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Polymerization of functionalized diallyl quaternary ammonium salt to poly(ampholyte–electrolyte)

M.M. Ali, H.P. Perzanowski, Sk.A. Ali*

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

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Abstract

The quaternary ammonium salt, *N*,*N*-diallyl-*N*-carboethoxymethyl-*N*-carbomethoxypentylammonium chloride **13**, on polymerization in aqueous solution using *tert*-butylhydroperoxide, afforded the polyelectrolyte **14**. The copolymer **15** of the monomer **13** and sulfur dioxide was synthesized in excellent yield. The polyelectrolytes **14** and **15** on acidic hydrolysis gave the poly(ampholyte–electrolytes) **16** and **17** which contain structural features common to both polyampholytes and conventional polyelectrolytes. The solution properties of these polymers are discussed in detail. The poly(ampholyte–electrolyte)s, **16** and **17** are shown to have considerably higher viscosity than their corresponding polyelectrolytes **14** and **15**. © 2000 Elsevier Science Ltd. All rights reserved.

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

1. Introduction

Butler [1] polymerized a large number of diallyl quaternary ammonium salts **1** to yield linear water-soluble polymers **3** via an intra-, inter-molecular chain propagation (termed cyclopolymerization) through the five-membered [2,3] cyclic structure **2** (Scheme 1). These cationic polyelectrolytes have found extensive industrial and commercial applications [4,5]. Poly diallyldimethylammonium chlorides, alone, account for over 1000 patents and publications. Polysulfones, the copolymers of the ammonium salts **1** and sulfur dioxide, are also produced commercially and used as adhesives, thickeners and paints [5]. There are only a few reports [6,7] in the literature of polyampholytes (polyzwitterions) derived from zwitterionic *N*,*N*-diallyl quaternary ammonium monomers (e.g. **4** and **5**) (Scheme 1). Recently, we have reported [8,9] a convenient synthetic route leading to polyampholytes **9** and **10** by polymerizing nonzwitterionic monomer **6** and the subsequent hydrolysis of the resultant polyelectrolytes **7** and **8** (Scheme 2). Polyampholytes have found applications in various fields. Polyampholytes can reduce the energy loss due to friction in turbulent flow [10], serve as biosensors, act as amphoteric buffers for electrophoresis [11] and used as a simple model [12–14] for understanding the complex behavior of proteins.

While the polyelectrolytes are usually soluble in water, the overwhelming majority of the reported polyampholytes [7,15,16] are known to be insoluble in water. This solubility behavior is attributed [17,18] to the collapsed coil conformation of the polyampholytes as a result of inter- and intrachain interactions leading to a three-dimensional ionic network. The presence of an inorganic salt (NaCl) neutralizes the ionically cross-linked network of the polyampholyte and causes the dissolution of the coiled polyampholyte. Unlike polyelectrolytes, the ampholytic polymers show “anti-polyelectrolyte behaviour” [17] and have greatly enhanced solubility and extensive chain expansion, hence higher viscosity, with increasing salt (NaCl) concentration.

To our knowledge, polyquaternary ammonium salts containing structural features common to both polyampholytes and conventional polyelectrolytes on each repeat unit, are not known to date. It would indeed be of tremendous theoretical and practical significance to determine the effect of this special structural feature (i.e. ampholyte–electrolyte) on the solubility and solution properties of the poly(ampholyte–electrolyte).

The present paper describes the synthesis of poly(ampholyte–electrolytes) **16** and **17** via hydrolysis of the polyelectrolytes **14** and **15**, which were prepared from the nonzwitterionic monomer **13** (Schemes 3 and 4). The

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* Corresponding author. Tel.: +966-3-860-3083; fax: +966-3-860-3586.
E-mail address: shaikh@kfupm.edu.sa (Sk.A. Ali).

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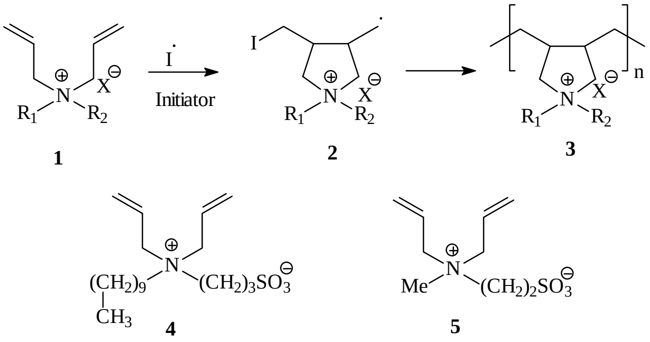


Scheme 1.

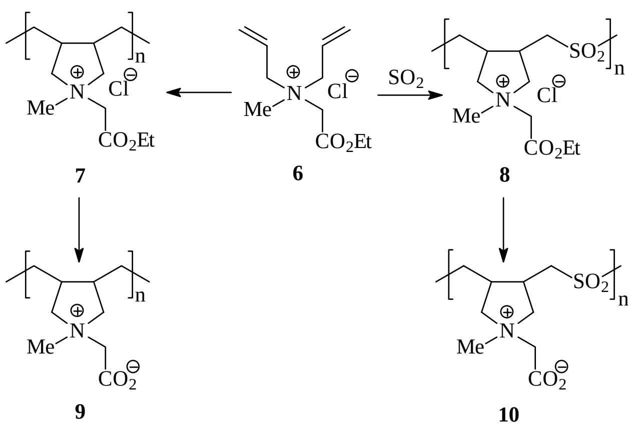
study provided an interesting opportunity to examine and compare the solution properties of a polyelectrolyte and its corresponding poly(ampholyte–electrolyte) having a similar degree of polymerization.

2. Experimental

2.1. Physical methods

All melting points 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). The ^1H 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 ($K = 0.005989$).

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 at a uniform rate of 10°C/min. The analyses were made over a temperature range of 20–1000°C, in an atmosphere of N_2 flowing at a rate of 100 ml/min.



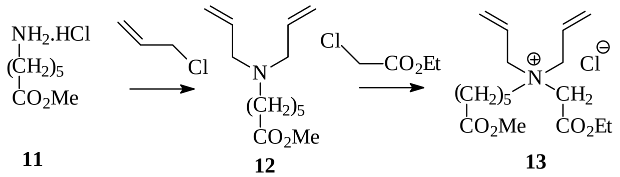
Scheme 2.

2.2. Materials

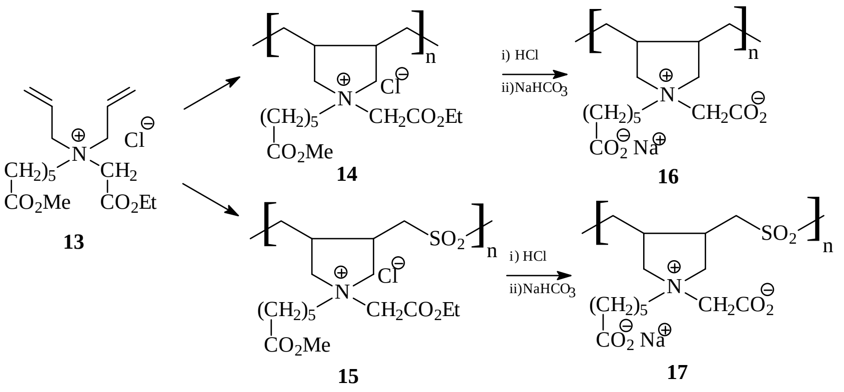
Ammonium persulfate (APS) from BDH Chemical Co. (Poole, UK), *t*-butylhydroperoxide (80% in ditertiarybutylperoxide) and 6-amino hexanoic acid from Fluka Chemie AG (Buchs, Switzerland) were used as received. Methyl 6-aminohexanoate hydrochloride **11** was prepared as described [19]. All the glasswares were cleaned using deionized water. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg).

2.3. Methyl 6-(N,N-diallylamino)hexanoate (**12**)

To a magnetically stirred solution of the hydrochloride salt (**11**) (138 g, 0.760 mol) in methanol (450 cm^3) under N_2 was added NaOH (30.4 g, 0.760 mol) in one portion followed by allyl chloride (58.2 g, 0.760 mol) dropwise over a period of 30 min during which the temperature was maintained at 50–55°C. After stirring an additional hour at 55°C, another 30.4 g of NaOH (0.760 mol) and allyl chloride (58.2 g, 0.760 mol) was added in a similar manner as described above and the mixture was stirred for a further 4 h at the same temperature. The resulting mixture was neutralized with K_2CO_3 (52.5 g, 0.38 mol) in water (75 cm^3) and the mixture was refluxed for 6 h. After removal of most of the methanol, enough water was added



Scheme 3.



Scheme 4.

to dissolve the inorganic salts. The aqueous layer was extracted with ether (3 × 200 cm^3). The organic layer was dried (Na_2SO_4), concentrated and chromatographed over silica using ether/hexane as eluent to obtain the diallyl compound **12** as a yellow liquid. The product was purified further by distillation at a reduced pressure through a 15 in Vigreux distilling column (b.p.$_{0.05\ \mathrm{mbar}}$ 83°C) to give **12** (102 g, 59.8%) as a colorless liquid. (Found: C, 69.1; H, 10.3; N, 6.21. $C_{13}H_{23}NO_2$ requires C, 69.29; H, 10.29; N, 6.22%); ν_{max} (neat) 3075, 2932, 2849, 2780, 1748, 1646, 1413, 1359, 1261, 1231, 1195, 1171, 1120, 999, and 921 cm^{-1}; δ_H ($CDCl_3$, TMS) 1.30 (2 H, quint, *J* 7.6 Hz), 1.47 (2 H, quint, *J* 7.6 Hz), 1.63 (2 H, quint, *J* 7.6 Hz), 2.31 (2 H, t, *J* 7.5 Hz), 2.41(2 H, app. t, *J* 7.5 Hz), 3.07 (4 H, d, J 6.6 Hz), 3.67 (3 H, s), 5.14(4 H, m), 5.84 (2 H, m); δ_C ($CDCl_3$) 24.89, 26.62, 27.02, 34.05, 51.48, 53.06, 56.86 (2C), 117.32 (2C), 135.79 (2C), 174.23. (middle C 77.02, TMS 0.00); *m/z*: 226 (M^+ + 1, 35.9%).

2.4. *N,N-diallyl-N-carboethoxymethyl-N-carbomethoxypentylammonium chloride* **13**

A solution of **12** (20.3 g, 0.090 mol) and ethyl chloroacetate (55.2 g, 0.45 mol) was stirred at 45°C for 72 h. The reaction mixture was cooled and agitated with ether (100 cm^3). The upper ether layer containing excess ethyl chloroacetate was decanted. The lower layer containing the quaternary salt **13** was agitated with ether (6 × 50 cm^3) after dissolving in dichloromethane each time. Finally, the thick viscous liquid was dried under vacuum at 50°C until constant weight (23.5 g, 75%). The NMR spectra revealed the presence of minor impurities which we were unable to remove and as such elemental analysis was not carried out. ν_{max} (neat) 3371, 3080, 2946, 2868, 1741, 1469, 1434, 1371, 1213, 1171, 1106, 1022, 948, and 855 cm^{-1}; δ_H ($CDCl_3$, TMS) 1.31 (3 H, t, *J* 7.1 Hz), 1.42 (2 H, quint, *J* 7.6 Hz), 1.68 (2 H, app. quint, *J* 7.6 Hz), 1.96 (2 H, app. quint, *J* 7.6 Hz), 2.35 (2 H, t, *J* 7.1 Hz), 3.67 (3 H, s and an overlapping 2 H, m), 4.25 (2 H, q, *J* 7.1 Hz), 4.50 (4 H, qd, *J* 7.4, 14.9 Hz), 4.67 (2 H, s), 5.77 (4 H, m), 6.12 (2 H, m); δ_C ($CDCl_3$) 13.93, 22.46, 24.13, 25.84, 33.55, 51.54, 56.81, 60.34, 62.72, 63.16 (2C), 124.60(2C), 129.64 (2C), 164.92, and 173.62 (middle C 77.53; TMS: 0.00).

2.5. *Attempted polymerization of the monomer* **13**, *using APS and hydrogen peroxide*

APS (15 mg) was added under N_2 to a solution containing

Table 1
Effect of concentration of monomer and initiator [tertiarybutylhydroperoxide (TBHP)] and comparison of intrinsic viscosity of polyelectrolyte (PE) **14**, and polyampholyte–electrolyte (PAE) **16**

Entry no.	Monomer concentration (%w/w)[a]	TBHP (mg g^{-1} monomer)[a]	Yield (%)	Intrinsic viscosity[b] (dl g^{-1}) of PE	Yield of hydrolysis reaction (%)	Intrinsic viscosity (dl g^{-1}) of PAE[c]
1	65	10	59	0.165	–	–
2	70	10	60	0.136	–	–
3	70	15	63	0.075	–	–
4	70	20	75	0.056	95	0.114
5	83	10	60	0.146	99	0.209
6	90	10	40	0.141	–	–

[a] Polymerization reactions were carried out in aqueous medium at 50°C for 18 h followed by 75°C for 48 h.

[b] Viscosity of 1–0.125% polymer solution on 0.1 N NaCl at 30°C was measured in Ubbelohde Viscometer (*K* = 0.005989).

[c] PE was converted to PAE by acidic hydrolysis.

Table 2
Solubility of homopolymer **14** and **16** and copolymer **15** and **17** (1% 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)

	ϵ	Polymer **14**	Polymer **16**	Polymer **15**	Polymer **17**
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	+	+	+	−

the monomer **13** (1.5 g) in dimethyl sulfoxide (1.65 g) in a 10 cm^3 round bottomed flask and the solution in the closed flask was stirred at 40°C for 120 h. Viscosity of the mixture remained unchanged and there seemed to be no polymerization. The ^{1}H NMR spectrum confirmed that polymerization had not occurred. This reaction was repeated in water (monomer concentration 75% w/w) using 8 mg ammonium persulfate/g of monomer at 90°C (1 h), still without any success.

The above reaction was also tried using 70% monomer

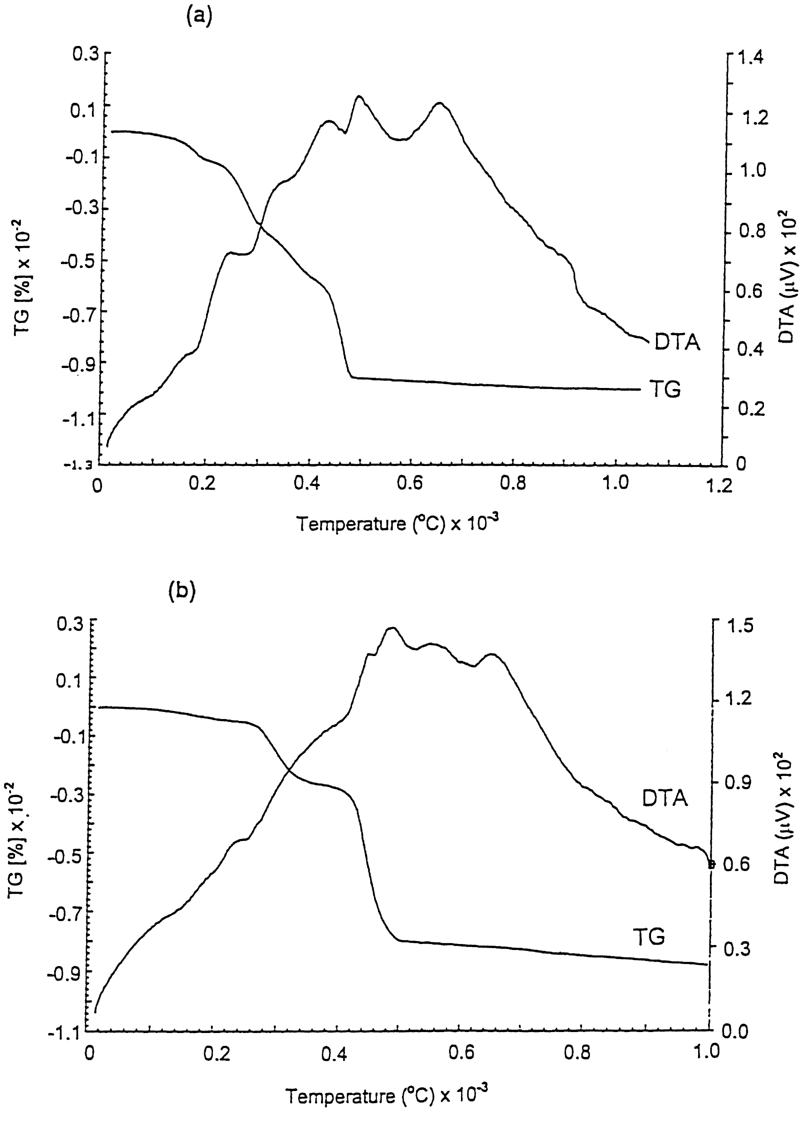


Fig. 1. Thermogravimetric analyses of: (a) polyelectrolyte **14**; and (b) poly(ampholyte–electrolyte) **16**.

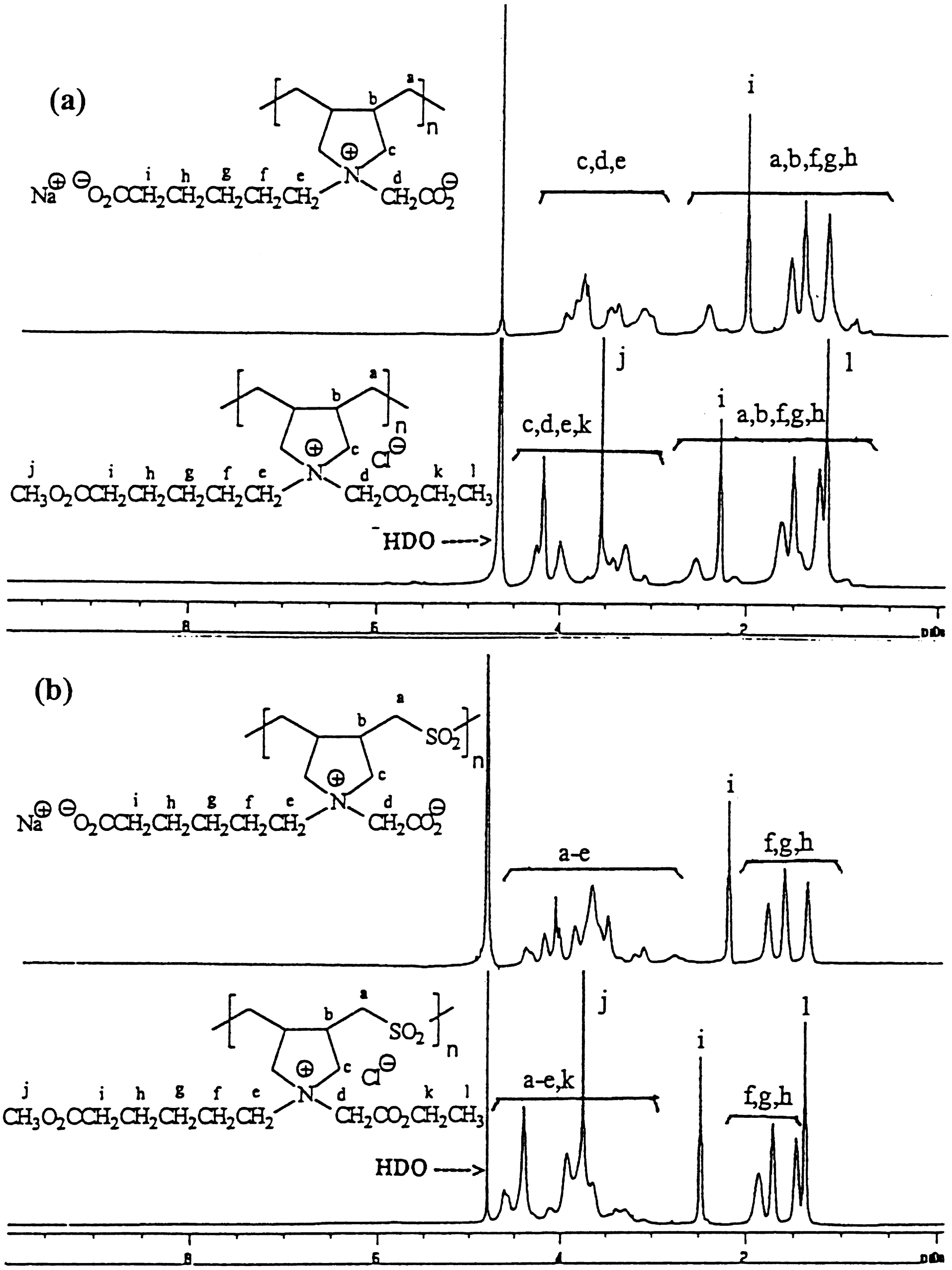


Fig. 2. ^1H NMR spectrum of: (a) polyelectrolyte **14** and poly(ampholyte–electrolyte) **16** in D_2O; and (b) polyelectrolyte **15** and poly(ampholyte–electrolyte) **17** in D_2O.

solution in water using hydrogen peroxide (6 drops, 24 mg/g of monomer) as initiator at 75°C for 72 h. However no polymerization product was obtained.

2.6. General procedure for the polymerization of **13** using tert-butylhydroperoxide

A solution of the monomer **13** 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 18 h and then for a further 48 h at 75°C. The reaction mixture became noticeably viscous after the first 6 h at 50°C and the magnetic stirrer stopped moving after 2 h at 75°C. 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 cream-colored polymer **14** was stored in a desiccator m.p. (closed capillary) 134–148°C with color darkening above 214°C. (Found: C, 58.2; H, 8.85; N, 4.20. $C_{17}H_{30}NO_4Cl$ requires C, 58.69; H, 8.69; N, 4.03%); ν_{max}.

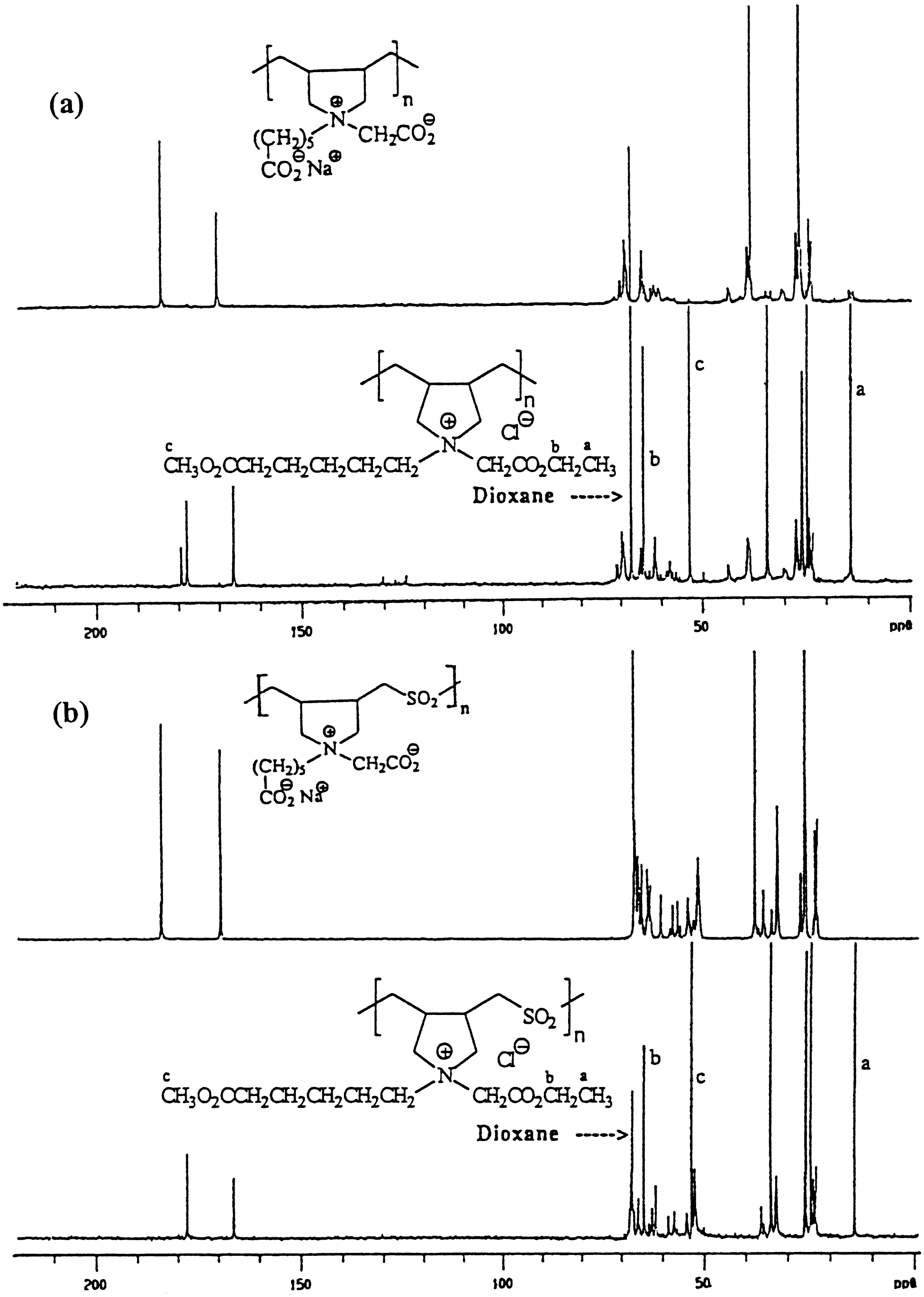


Fig. 3. ^{13}C NMR spectrum of: (a) polyelectrolyte **14** and poly(ampholyte–electrolyte) **16** in D_2O; and (b) polyelectrolyte **15** and poly(ampholyte–electrolyte) **17** in D_2O.

(KBr) 3431, 2942, 2859, 1744, 1630, 1448, 1384, 1303, 1218, 1096, 1042, and 1019 cm^{-1}.

*2.7. General procedure for the copolymerization of the monomer **13** with SO_2 using APS initiator*

In a typical experiment, SO_2 (1.92 g, 0.030 mol) was absorbed in a solution of the monomer **13** (10.4 g, 0.030 mol) in DMSO (5.8 g). The required amount of the initiator APS (as listed in Table 2) was then added under N_2 and the closed flask was magnetically stirred at 50°C for 20 h. The reaction mixture which remained transparent throughout the polymerization process, was then dialyzed against deionized water (8 h) to remove the unreacted monomer (checked by $AgNO_3$ test), SO_2, and the solvent DMSO. The copolymer solution was freeze-dried and then dried to a constant weight at 50°C under vacuum. The hygroscopic white polymer **15** was stored in a desiccator.

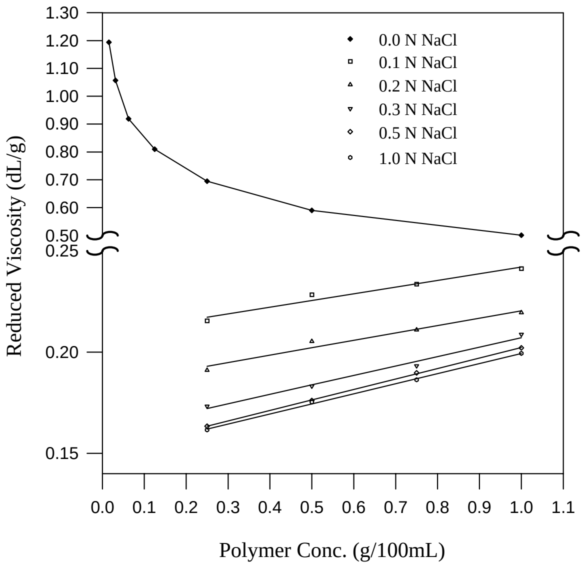


Fig. 4. Effect of added salt on the viscosity behavior of the poly(ampholyte–electrolyte) **16** in water at 30°C using an Ubbelohde Viscometer ($K = 0.005989$).

m.p. (closed capillary) 180–184°C (decomposes turning yellow and chars at 237°C). (Found: C, 49.2; H, 7.23; N, 3.32; S, 7.5. $C_{17}H_{30}NO_6SCl$ requires C, 49.56; H, 7.34; N, 3.40; S, 7.78%); ν_{max} (KBr) 3439, 2942, 1738, 1442, 1312, 1220, 1169, 1126, and 1018 cm^{-1}.

2.8. Acidic hydrolysis of the homopolymer 14

A solution of the homopolymer **14** (10.0 g) in 6 M HCl (200 cm^3) was stirred in a closed flask at 45°C for 120 h (or until the hydrolysis of the two ester groups was complete as indicated by the absence of the methoxy and ethoxy 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 dialysis continued to remove excess $NaHCO_3$ and NaCl (monitored by $AgNO_3$ test). The resulting solution was freeze dried and subsequently dried to a constant weight at 70°C. The cream-colored zwitterionic polymer **16** was stored in a dessicator. m.p. (closed capillary) 182–185°C (does not char up to 400°C). Yield 8.29 g (99%). (Found: C, 57.2; H, 7.85; N, 4.6. $C_{14}H_{22}NO_4Na$ requires C, 57.72; H, 7.61; N, 4.81); ν_{max} (neat) 3429, 2942, 1630, 1570, 1404, 1328, and 723 cm^{-1}.

2.9. Acidic hydrolysis of the copolymer 15

A solution of copolymer **15** (10 g) in 6 M HCl (200 cm^3) was stirred in a closed flask at 45°C for 144 h (or until the hydrolysis was complete as indicated by ^{1}H NMR spectrum). After about 2 h reaction time, the hydrolyzed copolymer started precipitating from the solution. Similar work up as described in the isolation of the polymer **16** afforded the white copolymer **17** (8.45 g, 98%). m.p. (closed capillary): 227–231°C (decomposes) and chars at 263°C. (Found: C, 46.8; H, 6.6; N, 3.74; S, 8.7. $C_{14}H_{22}NO_6SNa$ requires C, 47.31, H: 6.24, N: 3.94, S, 9.02%); ν_{max}. (neat): 3434, 2946, 1636, 1564, 1406, 1306, 1128, 910, 728, and 510 cm^{-1}.

2.10. Solubility measurements

Solubility of the homopolymers **14** and **16** and copolymers **15** and **17** 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

Methyl 6-aminohexanoate hydrochloride **11**, on reacting with two equivalents of allyl chloride in the presence of NaOH, afforded methyl 6-(*N*,*N*-diallylamino)hexanoate **12**, which on treatment with ethyl chloroacetate gave the quaternary monomer **13** as a thick liquid (Scheme 3). The monomer is found to be soluble in methanol, acetone and water.

Table 3
Effect of concentration of initiator [ammoniumpersulphate (APS)] and temperature on M/SO_2 copolymerization and comparison of intrinsic viscosity of polyelectrolyte (PE) **15**, with polyampholyte–electrolyte (PAE) **17**

Entry no.	APS[a] (mg g^{-1} monomer)	Temp. (°C)	Yield (%)	Intrinsic viscosity[b] (dl g^{-1}) of PE	Yield of hydrolysis reaction (%)	Intrinsic viscosity (dl g^{-1}) of PAE[c]
1	5.0	45	55	0.161	93	0.470
2	10	45	61	0.169	87	0.405
3	10	50	78	0.169	98	0.445
4	15	50	81	0.183	–	–
5	20	50	80	0.195	84	0.580
6	25	50	83	0.200	95	0.592

[a] Monomer (30 mmol), SO_2 (30 mmol), was polymerized in DMSO (5.8 g) for 20 h.
[b] Viscosity of 1–0.125% polymer solution on 0.1 N NaCl at 30°C was measured in Ubbelohde Viscometer ($K = 0.005989$).
[c] PE was converted to PAE by acidic hydrolysis.

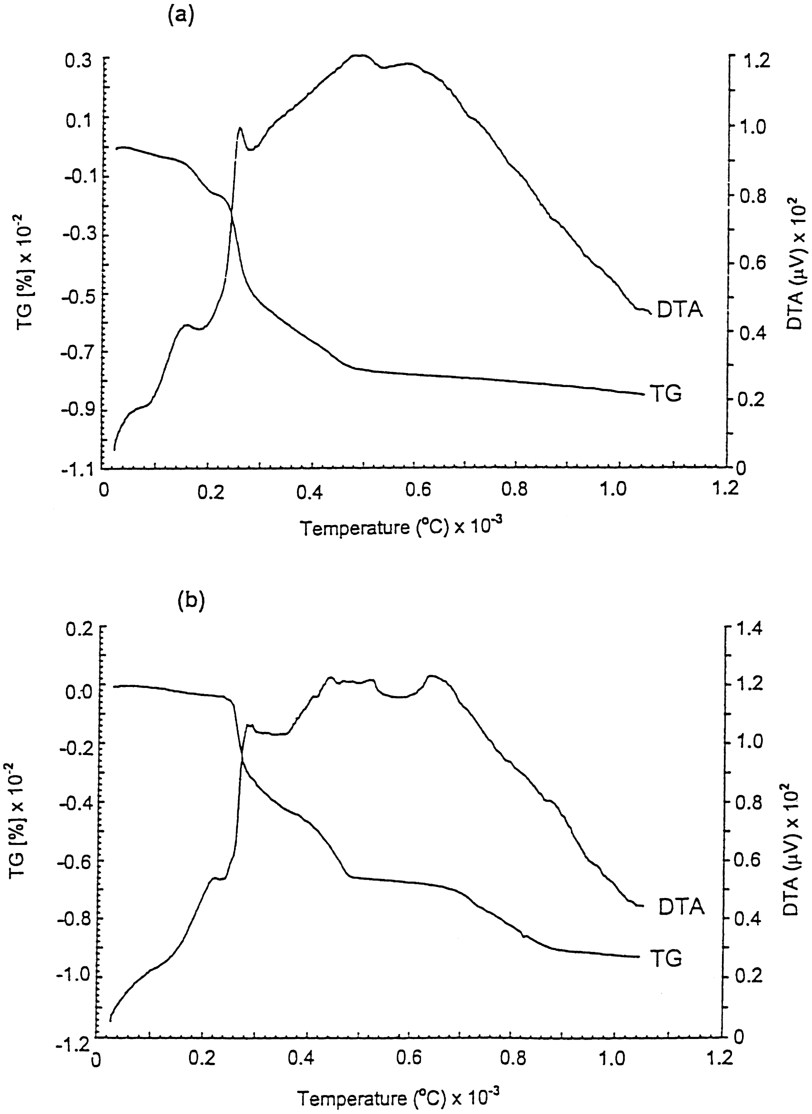


Fig. 5. Thermogravimetric analyses of: (a) polyelectrolyte **15**; and (b) poly(ampholyte–electrolyte) **17** with a scanning rate of 10°C per minute.

The monomer **13** was subjected to polymerization conditions using several initiators. While the initiators ammonium persulphate and hydrogen peroxide were found to be ineffective, 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 Table 1, the highest intrinsic viscosity was obtained for the polymerization under entry 1, with a monomer concentration of 65% w/w and 10 mg initiator/g of the monomer.

Polymer **14** (entries 4 and 5, Table 1) was hydrolyzed under acidic conditions (6 M HCl, 45°C), to give the hydrolyzed polymer **16** in excellent yield (>95%). The hydrolysis was found to be almost complete (vide infra). The differential thermal analysis and thermal gravimetric analysis of the polymers **14** and **16** are shown in Fig. 1. Absorption at 1744 cm^{-1} in the IR spectrum of **14** reveals the presence of ester group. The absorption around 1630 cm^{-1} indicates the presence of CO_2^- functionality in **16**. ^{1}H and ^{13}C NMR spectra of the polymers (**14** and **16**) are displayed in Figs. 2(a) and 3(a), respectively. It is evident after comparing the proton spectra of the polymers (Fig. 2(a)) that the CH_3–OC and the CH_3CH_2–OC protons that appeared at δ 3.70 ppm and δ 1.31 ppm, respectively, for the polyelectrolyte **14**, are not present in the spectrum of the poly(ampholyte–electrolyte) **16**, thus indicating the complete removal of the methyl and ethyl groups via hydrolysis. Similar observations are made from the ^{13}C NMR spectrum; the carbons of the ethyl and methyl group (Fig. 3(a)) were not present in the spectrum of the polymer **16**.

The pH of 1% solution of the polyelectrolyte **14** and poly(ampholyte–electrolyte) **16** was found to be 3.30 and 7.50, respectively. Both the polymers were found to be soluble in a range of solvents (Table 2). While the overwhelming majority of reported polyampholytes [7,15,17]

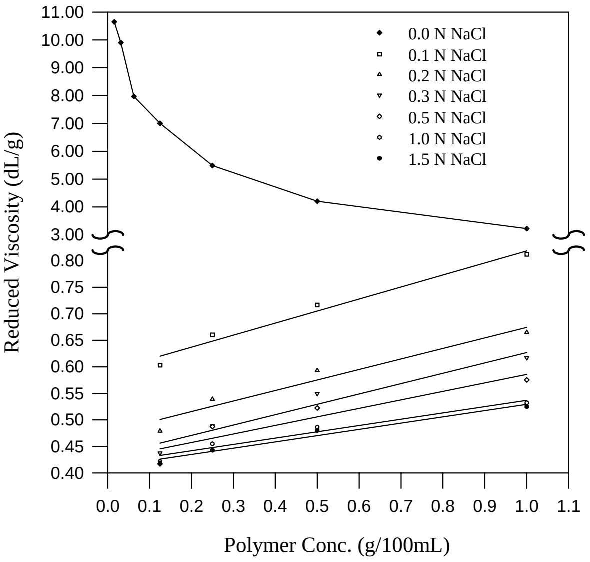


Fig. 6. Effect of added salt on the viscosity behavior of the poly(ampholyte–electrolyte) **17** in water at 30°C using an Ubbelohde Viscometer ($K = 0.005989$).

are known to be insoluble in water, the poly(ampholyte–electrolyte) **16** was found to be soluble in water as well as in several protic solvents. Viscosity data for the poly(ampholyte–electrolyte) **16** (entry 5, Table 1) are shown in Fig. 4. In the absence of added salt (NaCl), the viscosity plot for **14** as well as **16** is typical for an electrolyte, i.e. concave upwards. The addition of strong electrolytes, like sodium chloride, suppresses the ionization of the polyelectrolyte and the viscosity behavior becomes normal. By increasing the ionic strength, the viscosity decreases due to the screening of the charges on the macromolecular chain, thus leading to a decreased macromolecular expansion.

Next we focussed our attention on the copolymerization of the monomer **13** with SO_2. The results of the copolymerizations are shown in Table 3. The polyelectrolyte **15** (entries 1–3, 5, 6, Table 3) was hydrolyzed under acidic conditions to give the polyampholyte–electrolyte **17** in excellent yields (84–98%). The elemental analysis of the hygroscopic polymers **15** and **17** indicates the incorporation of monomer and SO_2 in an approximately 1:1 ratio, hence suggesting the formation of alternating copolymer.

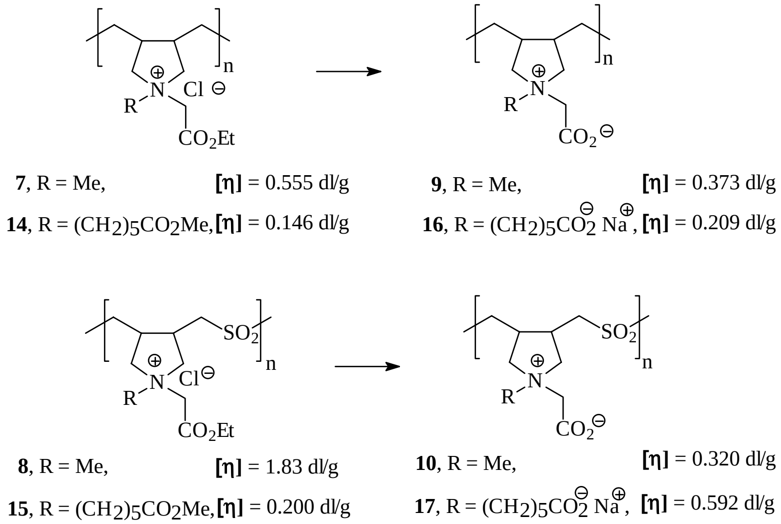
The thermogravimetric analyses of the polymers are shown in Fig. 5. The IR spectrum of the copolymer **15** indicates the presence of the SO_2 unit into the polymeric backbone. The two strong bands at 1312 and 1126 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit. ^1H and ^{13}C NMR spectra of the polymers **15** and **17** are displayed in Figs. 2(b) and 3(b), respectively. It is evident after comparing the proton spectra of the polymers (Fig. 2(b)) that the CH_3–OC and the CH_3CH_2–OC protons, which appeared at δ 3.75 ppm and δ 1.38 ppm, respectively, for the polyelectrolyte **15**, are not present in the spectrum of the poly(ampholyte–electrolyte) **17**. This indicates the removal of the ester groups by hydrolysis. A similar observation is made from the ^{13}C NMR spectra; the carbons of the ethyl and the methyl groups (Fig. 3(b)) are absent from the spectrum of **17**, indicating complete hydrolysis.

The pH of a 1% aqueous solution of the polyelectrolyte **15** and poly(ampholyte–electrolyte) **17** were found to be 3.11 and 9.79, respectively. While the polyelectrolyte **15** was found to be soluble in several protic solvents (as listed in Table 2), poly(ampholyte–electrolyte) **17** was insoluble in acetic acid. Viscosity data for poly(ampholyte–electrolyte) **17** (entry 6, Table 3) is presented in Fig. 6. In the absence of added salt (NaCl) the plot for **15** as well as **17** is typical for polyelectrolyte, i.e. concave upwards. In the presence of added salt (NaCl) the viscosity behavior becomes normal and an increasing salt concentration decreases the viscosity of the poly(ampholyte–electrolyte). The intrinsic viscosity of the poly(ampholyte–electrolyte) **17** in aqueous solutions containing various added salts were studied and is given in Table 4. It is observed that for common K^+ cation, the intrinsic viscosity does not change much from Cl^- to Br^- to I^-. This is contrary to what is expected of a polymer containing zwitterions as the sole functionality [8,9]. The divalent cation Ca^{2+}, which is known to precipitate anionic polyelectrolytes from aqueous solution even at low concentrations, did not precipitate the poly(ampholyte–electrolyte) **17**.

Both the poly(ampholyte–electrolyte)s, **16** and **17**, behave more like a polyelectrolyte than a polyampholyte as far as viscosity is concerned. It is interesting that while the intrinsic viscosity in 0.1 M NaCl of the polyelectrolytes **7** and **8** is considerably higher than their corresponding polyampholytes **9** and **10**, the reverse is the case with the polyelectrolytes **14** and **15**, which on hydrolysis gave the poly(ampholyte–electrolytes) **16** and **17** with significant increase in their viscosity (Scheme 5). Repulsion between the positive charges in the cationic backbone in polyelectrolytes **7** and **8** increases the hydrodynamic volume, hence viscosity. In polyampholytes **9** and **10**, however, the anionic moiety because of its proximity neutralizes and screens the positive charges in the backbone, thus reduces the hydrodynamic volume and viscosity. The poly(ampholyte–electrolytes) **16** and **17**, as the name implies, possess dual type of structural character and it is the electrolytic portion of the structure that dictates the solubility and viscosity behavior of the polymers. Even though the

Table 4
Effect of cation on the viscosity behavior of polyampholyte–electrolyte **17**

Solvent (0.1 M)	Intrinsic viscosity (dl g^{-1})
KCl	0.577
KBr	0.576
KI	0.512
NaCl	0.592
$CaCl_2$	0.234



7, R = Me, [η] = 0.555 dl/g

14, R = $(CH_2)_5CO_2Me$, [η] = 0.146 dl/g

9, R = Me, [η] = 0.373 dl/g

16, R = $(CH_2)_5CO_2^{\ominus}\,Na^{\oplus}$, [η] = 0.209 dl/g

8, R = Me, [η] = 1.83 dl/g

15, R = $(CH_2)_5CO_2Me$, [η] = 0.200 dl/g

10, R = Me, [η] = 0.320 dl/g

17, R = $(CH_2)_5CO_2^{\ominus}\,Na^{\oplus}$, [η] = 0.592 dl/g

Scheme 5.

zwitterionic portion diminishes the hydrodynamic volume, the more dominant repulsion between the anionic pendants in the poly(ampholyte–electrolytes) **16** and **17** increases the hydrodynamic volume and viscosity of the polymer.

4. Conclusion

The monomer **13** is prepared from inexpensive starting materials. Efforts are underway to improve the viscometric behavior of the polymers by using other initiators. The study has demonstrated a simple way to convert polyelectrolytes to poly(ampholyte–electrolyte)s and thus provides an opportunity for the direct comparison of the solution properties of a polyelectrolyte and poly(ampholyte–electrolyte) having the same degree of polymerization.

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