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Synthesis of a terpolymer and a tetrapolymer using monomers of diallylamine salts and SO$_2$ and their application as antiscalants

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Abstract An aqueous solution of diallylammonium salts $(CH_2 = CHCH_2)_2NH^+(CH_2)_3A^-$ having A^- as: CO_2^- (**I**), $PO_3H_2\,Cl^-$ (**II**) and SO_3^- (**III**) in 1:1:1 mol ratio underwent ammonium persulfate-initiated ter cyclopolymerization to yield pH-responsive zwitterionic polymer **IV** with random placements of the monomers in the same ratio. During dialysis, $PO_3H_2Cl^-$ of the incorporated monomer units of **II** upon depletion of HCl became PO_3H^-. Likewise, azobisisobutyronitrile-initiated cyclopolymerization of **I**, **II**, **III**, and SO$_2$ in a mole ratio of 1:1:1:3 provided pH-responsive tetrapolymer **V** in over 90 % yield with random and alternative placements of **I–III** and SO$_2$ units, respectively, in the same ratio as the feed. Polyzwitterions (PZs) **IV** and **V** were insoluble in salt-free water but soluble in the presence of salts. The critical salt concentrations required to promote water solubility of PZ **IV** were determined to be 0.356 M NaCl, 0.237 M NaBr and 0.128 M NaI, whereas for PZ **V** the corresponding values were found to be 2.25, 1.26 and 0.862 M, respectively. PZs **IV** and **V** were converted into anionic polyelectrolytes **VI** and **VII** upon basification with NaOH. The viscosity and antiscalant behaviors of **VI** and **VII** were examined. The polymers demonstrated remarkable scale inhibition efficacies; at a dose of 10 ppm, both **IV** (+NaOH) and **V** (+NaOH) delayed the precipitation of CaSO$_4$ from its supersaturated solution up to 920 and over 4000 min, respectively. For a small concentration of 5 ppm of polymer **V**, a scale inhibition of 100 % over 100 min verified it to be a potential effective antiscalant additive in reverse osmosis plants.
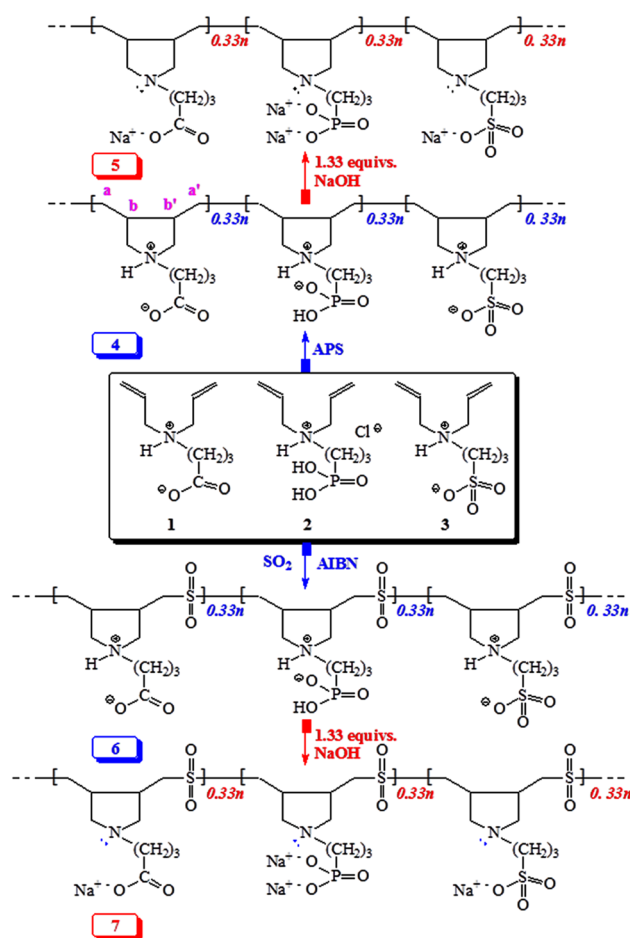
Introduction

Scaling is one of the major problems in membrane-based desalination plants which incorporate reverse osmosis (RO) protocol in desalting seawater and aquifer brackish waters [1–3]. The deposition of scale on the membranes leads to the reduction of their efficacy of product recovery and salt rejection. Antiscalants are used to mitigate the scaling on the membrane surface, which is owing to the precipitation of very low water-soluble salts such as CaCO$_3$, Mg(OH)$_2$, CaSO$_4$, SrSO$_4$, etc. [4–6]. Several research groups have attempted to understand the mechanism of scale inhibition which is a matter of paramount importance in desalination plants [7–9]. The interactions among the pendant negatively charged functional motifs on the antiscalants such as polyphosphates, polysulfonates, polyacrylates and Ca^{2+} ions impart changes in precipitate morphologies, thereby leading to scale inhibition [10].

It is one of our objectives to synthesize terpolymer **5** and tetrapolymer **7** using Butler's cyclopolymerization protocol [11–13]. The novelty of the work lies with the assembly of three different functional motifs of amino-phosphonate, -carboxylate and –sulfonate in a single molecular backbone. It would give us an opportunity to investigate the efficacies of the newly synthesized polymers as novel antiscalants to exploit the varying chelating abilities of a multitude of anionic centers in scavenging metal cations (Scheme 1). Note that the three monomer units incorporated in **5** and **7** have seven chelating centers (of three N and four O$^-$) with different basicity constants. In addition, the latter contains

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Scheme 1 Synthesis of pH-responsive cyclopolymers

weight cutoff (MWCO) of 6000–8000 Da was purchased from Spectrum Laboratories Inc., (Rancho Dominguez, CA, USA). 2,2′-Azobisisobutyronitrile (AIBN) purchased from Fluka AG (Buchs, Switzerland) was crystallized (C_2H_5OH–$CHCl_3$). The monomers **1** [19], **2** [15] and **3** [14] were synthesized using known procedures.

Physical methods for structural characterization

An elemental analysis was carried out in a Perkin Elmer Series II Model 2400. The IR spectra were recorded by a Fourier transform infrared (FTIR) spectrometer (Perkin Elmer 16F PC). The NMR spectra were recorded on a 500-MHz Jeol LA spectrometer using the residual proton resonance of D_2O at δ 4.65 ppm, and the dioxane ^{13}C peak at δ 67.4 ppm as internal and external standards, respectively. ^{31}P was referenced with H_3PO_4 (85 %) in dimethyl sulfoxide (DMSO). The zeta potentials of the zwitterionic polymers were measured on a Zetatrac zeta potential charge analyzer (Microtrac Inc., USA) using ethanol as a solvent. Thermogravimetric analysis (TGA) was carried out in an SDT analyzer (Q600: TA Instruments, New Castle, DE, USA) under N_2 atmosphere. Polymer/CO_2-free water solutions were used to measure viscosities under N_2 using an Ubbelohde viscometer having a viscometer constant of 0.005573 mm^2/s^2. The conductivity measurements were carried out using an Orion Versa Star benchtop conductivity meter (Thermoscientific, Beverly, MA, USA).

Polymer synthesis

Terpolymerization of 1, 2 and 3

As described in Table 1, to a solution of **1** (1.83 g, 10 mmol), **2** (2.55 g, 10 mmol), and **3** (2.19 g, 10 mmol) in 1 M NaCl (3.0 mL) at 90 °C in a RB-flask fitted with a condenser, APS (0.50 g) was added and stirred under N_2 for 10 min. The exothermic reaction started within a minute and after the time elapsed, the crude mixture was cooled to room temperature, transferred to a dialysis bag with the help of 2 M NaCl solution (since the terpolymer was insoluble in salt-free water) and dialyzed against deionized water with frequent exchange of fresh water. During dialysis as a result of depletion of NaCl, the polymer started to come out of the solution as a jelly-type material. After the complete removal of NaCl (as confirmed by AgNO$_3$ test), the entire heterogeneous mixture was freeze-dried to obtain terpolymer **4** as a white powder (5.0 g, 80.4 %). δ_P (202 MHz, D_2O): 21.60 (95 %); 23.89 (5 %); $\nu_{max.}$ (KBr): 3445 (v br), 2962, 1707, 1653, 1576, 1462, 1401, 1261, 1210, 1153, 1117, 1037, 900, 797, 731, 704, and 605 cm^{-1}; (Found: C, 52.5; H, 8.6; N, 6.5; S, 4.9 %. Repeating unit of **1**, **2**, **3** in a 1:1:1 ratio requires C, 54.09; H, 8.43; N, 6.76; S, 5.16 %).

weak ligand center in SO$_2$ [14–16]. While the pK_as of the conjugate acid functionalities of –CO$_2$H [17] and diprotic –PO$_3$H$_2$ [18] are reported to be 4, 2.4 and 6, respectively, –SO$_3$H is known to have a pK_a value −2.1. The pK_a of the conjugate acid of the protonated amine is known to vary in the range of 10.5–10.8 [14–16].

Sulfonates, phosphonates and carboxylates, as discussed above, on their own act as antiscalants. It is anticipated that the combined efforts of these functionalities working in synergy may effectively mitigate the nuisance caused by scaling in the RO process. In addition, the polymers having so many functional motifs are expected to have interesting solutions properties.

Experimental

Materials

Ammonium persulfate (APS) was from Sigma-Aldrich. For dialysis, a membrane (Spectra/Por) with a molecular

Table 1 Cyclopolymerization[a] of monomers **1**, **2**, **3** and SO_2

Entry no.	Monomer (mmol)				1 M NaCl (mL)	DMSO (g)	Temp (°C)	Time	Initiator (mg)	Yield[a] (%)	$[\eta]$[b] (dL g^{-1})
	1	**2**	**3**	SO_2							
1	10	10	10	–	3	–	90	10 min	APS (500)	**4**:80	0.244
2	10	10	10	–	3	–	90	10 min	APS (190)	**4**:68	0.253
3	10	10	10	30	–	8.4	60	48 h	AIBN (150)	**6**:92	0.223

[a] Polymer number is written in bold followed by its %yield

[b] Viscosity of 1-0.125 % polymer solutions of **5** (i.e., **4** + 1.33 equivs. NaOH) and **7** (i.e., **6** + 1.33 equivs. NaOH) in 0.1 M NaCl was measured with Ubbelohde viscometer (having viscometer constant of 0.005573 mm^2/s^2) at 30 °C using CO_2-free water under N_2 to avoid CO_2 absorption that may affect the viscosity data

Tetrapolymerization of *1*, *2*, *3* and SO_2

As described in Table 1, to a solution of **1** (1.83 g, 10 mmol), **2** (2.55 g, 10 mmol), and **3** (2.19 g, 10 mmol) in DMSO (8.4 g), SO_2 (1.92 g, 30 mmol) was absorbed. After adding AIBN (150 mg), the mixture was stirred under N_2 at 60 °C for 48 h. The reaction mixture became immobile within an hour; at the end the reaction mixture was soaked in water, filtered and washed with acetone. The white polymer **6** was then grounded with a mortar and pestle and soaked in methanol, filtered, and dried under vacuum at 60 °C to a constant weight (7.5 g, 92 %). (Found: C, 41.0; H, 6.6; N, 5.0; S, 15.3 %. Repeating unit of **1**, **2**, **3** and SO_2 in a 1:1:1:3 ratio requires C, 41.32; H, 6.44; N, 5.16; S, 15.76 %); ν_{max}. (KBr): 3470 (v br), 2973, 1717, 1647, 1575, 1465, 1418, 1309, 1213, 1127, 1037, 950, 906, 782, and 732 cm^{-1}; δ_p (202 MHz, D_2O): 22.87 (95 %) and 24.66 (5 %).

Solubility measurements

The critical (minimum) salt concentration (CSC) required to promote solubility was determined by titrating a 1 % w/w aqueous solution of **4** and **6** containing salts at a higher concentration than their CSC values at 23 °C. The average of the triplicate results of the CSCs was determined with approximate accuracies of ±1–2 %. The results are given in Table 2.

Evaluation of antiscalant behavior

Evaluation of antiscalant behavior was carried out at 40 ± 1 °C as described [16] using supersaturated solution of 2598 mg L^{-1} of Ca^{2+} and 6300 mg L^{-1} of SO_4^{2-} in the absence and presence of **4** (entry 1, Table 1) and **6** (entry 3, Table 1). The time, when a rapid increase in precipitation of $CaSO_4$, as indicated by a rapid decrease in conductivity, was assigned as the induction time (Table 3). The aqueous stock solutions of **4** and **6** were prepared by treating them with minimum quantity of $NaHCO_3$.

Table 2 Critical salt concentration for aqueous solutions of terpolymer **4** and tetrapolymer **6** at 23 °C

Salt	CSC (M)	
	4	**6**
NaCl	0.356	2.25
NaBr	0.237	1.26
NaI	0.128	0.862

Results and discussion

Synthesis and characterization of the ionic polymers

The results of ter and tetrapolymerizations are summarized in Table 1 (Scheme 1). To our satisfaction, both polymers **4** and **6** are obtained in excellent yields. Monomers **1**, **2** and **3** underwent APS-initiated terpolymerization to give terpolymer **4** (entries 1 and 2, Table 1), while in the presence of the fourth monomer SO_2, AIBN-initiated tetrapolymerization afforded tetrapolymer **6** (entry 3, Table 1). Note that the terpolymerization was carried out in 1 M NaCl instead of water used for usual cyclopolymerization process. The use of NaCl not only prevented precipitation of the polymer during the reaction, it also expanded the backbone, thereby exposing the propagating terminal for further propagation; in its absence, the chain terminal would otherwise be cocooned inside the globular polyzwitterions [14]. Also, note that during dialysis, the cationic monomer **2** became a zwitterionic unit in the polymers upon depletion of HCl. The zeta potentials of 3.26 and 6.34 mV for the terpolymer **4** and tetrapolymer **6**, respectively, confirmed the overall positive charge density on the polymer surface. The polymerization of monomers **1**, **2** and **3** was initially expected to generate terpolymer **4**.1/3HCl which on depletion of HCl during dialysis would equilibrate to **4** (Scheme 2). Similarly, in case of tetrapolymerization, soaking in water would lead to the formation of **6** (Scheme 1). Note that $-PO_3H_2$ with pK_1 and pK_2 values of ~2.0 and 6.5 is a stronger acid than $-CO_2H$ with a pK_a value of ~4.23 and as such, the

Table 3 Percent inhibition against precipitation at various times in the presence of various concentrations of the synthesized polymers in 3 CB supersaturated CaSO$_4$ solution at 40 °C

Sample	Conc (ppm)	Percent inhibition at times (min)							Induction time (min)
		30	100	200	500	800	1000	4000	
4	5	81	3	–	–	–	–	–	30
	10	99	99	99	99	95	3	–	920
	15	100	100	100	99	97	93		NO[a]
6	5	100	100	6	–	–	–	–	160
	10	100	100	99	99	99	98	96	NO[a]

[a] Not observed

initial product was assigned the structure **4**. 1/2HCl having the functional motifs of –CO$_2$H and –PO$_3$H$^-$. While the phosphonate and sulfonate functionalities would definitely remain as part of the zwitterionic forms, any incomplete removal of HCl from **4**.1/3HCl would generate a slightly excess positive charge on the polymer surface. The intrinsic viscosity [η] values in 0.1 M NaCl of anionic polyelectrolytes (APE) **5** and **7**, generated by treating water-insoluble polymers **4** and **6** with 1.33 equivalents of NaOH, are given in Table 1. The [η]s of ter and tetrapolymers are both similar and relatively high, as chain transfers involving abstraction of underlined allylic (C=CC$\underline{H}_2$) protons are known to give polymers having low molar masses [20].

All three monomeric units in polymers **4** and **6** are zwitterionic, and as such the polyzwitterions (PZs) are found to be insoluble in salt-free water owing to the formation of three-dimensional network by the physical interactions of intra-group, intra- and inter-chain polymers [12]. However, the PZs are found to be soluble in the presence of added salts, which can disrupt the zwitterionic interactions by neutralizing the dipolar charges, thereby imparting water solubility as a result of expansion of the polymer backbone and globule-to-coil transition [21, 22]. The CSCs required to promote water solubility of PZ **4** were determined to be 0.356 M NaCl, 0.237 M NaBr and 0.128 M NaI, whereas for PZ **6** the corresponding values were found to be 2.25, 1.26 and 0.862 M, respectively (Table 2). The iodide ions being the softest and the most polarisable can neutralize the positive charges on the zwitterionic dipoles most effectively, thereby requiring the least amount of NaI. Higher CSC values for PZ **6** can be attributed to the presence of SO$_2$ in its backbone; the positive charges on its dipoles are more dispersed and less hydrated owing to the electron-withdrawing SO$_2$ units, thereby evoking stronger zwitterionic attractions with the negative centres in the CO$_2^-$, PO$_3$H$^-$ and SO$_3^-$ motifs. Needless to say, the anionic counterparts **5** and **7** were found to be water-soluble as expected of any polyelectrolytes.

Attempts to determine the molar masses of the polymers by GPC were unsuccessful, presumably as a result of strong adsorption to the column materials as observed with some polymers containing amine and carboxy motifs [23].
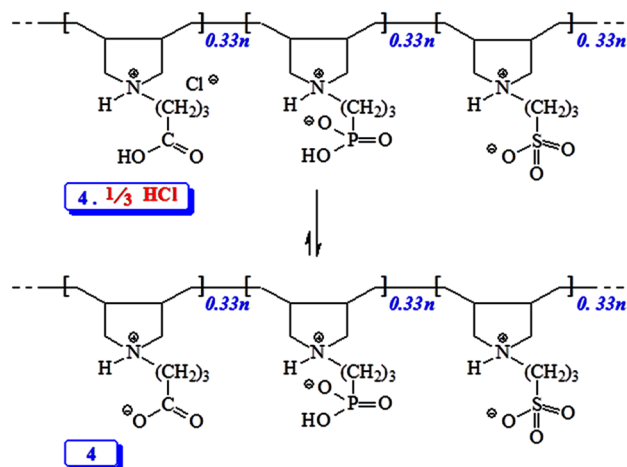
Scheme 2 Dissociation of carboxylic acid groups in terpolymer **4**.1/3HCl
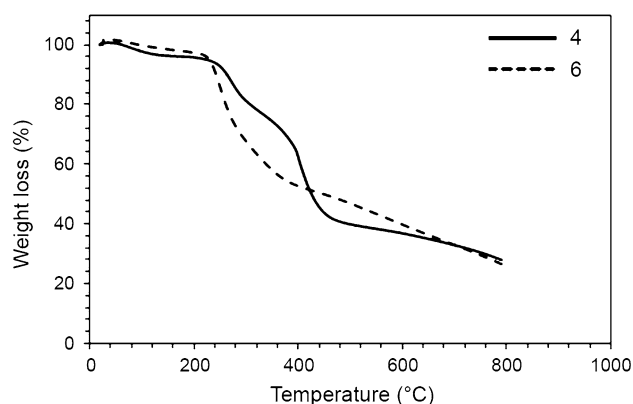
Fig. 1 TGA curve of ter and tetrapolymers **4** and **6**

The TGA curves of terpolymer **4** and tetrapolymer **6** are shown in Fig. 1. Both ter and tetrapolymer are stable up to 230 °C and exhibited a loss of 5 % attributed to the departure of moisture. As for terpolymer **4**, a rapid loss of 15 % in the range 230–310 °C was accounted for the departure of propylcarboxylate pendant as γ-butyrolactone (its calculated value is 14 %). A gradual loss of 17 % and a rapid loss of 22 % in the ranges 310–400 and 400–480 °C,

respectively, are associated with the departure of propyl-phosphonate and -sulfonate pendants each of which is calculated to have mass of 20 %. The mass remained at 800 °C was found to be 28 %. For tetrapolymer **6**, a rapid loss of 39 % in the temperature window of 230–360 °C was accounted for the combined loss of SO_2 and propylcarboxylate pendant which are calculated to have masses of 24 and 11 %, respectively. A gradual loss of 30 % in the range 360–800 °C was accounted for the loss of propyl-phosphonate and -sulfonate pendants each of which is calculated to have mass of 15 %. The mass remained at 800 °C was found to be 27 %.

IR and NMR spectra

The presence of IR absorption at 1037 cm^{-1} is attributed to the phosphonate functionality in **4** and **6**. The absorption bands at 1707 and 1717 cm^{-1} for **4** and **6**, respectively, indicate the presence of COOH (at least to some extent) owing to equilibration involving the phosphonate and carboxyl motifs as: $-CO_2^- + -PO_3H^- \leftrightharpoons -CO_2H + -PO_3^{2-}$. While the symmetric stretching vibration of COO^- in the zwitterionic form in **4** and **6** appeared at 1401 and 1418 cm^{-1}, respectively. The vibration at 1576 cm^{-1} in **4** is assigned to its antisymmetric stretching. The absorption peaks are in agreement with those observed for simple amino acids [24]. The presence of sulfonate motifs in the polymers **4** and **6** is ascertained by absorption at 1037 and ~1210 cm^{-1}, the later polymer also displayed the absorption bands at 1309 and 1127 cm^{-1} attributed to the asymmetric and symmetric vibrations of SO_2 units.

Figures 2 and 3 display the ^1H and ^{13}C NMR spectra of monomers **1–3** and polymers **4** and **6**, respectively. The signals for alkene protons and carbons of monomers **1–3** disappeared upon polymerization, confirming the termination happening via coupling and chain transfer processes [20, 25]. The ^{31}P NMR signals at 21.60 (major) and 23.89 ppm (minor) for **4**, and 22.87 (major) and 24.66 ppm (minor) for **6** revealed the incorporation of monomer **2** into the polymer backbone. The minor peak integrated for 5 % may presumably account for the presence of six-membered piperidine ring skeleton embedded in the backbone along with the major pyrrolidine rings. Figure 3d, e also ascertain the incorporation of all three monomers into the polymer chains as evident from the presence of carbon signals marked f(CO_2^-), f(PO_3H^-) and f(SO_3^-) attached to CO_2^-, PO_3H^- and SO_3^-, respectively. The ^{31}P and ^{13}C NMR spectra thus confirmed the incorporation of all three monomers into the polymer chain. The similar steric environment of the monomers to impart equal reactivity as well as high conversions is expected to incorporate all three monomers into the polymer chains in a ratio of 1:1:1 to match the feed ratio as corroborated by elemental analyses. The

area integration of the relevant carbon signals revealed a 75:25 *cis/trans* ratio of the substituents at $C_{b,b'}$ similar to the findings reported earlier (Fig. 3d, e) [11, 26]. We cannot provide any proof of the arrangement of the incorporated monomers **1–3** in the polymer backbone of either **4** or **6**; however, structural similarity of the monomers is expected to impart similar reactivity, thereby leading to their random placements. The incorporation of SO_2 unit must alternate between itself and the monomers **1–3**.

Viscosity measurements

Huggins viscosity equation: $\eta_{sp}/C = [\eta] + k[\eta]^2 C$ was used to investigate the viscosity behavior of the synthesized polymers. The viscosity plots for APE **5** and **7** are concave upwards as expected of any polyelectrolytes (Fig. 4a-i, b-i), while it became linear in 0.1 M NaCl (Fig. 4a-ii, 4b-ii). Plots (iii) and (iv) in Fig. 4a, b represent the viscosity behavior of PZs **4** and **6** in the presence of various concentrations of NaCl. The viscosity increases with increasing salt concentrations of added salts because of antipolyelectrolyte effects [25, 27, 28]. While the Cl^- ions can effectively neutralize the positive nitrogens, Na^+ ions having smaller ionic radius and larger hydration shell cannot approach the negative charges close enough to effectively bind them. As a result, the zwitterionic dipoles which carry overall negative charges lead to expansion of the polymer chains.

Scale inhibition

The percent scale inhibition (PSI), given in Table 3, was determined using Eq. (1):

$$\% \text{ Scale inhibition} = \frac{[Ca^{2+}]_{\text{inhibited}(t)} - [Ca^{2+}]_{\text{blank}(t)}}{[Ca^{2+}]_{\text{inhibited}(t_0)} - [Ca^{2+}]_{\text{blank}(t)}} \times 100 \tag{1}$$

which uses the concentration of $[Ca^{2+}]$ at time zero and time t in the inhibited (with antiscalant) and blank (without antiscalant) solutions. In the calculation of PSI, it is assumed that the conductance is proportional to the concentration of the ions. The study was intended to examine the precipitation behavior of $CaSO_4$ from its supersaturated solutions containing 2598 mg L^{-1} of Ca^{2+} and 6300 mg L^{-1} of SO_4^{2-} which are three times the concentration found in the reject brine in our university's desalination plant. When an equal volume of $CaCl_2$ and Na_2SO_4 solutions containing 2×2598 mg L^{-1} of Ca^{2+} and 2×6300 mg L^{-1} of SO_4^{2-} were mixed, an immediate drop in conductivity indicating the precipitation of $CaSO_4$, also confirmed by visual inspection (Fig. 5-blank). Figure 5b, d represent the expanded conductivity

Fig. 2 ^{1}H NMR spectra of **a1**; **b2**; **c3**; **d4**; and **e6** in D$_2$O
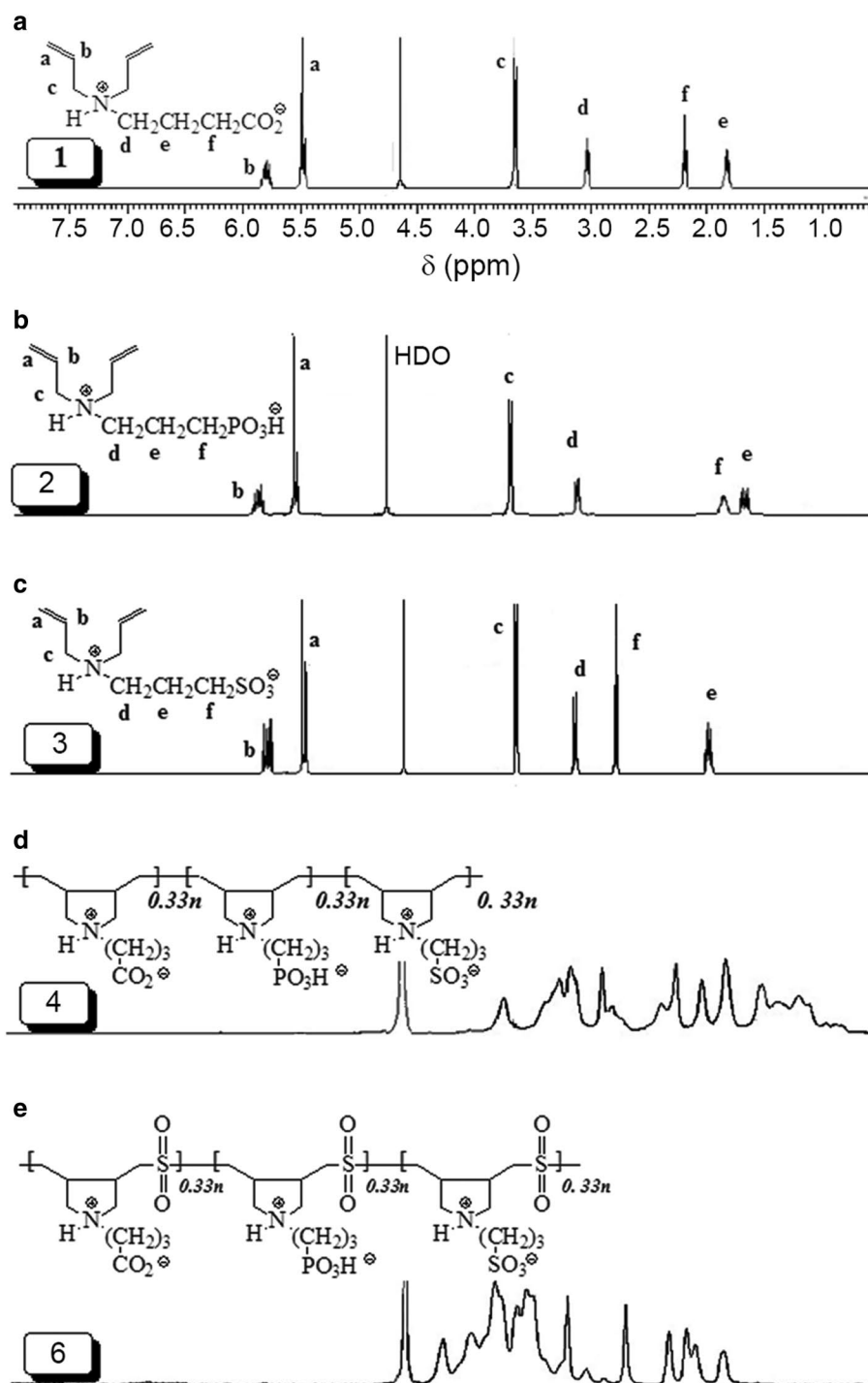
versus time plots of 5a and 5c, respectively, for a shorter time scale. In the presence of 5 and 10 ppm of terpolymer **4**, while there was an induction period (IP) of 30 and 950 min, respectively, before the sudden drop in the conductivity, no such IP was observed in the duration of 1150 min in the presence of 15 ppm of the antiscalant (Fig. 5a; Table 3).The tetrapolymer **6** performed even much better; an IP of 160 min and no IP for a duration of

4220 min were observed in the presence of 5 and 10 ppm of the tetrapolymer (Fig. 5c). Note that for a small concentration of 5 ppm, tetrapolymer **6** imparted a scale inhibition of ~100 % for over 100 min (Fig. 5d), while in the presence of 10 ppm, it imparted a remarkable scale inhibition of 96 % (Table 3).

Induction period depends on the concentration of the antiscalant; it prevents the growth of the CaSO$_4$ by

Fig. 3 ^{13}C NMR spectra of **a1**; **b2**; **c3**; **d4**; and **e6** in D_2O
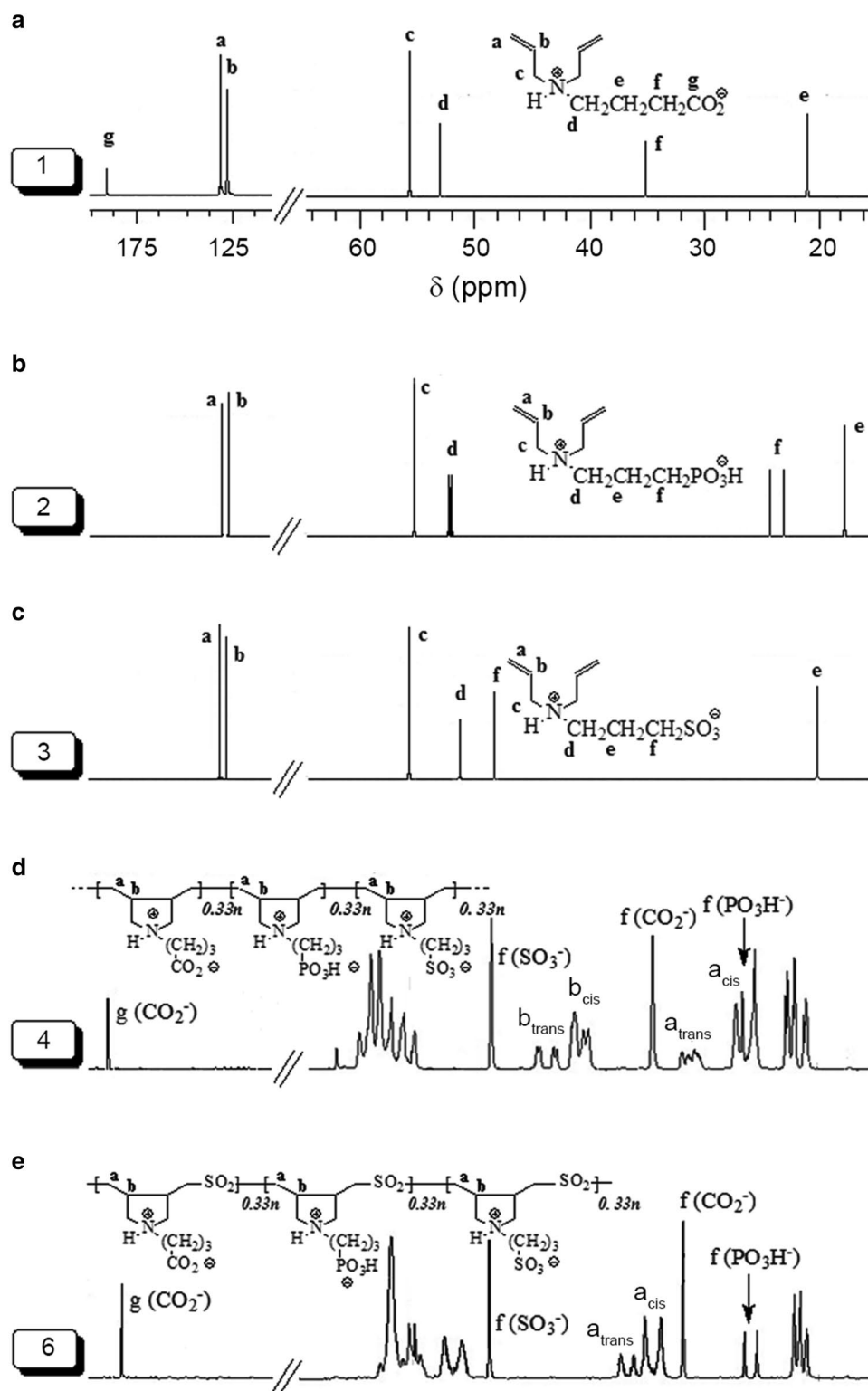
poisoning the active sites of the crystals. Alteration in crystal shape does not allow it to grow normally; the increased distortion and internal stress of crystals result in crystal fractures and prevention of crystal deposition [29]. However, after all the polymer chains are adsorbed, the crystal

growth resumes at a rate like that of the unpoisoned (blank) systems.

The residence time of the saline water inside the RO desalination chamber is less than 15 min; as such the newly synthesized antiscalants **4** and **6** can very well keep
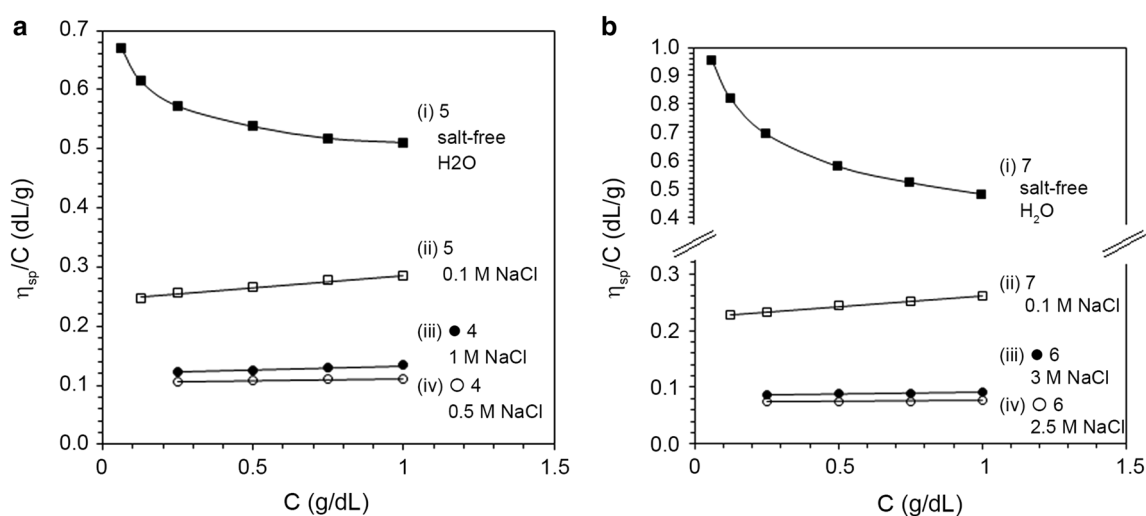
Fig. 4 Using an Ubbelohde viscometer at 30 °C. The viscosity behavior of **a**: (*i*) *filled square* **5** in salt-free water, (*ii*) *empty square* **5** in 0.1 M NaCl, (*iii*) *filled circle* **4** in 1 M NaCl, (*iv*) *empty circle* **4** in 0.5 M NaCl; and **b:** (*i*) *filled square* **7** in salt-free water, (*ii*) *empty square* **7** in 0.1 M NaCl, (*iii*) *filled circle* **6** in 3 M NaCl, (*iv*) *empty circle* **6** in 2.5 M NaCl
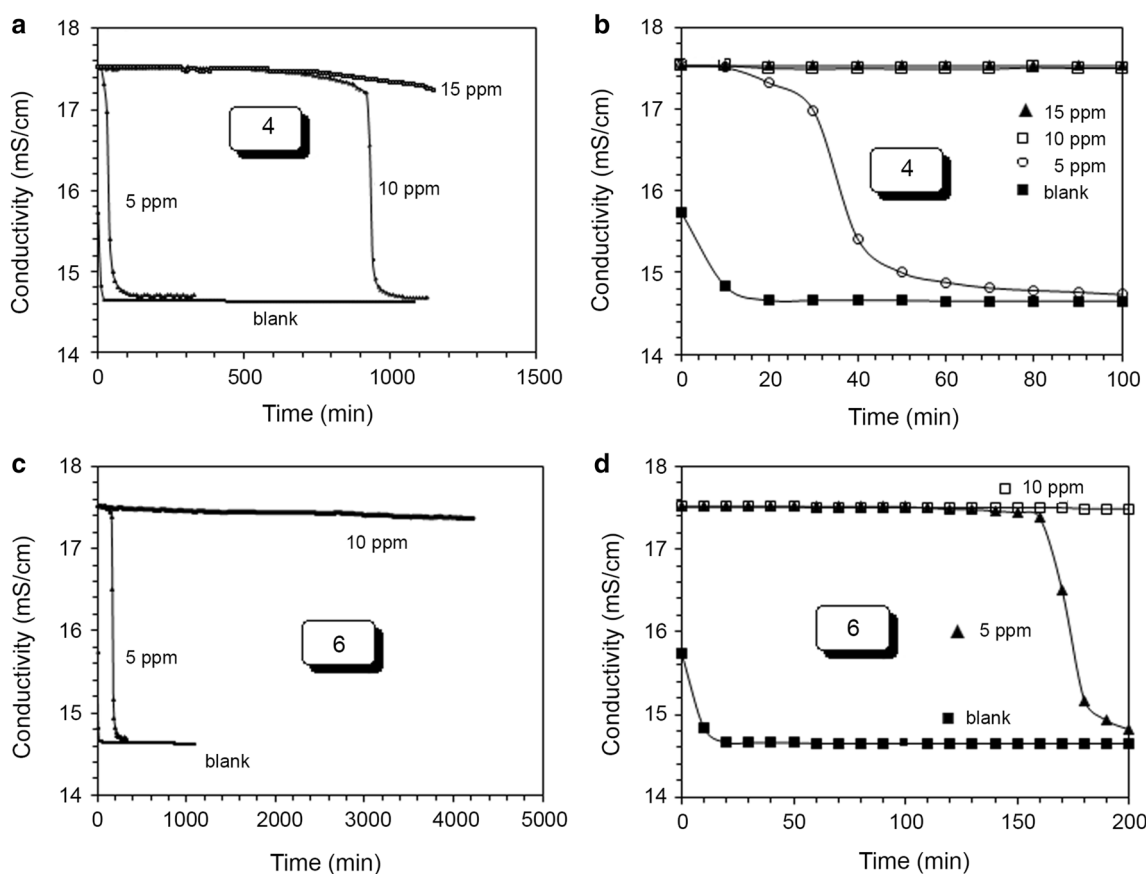

Fig. 5 Precipitation behavior of a supersaturated solution of CaSO$_4$ in the presence of: 0, 5, 10 and 15 ppm of **4** using a time scale of **a** 0–1500 min; **b** 0–100 min and 0, 5 and 10 ppm of **6** using a time scale of **c** 0–5000 min; and **d** 0–200 min

a scale-forming $CaSO_4$ in solution for much longer than the induction period of 15 min [30]. Therefore, the current polymers can be considered as effective inhibitors since they can scavenge metal ions and disrupt the nucleation and crystallization processes, thus minimize the fouling of membranes by $CaSO_4$ [29, 31, 32].

Conclusion

Butler's cyclopolymerization is used for the first time to synthesize pH-responsive linear ter and tetrapolymers **4** and **6** containing the functionalities of carboxylate, phosphonate and sulfonate in the same polymer backbone. The strong zwitterionic interactions imparted water-insolubility in these polymers which were, however, found to be water-soluble in the presence of added salts or NaOH. The functionalities along with the unquenched nitrogen valency provided potent chelation centers of a range of chelating abilities for the formation of metal-chelate complex. This was demonstrated by the remarkable scale inhibition efficacies by **4** and **6** both of which at a dose of 10 ppm delayed the precipitation of $CaSO_4$ from its supersaturated solution up to 920 and over 4000 min, respectively. For an insufficient concentration of 5 ppm, polymer **6** achieved a PSI of 100 % for a duration over 100 min, thereby making it a potentially effective antiscalant additive in RO plants.

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