsic viscosity (dl/g)	k'
0.1	0.324	0.709
0.2	0.425	0.602
0.3	0.534	0.458
0.5	0.652	0.382
1.0	0.810	0.354
1.5	0.917	0.340
2.0	1.02	0.324

Table 5
Effect of anion and cation on the viscosity behavior of the polyampholyte **8** at 30°C in water containing 0.5 M

H_2O (0.5 M)	Intrinsic viscosity (dl/g)
KCl	0.652
KBr	0.811
KI	0.833
LiCl (1.5 N)	0.178
NaCl (1.5 N)	0.917
NaCl	0.652
NH_4Cl	0.623
$CaCl_2$	0.474
$(C_3H_7)_4NBr$	0.874
Formamide	0.859

corresponding polyampholyte **8** are presented in Fig. 4. In the absence of an added salt (NaCl) the plot for **7** is typical for polyelectrolyte i.e., concave upwards. The addition of strong electrolytes such as NaCl causes dissolution of the polyampholyte **8** and the viscosity behavior of polymer **7** and **8** becomes normal as can be seen in Fig. 4. By increasing the ionic strength, the viscosity of the polyelectrolyte **7** decreases because of the screening of the charges on the macromolecular chain thus leading to a decreased coil dimension. The intrinsic viscosity of polymer **7** in 0.1, 0.5 and 1.0 N NaCl solution becomes 1.83, 0.685 and 0.567 dl/g, respectively. For the polyampholyte **8**, however, increasing the NaCl concentration increases the intrinsic viscosity of the polyampholyte. In Figs. 4 and 5 and Table 4 the effect of NaCl concentration on intrinsic viscosity is illustrated. Fig. 5 is composed of two straight lines. The first line with the higher slope may be attributed to the site binding [15,16] of the chloride ion by the quaternary ammonium center. This line reflects the relatively rapid change in the intrinsic viscosity as the chloride ion concentration is increased. The second line, characterized by a slower rate of change in intrinsic viscosity, may be because of atmospheric binding of the Cl^- by the polyampholyte. Huggin's constant, k', which is a measure of solvent–polymer interaction, decreases with increasing concentration of the added salt (Table 4). This observation supports the explanation given earlier concerning the gradual depletion of the potential binding sites. The presence of an inorganic salt (NaCl) disrupts the intra-chain interaction of the quaternary ammonium and carboxylate groups, thus causing the tightly coiled polyampholyte to behave as a flexible coil. The addition of a salt allows the polyampholyte to achieve a more rod-like conformation [15] in order to relieve the repulsion between pendent 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 pendent group 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 rod-like. An increase in the intrinsic viscosity of the polyampholyte with increasing salt concentration was characterized as "anti-polyelectrolyte" behavior [7].

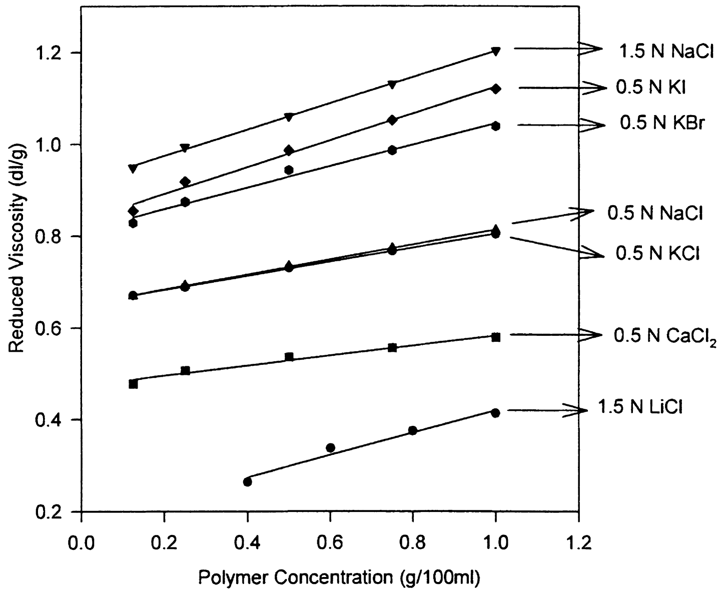


Fig. 6. Effect of added salt on the viscosity behavior of the polyampholyte **8** in water at 30°C using a Ubbelohde viscometer.

The reduced viscosities of the polyampholyte in aqueous solutions containing various added salts were studied and are illustrated in Fig. 6 and Table 5. It is observed that for the common K^+ cation, the intrinsic viscosity increases as the anion is changed from Cl^- to Br^- to I^-. However, for the common Cl^- anion, the viscosity behavior for the Na^+, K^+ and NH_4^+ salts are very similar, whereas that for the Li^+ and Ca^{2+} salts are found to be very different. It is noteworthy that the salt effects on the viscosity and CSC values are very similar. The divalent cation Ca^{2+}, which is known to precipitate anionic polyelectrolytes from aqueous solutions even at low concentrations, did not precipitate the polyampholyte **9**.

4. Conclusion

A very convenient synthetic route for obtaining polyampholytes using inexpensive starting materials is described. Polyampholytes offer a great potential for applications because of their interesting aqueous solution properties [18]. Their solubility in water is controlled by electrostatic interactions and enhanced viscosities with increasing ionic strength which makes the polymer well suited to applications involving high salinity media. The anti-polyelectrolyte effect observed for polyampholyte **8** can be enhanced by proper hydrophobic modification of the polyampholyte, i.e. by incorporating a few mole percent of a long chain hydrocarbon attached to the nitrogen in place of the *N*-methyl group.

Monomer **7** is prepared [12] from inexpensive starting materials and in an almost quantitative yield. A simple method to convert a polyelectrolyte into a polyampholyte is described and thus provides an opportunity for the direct comparison of the solution properties of a polyelectrolyte and a polyampholyte having the same degree of polymerization. It is noteworthy that, in 0.1 N NaCl, polyelectrolyte **7** has a much higher viscosity than the corresponding polyampholyte **8**, hence the former has a more expanded hydrodynamic volume. Interestingly, unlike many sulfobetaines, the viscosities of the polyampholyte **8** do not level off (Fig. 5) in the concentration range (up to 2 N NaCl) of the added salt.

Acknowledgements

Facilities provided by the King Fahd University of Petroleum and Minerals, Dhahran, are gratefully acknowledged.

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 HP. J Polym Sci, Polym Lett Ed 1976;14:549.

[4] Chemical Economics Handbook, Menlo Park, CA: Stanford Research Institute, 1983 pp. 581–10111, 581–5022L, 581–1012D.

[5] Ottenbrite RM, Ryan, Jr WS. Ind Eng Chem Prod Res Develop 1980;19:528.

[6] Armstrong RW, Strauss UP. Encyclopedia of polymer science and technology, vol. 10. New York: Interscience, 1969 pp. 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] Ali SA, Rasheed A, Wazeer MIM. Polymer 1999;40:2439.

[13] Ali SA, Wazeer MIM, Ahmed SZ. J Appl Polym Sci 1998;69:1329.

[14] Ali SA, Ahmed SZ, Wazeer MIM, Hamad EZ. Polymer 1997;38:3385.

[15] Salamone JC, Volksen W, Olson AP, Israel SC. Polymer 1978;19:1157.

[16] Monroy Soto VM, Galin JC. Polymer 1984;25:254.

[17] Salamone JC, Volksen W, Israel SC, Olson AP, Raia DC. Polymer 1977;18:1058.

[18] Skouri M, Munch JP, Candau SJ, Neyret S, Candau F. Macromolecules 1994;27:69.