

Bis[3-(diethoxyphosphoryl)propyl]diallylammonium Chloride: Synthesis and Use of Its Cyclopolymer as an Antiscalant

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ABSTRACT: A new symmetrically substituted cationic monomer bis[3-(diethoxyphosphoryl)propyl]diallylammonium chloride has been synthesized and cyclopolymerized to give the corresponding cationic polyelectrolyte (+) (CPE) bearing two identical (diethoxyphosphoryl)propyl pendants on the pyrrolidinium repeating units. The hydrolysis of the phosphonate ester in (+) (CPE) gave a pH-responsive cationic polyacid (+) (CPA) bearing the motifs of a tetrabasic acid. The (+) (CPA) under pH-induced transformation was converted into a water-insoluble polyzwitterion acid (\pm) (PZA) or water-soluble polyzwitterion/monoanion ($\pm -$) (PZMAN) or polyzwitterion/dianion ($\pm =$) (PZDAN) or polyzwitterion/trianion ($\pm \equiv$) (PZTAN), all having identical degree of polymerization. The interesting solubility and viscosity behaviors of the polymers have been investigated in some detail. The apparent protonation constants of the anionic centers in ($\pm \equiv$) (PZTAN) and its corresponding monomer ($\pm \equiv$) (ZTAN) have been determined. Evaluation of antiscaling properties of the PZA using supersaturated solutions of CaSO_4 revealed $\approx 100\%$ scale inhibition efficiency at a meager concentration of 10 ppm for a duration over 71 h at 40°C . The PZA has the potential to be an effective antiscalant in Reverse Osmosis plants. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40615.

KEYWORDS: polyelectrolytes; properties and characterization; radical polymerization; stimuli-sensitive polymers; synthesis and processing

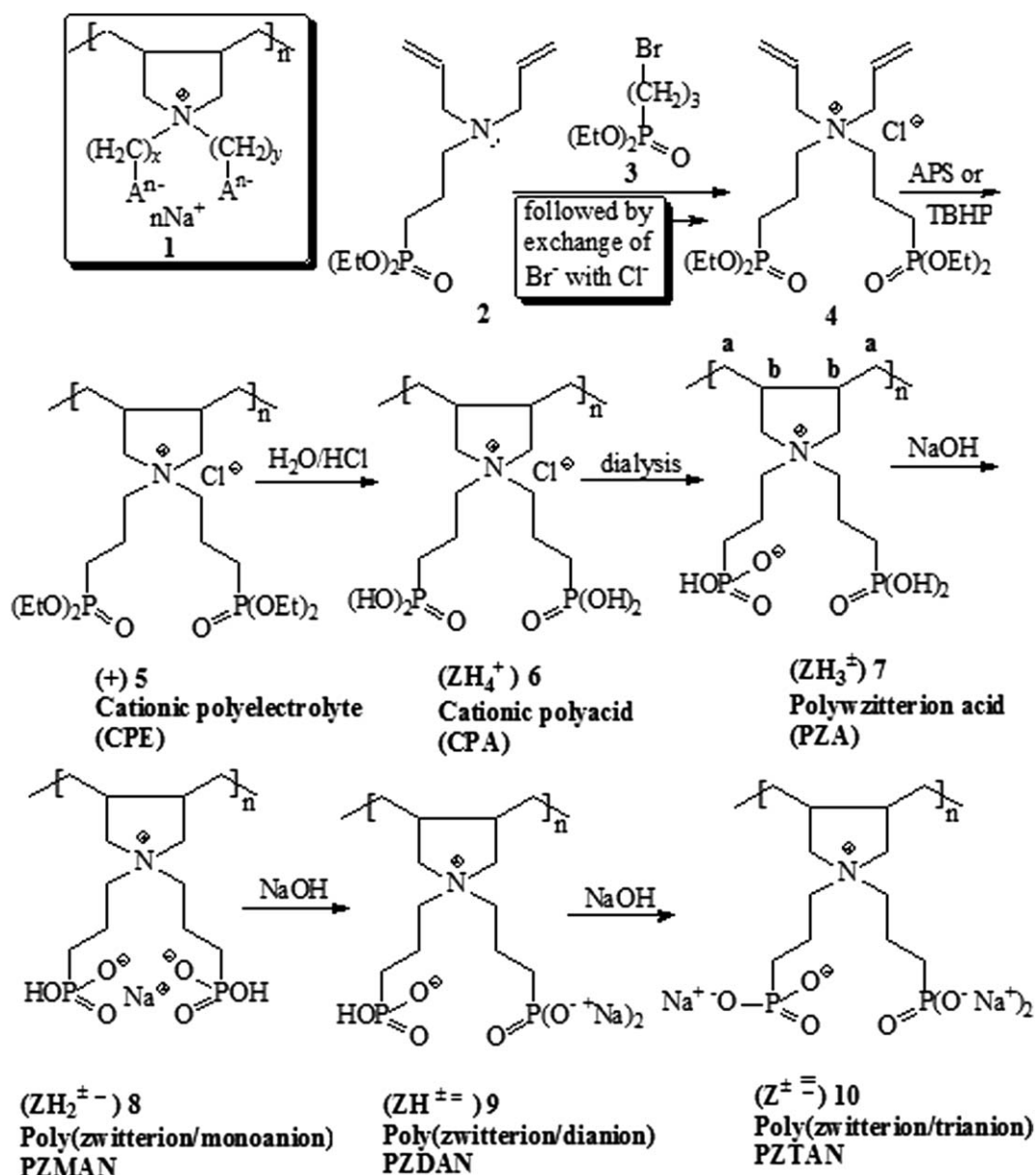
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INTRODUCTION

Butler's cyclopolymerization protocol^{1–4} using pH-responsive diallylamine salts bearing aminoalkylphosphonate motifs has been utilized in the synthesis of linear^{5–7} cyclopolymers as well as cross-linked resins.⁸ Aminophosphonic acids are structural analogues of amino acids, and as such are suitable for various biological applications.⁹ Phosphonates have found application in chelating divalent cations such as Ca^{2+} and Ba^{2+} ions in detergents and inhibiting the deposition of scale.^{10,11} Polymers having phosphonate functionality have been explored for proton conducting membranes.¹² Some phosphonates are used as medicines: Antiretroviral drug Tenofovir is used in the treatment of viral diseases such as HIV and hepatitis B.¹³ Phosphonates are utilized as adhesion promoters to dental tissue^{14,15} and bone.^{16–18} Two recent reports describe the polymerizations of phosphonated-bis(methacrylamide)s for dental applications.^{19,20} While some linear polyaminophosphonates, prepared by Butler's cyclopolymerization technique,^{1–4} have been used as antiscalants^{21,22} and as polymer components in the construction of aqueous two-phase systems,²³ the amino-phosphonate resins are found to be very effective in the removal of toxic metal ions.^{8,24–26}

pH-Responsive bisphosphonates $\text{R}^1\text{R}^2\text{C}(\text{PO}_3\text{H})_2$, analogues of pyrophosphates $\text{O}(\text{PO}_3\text{H})_2$, have also significant industrial importance: They are used as corrosion inhibitors²⁷ in concrete, complexing agents in oil industries,²⁸ and inhibitors of bone resorption²⁹ in bone-related diseases. To date, only a single report describes the cyclopolymerization of a diallyl amine salt $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}^+\text{CH}(\text{PO}_3\text{H})(\text{PO}_3^-)]$ bearing bisphosphonate functionality having both the phosphorous attached to the same carbon.⁷ To our knowledge, cyclopolymerization of a symmetric bisphosphonate diallyl quaternary ammonium salt (like **1**, Scheme 1) having phosphorous atoms attached to two different carbons is yet to be reported. Keeping in view the importance of the phosphonates and in our continuing studies of aminophosphonate polymers, herein we report the synthesis and cyclopolymerization of new bisphosphonate monomer **4** bearing bis-3-phosphorylpropyl substituents (Scheme 1). Ester hydrolysis of cyclopolymer cationic polyelectrolyte (**5**) to pH-responsive **6** would give us the opportunity to examine its solution properties, determine acid dissociation constants and test its efficiency as an antiscalant to inhibit CaSO_4 scale formation in desalination plants. The cyclopolymer having bisphosphonate motifs with multiple adsorption sites is expected to sequester Ca^{2+} ions effectively to inhibit scale formation.



Scheme 1. Cyclopolymerization of diallylbisphosphonate monomer.

EXPERIMENTAL

Physical Methods

A Perkin Elmer Elemental Analyzer Series II Model 2400 and a Perkin Elmer 16F PC FTIR spectrometer were used to carry out Elemental analyses and record IR spectra, respectively. The ¹³C, ¹H, and ³¹P NMR spectra have been measured in D₂O (using HOD signal at δ 4.65 and dioxane ¹³C peak at δ 67.4 as internal standards) on a JEOL LA 500 MHz spectrometer. ³¹P was referenced with 85% H₃PO₄ in DMSO. Viscosity measurements have been made by Ubbelohde viscometer using CO₂-free water under N₂. A Sartorius pH meter PB 11 was used to measure pH of the solutions. Conductivity measurements were recorded by a Conductivity meter (Thermo Scientific Model: ORION STAR A212). Molecular weights were determined by the GPC measurement performed on an Agilent 1200 series apparatus having a RI detector and PL aquagel-OH MIXED column using

polyethylene oxide/glycol as a standard and water as eluent at a flow rate of 1.0 mL/min at 25°C.

Materials

Ammonium persulfate (APS) and tertiary butyl hydroperoxide (TBHP) (70 w/w % in water) from Fluka AG (Buchs, Switzerland) were used as received. A Spectra/Por membrane with a molecular weight cut off (MWCO) value of 6000 to 8000 (Spectrum Laboratories, Inc) was purchased for dialysis. Tertiary amine 2 was prepared by reacting diallylamine and 1-bromo-3-(diethylphosphonato)propane (3).⁶

N-Allyl-N,N-bis[3-(diethoxyphosphoryl)propyl]prop-2-en-1-Aminium Chloride (4)

A mixture of 2 (20.2 g, 73.4 mmol) and 3 (31.0 g, 119.7 mmol), K₂CO₃ (10.57 g, 76.6 mmol) in acetonitrile (120 mL) was stirred under N₂ at an oil-bath temperature of 95°C for

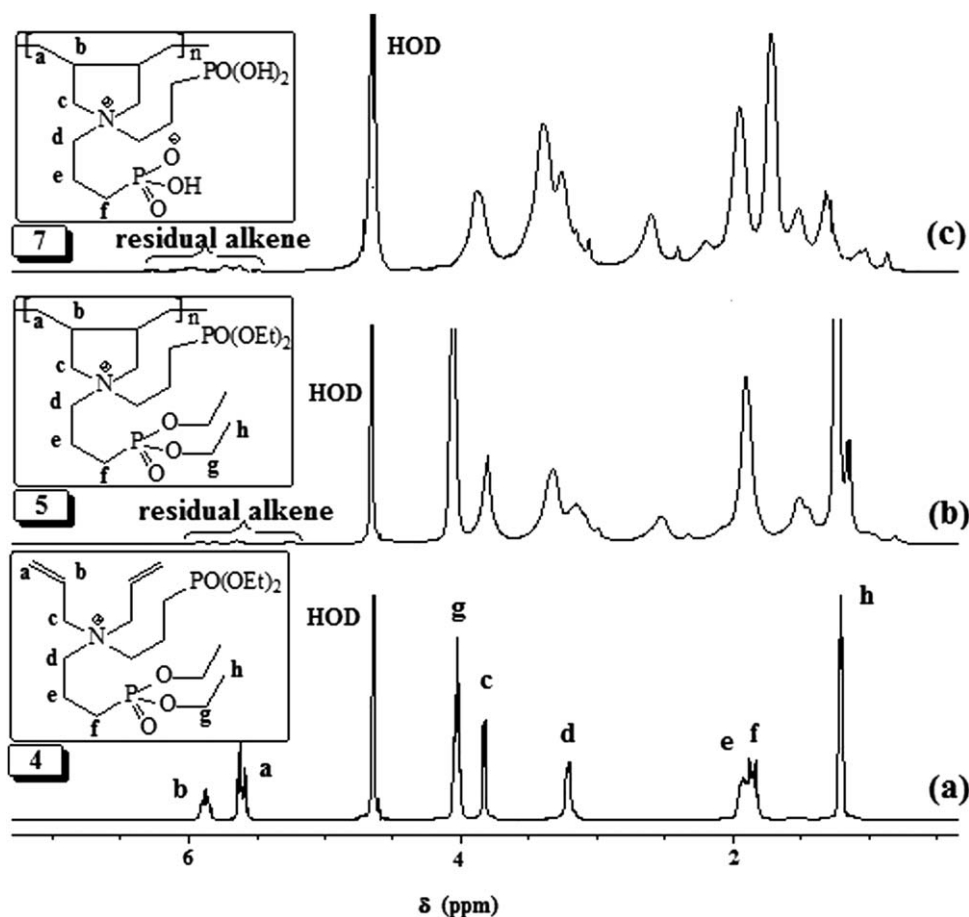


Figure 1. ^1H NMR spectrum of (a) 4, (b) 5, and (c) 7 (+NaCl) in D_2O .

96 h. After concentration, the residual liquid was taken up in water (40 mL) and washed with ether (3×50 mL). After saturating the aqueous layer with NaCl and adding concentrated HCl (15 mL), the mixture was stirred for 10 min. The aqueous layer was extracted with CHCl_3 (3×50 mL). After removal of CHCl_3 , the residual liquid in saturated NaCl solution (30 mL) was stirred for 30 min. The aqueous layer was then washed with a 2 : 1 ether/ CH_2Cl_2 mixture (3×50 mL) and finally, extracted with CH_2Cl_2 (3×100 mL). The CH_2Cl_2 -extract was dried (Na_2SO_4) and concentrated to obtain **4** as a pale yellow liquid (25.4 g, 71%). (Found: C, 48.6; H, 8.8; N, 2.7%. $\text{C}_{20}\text{H}_{42}\text{ClNO}_6\text{P}_2$ requires C, 49.03; H, 8.64; N, 2.86%); ν_{max} (KBr): 3422, 3081, 2984, 2909, 1644, 1471, 1444, 1242, 1163, 1026, 964, 875, 792, 752, and 661 cm^{-1} ; δ_{H} (D_2O) 1.21 (12 H, t, $J = 7$ Hz), 1.80–2.00 (8H, m), 3.20 (4H, m), 3.83 (4H, d, $J = 7.0$ Hz), 4.03 (8H, m), 5.61 (4H, m), 5.88 (2H, m), (HOD: 4.65); δ_{C} (D_2O) 15.52 (s, PCH_2CH_2), 16.10 (d, 2C, Me , 3J (PC) 6.2 Hz), 21.10 (d, PCH_2 , 1J (PC) 142 Hz), 57.92 (d, $\text{PCH}_2\text{CH}_2\text{CH}_2$, 3J (PC) 16.5 Hz), 61.44 (2C, $=\text{CH}-\text{CH}_2$, s), 63.99 (d, 2C, OCH_2CH_3 , 2J (PC) 6.2 Hz), 124.10 (2C, s, $\text{CH}_2=\text{CH}$), 129.42 (2C, s, $\text{CH}_2=\text{CH}$) (dioxane: 67.40 ppm); δ_{P} (202 MHz, D_2O): 30.94 (s). The ^1H and ^{13}C NMR spectra are shown in Figures 1 and 2, respectively. ^{13}C DEPT 135 analysis supported the spectral assignments.

Acid Hydrolysis of **4** to Cationic Acid (CA) **11**

A mixture of **4** (15 g, 30.6 mmol), water (25 mL) and concentrated HCl (22 mL) was heated in a flask under N_2 at 95°C for 48 h. The residual liquid after removal of the solvent was dissolved in methanol and poured into acetone to give **11** as a thick liquid (11.0 g, 95%) which crystallized in a freezer as a hygroscopic white solid. Mp. 75 to 80°C (methanol/acetone). (Found: C, 37.8; H, 7.2; N, 3.6%. $\text{C}_{12}\text{H}_{26}\text{ClNO}_6\text{P}_2$ requires C, 38.16; H, 6.94; N, 3.71%); ν_{max} (neat) 3500 to 2500 (very broad), 2959, 1702, 1642, 1475, 1418, 1368, 1230, 1169, 995, 874, and 714 cm^{-1} . δ_{H} (D_2O) 1.51 (4H, dt, $J = 18.3$ and 7.4 Hz), 1.75 (4H, m), 3.04 (4H, m), 3.64 (4H, d, $J = 7.3$ Hz), 5.42 (4H, m), 5.72 (2H, m), (HOD: 4.65); δ_{C} (D_2O) 15.87 (2C, s, PCH_2CH_2), 23.32 (2C, d, PCH_2 , 1J (PC) 140 Hz), 58.28 (2C, d, $\text{PCH}_2\text{CH}_2\text{CH}_2$, 3J (PC) 18.6 Hz), 61.37 (2C, $=\text{CH}-\text{CH}_2$, s), 124.10 (2C, s, $\text{CH}_2=\text{CH}$), 129.20 (2C, s, $\text{CH}_2=\text{CH}$) (dioxane: 67.40 ppm); δ_{P} (202 MHz, D_2O): 26.00 (m). The DEPT 135 NMR analysis supported the ^{13}C spectral assignments.

Procedure for the Cyclopolymerization of **4** or **11**

A solution of monomer **4** (7.35 g, 15 mmol, entry 5, Table I), water (3.15 g) and initiator APS (200 mg) in a 25-mL closed vessel under N_2 was stirred at 90°C for 4 h. The reaction mixture after dialysis against deionized water for 24 h was freeze-dried to obtain CPE **5** as a light brown hygroscopic polymer. The thermal

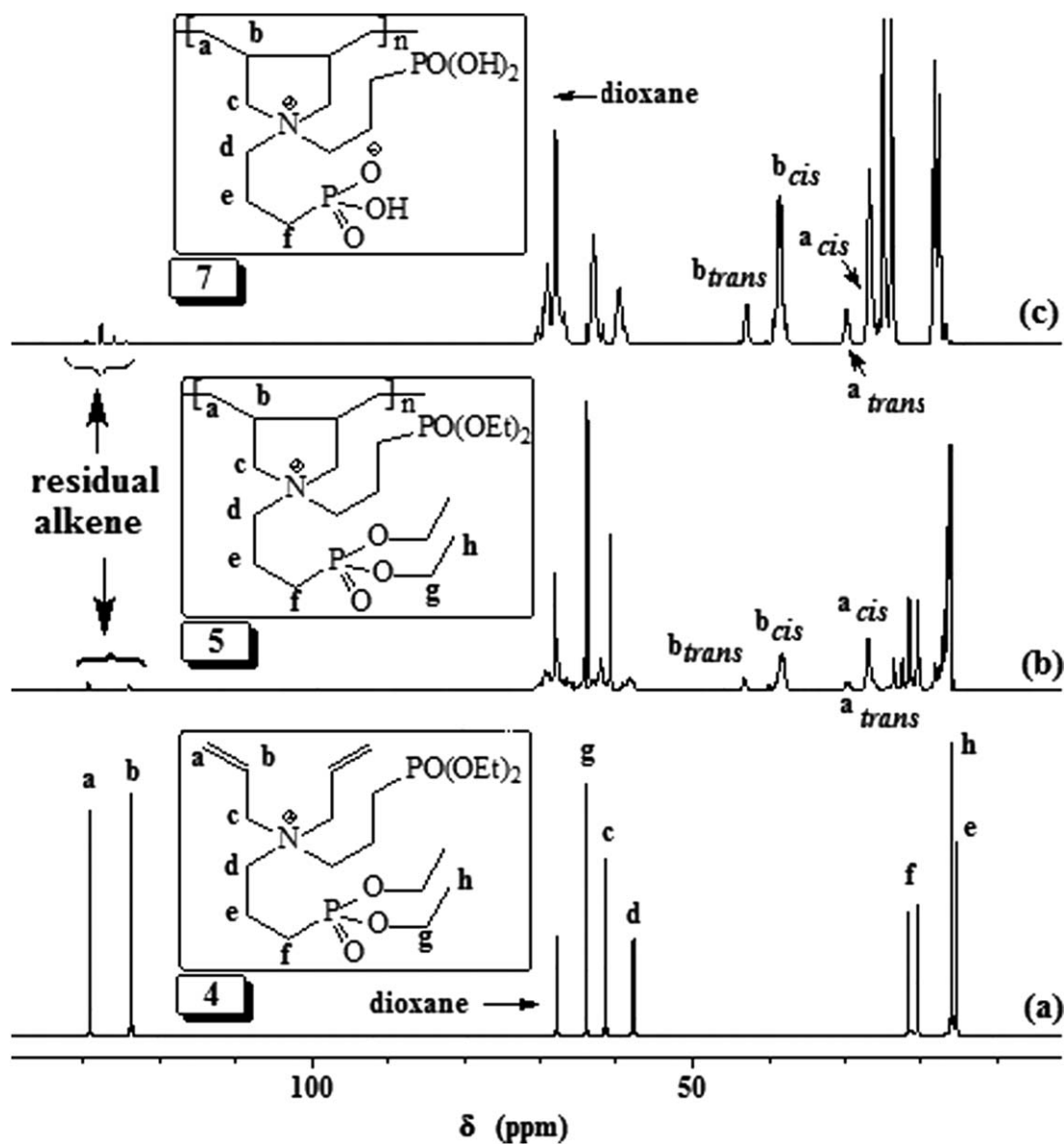


Figure 2. ^{13}C NMR spectrum of (a) 4, (b) 5, and (c) 7 (+NaCl) in D_2O .

Table I. Cyclopolymerization^a of Monomers 4 and 11

Entry No.	Monomer (mmol)	Water (% w/w)	Initiator ^a (mg)	Temp (°C)	Time (h)	Yield (%)		$[\eta]^b$ (dL g ⁻¹)
						NMR	isolated	
1	4 (7.5)	30	APS (100)	90	48	65	37	0.0545
2	4 (7.5)	30	APS (140)	90	4	70	51	0.0475
3	4 (7.5)	25	APS (380)	95	3	72	45	0.0417
4	4 (7.5)	20	TBHP (200)	105	48	75	44	0.0496
5	4 (1.5)	30	APS (200)	90	4	76	63	0.0484
6	11 (7.5)	30	APS (300)	95	5	77	61	0.0632

^aPolymerization reactions were carried out in aqueous solution of monomer 4 or 11 in the presence of ammonium persulfate (APS) or tert-butyl hydroperoxide (TBHP) at specified temperatures to give respective polymers of 5 and 7.

^bViscosity of 1 to 0.25% solution of 5 in 0.1M NaCl and 7 in 1.0M NaCl at $30.0 \pm 0.1^\circ\text{C}$ was measured with Ubbelohde Viscometer ($K = 0.005718$).

Table II. Solubility^{a,b} of CPE (+) **5** and PZA (\pm) **7**

Solvent	ϵ	5	7
Formamide	111	+	\pm
Water	78.4	+	–
Formic acid	58.5	+	+
DMSO	47.0	+	–
Ethylene glycol	37.3	+	–
DMF	37.0	+	–
Methanol	32.3	+	–
Triethylene glycol	23.7	+	–
Acetic acid	6.15	+	–

^a Polymer-water mixture (solution) [2% (w/w)] was made after heating the mixture at 70°C for 1 h and then cooling to 23°C.

^b "+" indicates soluble, "–" indicates insoluble, and " \pm " indicates partially soluble.

decomposition: the color changed to dark brown and black at respective temperatures of 260°C at 320°C. (Found: C, 48.7; H, 8.8; N, 2.8%. $C_{20}H_{42}ClNO_6P_2$ requires C, 49.03; H, 8.64; N, 2.86%); ν_{max} (KBr) 3420 (br), 2984, 2933, 2905, 1650, 1460, 1394, 1369, 1221, 1160, 1123, 1050, 1017, 968, 786, 698, 620 and 544 cm^{-1} . δ_p (202 MHz, D_2O): 32.89 (4%), 30.96 (72%), and 22.96 (24%). 1H NMR and ^{13}C NMR spectra are shown in respective Figures 1 and 2. Cyclopolymerization of **11** (entry 6, Table I) followed by dialysis afforded PZA **7**.

Acid Hydrolysis of CPE **5** to Poly(zwitterion acid) (PZA) **7**

A solution of CPE **5** (3.5 g, 7.14 mmol) (from entry 5, Table I) in water (20 mL) and concentrated HCl (25 mL) was heated at 95°C for 24 h. The homogeneous mixture was dialyzed against deionized water for 24 h. During dialysis, the polymer started to precipitate out as an oily material within 1 h. The resulting mixture was freeze-dried to obtain PZA **7** as a white solid (2.3 g, 94%). The thermal decomposition: the color changed to brown and black at respective temperatures of 260°C and 310 to 320°C. (Found: C, 41.9; H, 7.5; N, 3.9%. $C_{12}H_{25}NO_6P_2$ requires C, 42.23; H, 7.38; N, 4.10%); ν_{max} (KBr) 3425 (br), 2952, 1651, 1463, 1416, 1234, 1146, 1058, 936, 756, 710 and 531 cm^{-1} . δ_p (202 MHz, D_2O): 23.78. 1H NMR and ^{13}C NMR spectra are shown in Figures 1 and 2, respectively.

Solubility Measurements

After stirring a mixture of CPE **5** or PZA **7** (2 w/w %) in a solvent at 70°C (1 h), the solubility behavior was checked at 23°C. The results are given in Table II. To a stirred mixture of PZA **7** (10 mg, 1 wt %) in deionized water (1 mL) was added NaCl in portions until it became soluble in the presence of 0.71M NaCl.

Potentiometric Titrations

Procedure for the determination of the protonation constants by potentiometric titrations under N_2 in CO_2 -free water is described elsewhere.^{6,30} A certain mmol of PZA **7** (ZH_3^{\pm}) or **11** (ZH_4^+) in 0.0175M NaCl (200 mL) was used in each trial (Tables III and IV). The water-insoluble zwitterionic polymer **7**

Table III. Experimental Details for the Determination of Basicity Constants Using Polymer PZA **7** (ZH_3^{\pm}) in 0.0175M NaCl at 23°C

run	ZH_3^{\pm} (mmol)	C_7^a (mol dm^{-3})	α -range	pH-range	Points ^b	Log $K_1^{\circ c}$	n_1^c	R^{2d}
Polymer 7								
1	0.2959 (7 : ZH_3^{\pm})	–0.09690	0.88–0.34	9.15–11.25	16	10.78	1.88	0.9981
2	0.2652 (ZH_3^{\pm})	–0.09690	0.84–0.39	9.36–11.12	18	10.69	1.90	0.9946
3	0.2324 (ZH_3^{\pm})	–0.09690	0.79–0.39	9.66–11.14	18	10.75	1.98	0.9963
Average						10.74 (5)	1.92 (5)	
Log $K_1^{\circ} = 10.74 + 0.92 \log [(1-\alpha)/\alpha]$			For the reactions: $Z^{\pm} + H^+ \rightleftharpoons ZH^{\pm}$					
Polymer 7								
1	0.2959 (7 : ZH_3^{\pm})	–0.09690	0.87–0.20	7.38–8.64	12	8.10	0.91	0.9975
2	0.2652 (ZH_3^{\pm})	–0.09690	0.92–0.14	7.30–8.78	15	8.14	0.85	0.9941
3	0.2324 (ZH_3^{\pm})	–0.09690	0.92–0.19	7.31–8.67	13	8.11	0.87	0.9877
Average						8.12 (2)	0.88 (3)	
Log $K_2^{\circ} = 8.12 - 0.12 \log [(1-\alpha)/\alpha]$			For the reactions: $ZH^{\pm} + H^+ \rightleftharpoons ZH_2^{\pm}$					
Polymer 7								
1	0.2959 (7 : ZH_3^{\pm})	–0.09690	0.58–0.31	3.21–4.65	17	3.56	3.06	0.9914
2	0.2652 (ZH_3^{\pm})	–0.09690	0.56–0.32	3.23–4.55	16	3.51	3.07	0.9959
3	0.2324 (ZH_3^{\pm})	–0.09690	0.55–0.31	3.28–4.55	14	3.45	3.05	0.9924
Average						3.51 (6)	3.06 (1)	
Log $K_3^{\circ} = 3.51 + 2.06 \log [(1-\alpha)/\alpha]$			For the reactions: $ZH_2^{\pm} + H^+ \rightleftharpoons ZH_3^{\pm}$					

^a Titrant concentration (negative values indicate titrations with NaOH).

^b Number of data points from titration curve.

^c Values in the parentheses are standard deviations in the last digit.

^d R = Correlation coefficient.

^e $\log K_i = \log K_i^{\circ} + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

Table IV. Experimental Details for the Determination of Basicity Constants Using Monomer (ZH₄⁺) **11** in 0.0175M NaCl at 23°C

run	ZH ₄ ⁺ (mmol)	C _T ^a (mol dm ⁻³)	α-range	pH-range	Points ^b	Log K ₁ ^{o c}	n ₁ ^c	R ^{2d}
Monomer 11								
1	0.2912 (6 : ZH ₄ ⁺)	-0.09690	0.91-0.17	8.70-10.65	18	9.84	1.07	0.9937
2	0.2507 (ZH ₄ ⁺)	-0.09690	0.84-0.12	9.00-10.6	16	9.76	1.04	0.9903
3	0.2102 (ZH ₄ ⁺)	-0.09690	0.90-0.17	8.85-10.5	14	9.80	1.05	0.9956
Average						9.80 (4)	1.05 (2)	
Log K ₁ ^e =9.78			For the reaction : Z ^{±=} +H ⁺ ⇌ ZH ^{±=}					
Monomer 11								
1	0.2912 (11 : ZH ₄ ⁺)	-0.09690	0.84-0.16	6.75-8.30	17	7.48	1.03	0.9935
3	0.2507 (ZH ₄ ⁺)	-0.09690	0.91-0.14	6.50-8.20	16	7.42	0.97	0.9934
2	0.2102 (ZH ₄ ⁺)	-0.09690	0.93-0.23	6.40-7.95	14	7.41	0.94	0.9960
Average						7.44 (4)	0.98 (5)	
Log K ₂ ^e =7.43			For the reaction : ZH ^{±=} +H ⁺ ⇌ ZH ₂ ^{±-}					
Monomer 11								
1	0.2912 (11 : ZH ₄ ⁺)	-0.09690	0.31-0.21	2.70-2.93	14	2.38	0.95	0.9917
2	0.2507 (ZH ₄ ⁺)	-0.09690	0.27-0.19	2.74-2.94	10	2.34	0.96	0.9941
3	0.2102 (ZH ₄ ⁺)	-0.09690	0.25-0.16	2.80-3.04	8	2.27	1.06	0.9795
Average						2.33 (6)	0.99 (6)	
Log K ₄ ^e =2.30			For the reaction : ZH ₃ [±] +H ⁺ ⇌ ZH ₄ [±]					

^a Titrant concentration (negative values indicate titrations with NaOH).^b Number of data points from titration curve.^c Values in the parentheses are standard deviations in the last digit.^d R = Correlation coefficient.^e log K_i = log K_i^o

(≈100 mg) was dissolved in 1M NaCl (3.5 mL), diluted to 200 mL to make the solution in 0.0175M NaCl. The log K₁, log K₂, and log K₃ of the respective protonation of ²⁻O₃P-X⁺-PO₃²⁻ [in **10**], ²⁻O₃P-X⁺-PO₃H⁻ [in **9**] and ⁻HO₃P-X⁺-PO₃H⁻ [in **8**] were calculated at each pH value by the Henderson-Hasselbalch eq. (2) (Scheme 2). The degree of protonation (α) of **10**, **9**, and **8** is the ratio [ZH^{±=}]_{eq}/[Z]_o, [ZH₂^{±-}]_{eq}/[Z]_o, and [ZH₃[±]]_{eq}/[Z]_o, respectively, where [ZH^{±=}]_{eq}, [ZH₂^{±-}]_{eq} and [ZH₃[±]]_{eq} represent the respective equilibrium concentrations of the first (**9**), second (**8**) and third protonated species (**7**), and [Z]_o describes the initial concentration of repeating units.

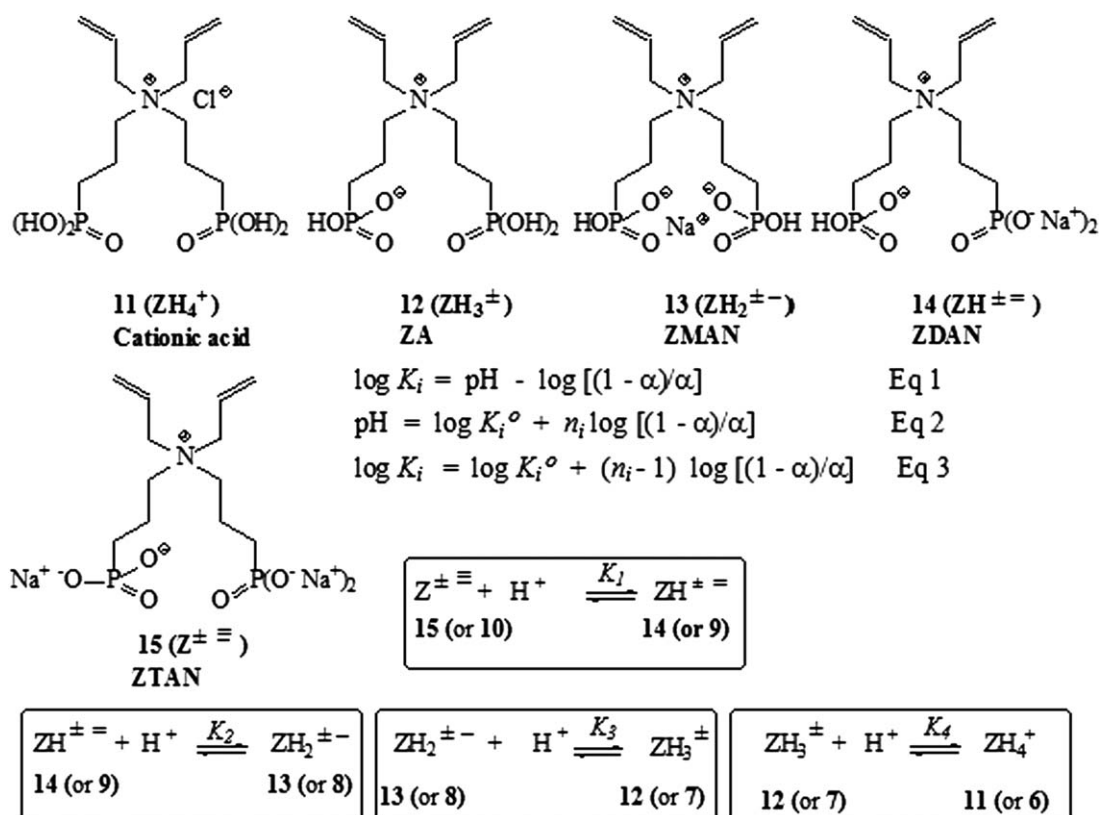
For the determination of the third step [**8** (ZH₂^{±-}) + H⁺ ⇌ **7** (ZH₃[±])] protonation constant (log K₃) using the titration of PZA **7** [ZH₃[±]] with NaOH, [Z]_o and [ZH₃[±]]_{eq} are related by [ZH₃[±]]_{eq} = [Z]_o - C_{OH⁻} - [H⁺] + [OH⁻], where C_{OH⁻} represents the added NaOH concentration. The equilibrium [H⁺] and [OH⁻] values were calculated from the pH value.^{30,31} Continuing the titration, the second step [**9** (ZH^{±=}) + H⁺ ⇌ **8** (ZH₂^{±-})] protonation constant (log K₂) was determined using volume of the titrant after deducting the equivalent volume from the total volume. Finally, the titration is ended by determination of the first step [**10** (Z^{±=}) + H⁺ ⇌ **9** (ZH^{±=})] protonation constant (log K₁) using volume of the titrant after deducting the two-equivalent volume from the total volume. The fourth step [**7** (ZH₃[±] + H⁺ ⇌ **6** (ZH₄⁺)] protonation constant (log K₄) using the titration of PZA **7** [ZH₃[±]] with HCl was not carried out

since PZA **7** [ZH₃[±]] is simultaneously involved in two equilibria: [**8** (ZH₂^{±-}) + H⁺ ⇌ **7** (ZH₃[±])] for log K₃ and [**7** (ZH₃[±]) + H⁺ ⇌ **6** (ZH₄⁺)] for log K₄. Simultaneous protonation and deprotonation of PZA **7** owing to the proximity of the log K₃ and log K₄ values made it difficult to determine the later.

For the monomeric unit, log K₄ for the fourth step protonation [**12** (ZH₃[±]) + H⁺ ⇌ **11** (ZH₄⁺)] was determined in a small window of α using 2[Z]_o instead of [Z]_o as the initial concentration of the monomer since both the PO₃H₂ in **11** (H₂O₃P-X⁺-PO₃H₂) Cl⁻ are involved in deprotonation to an extent to make the initial combined H⁺ concentration higher than that of [Z]_o. Log K₃ for the monomer could not be determined.

Evaluation of Antiscalant Behavior

Antiscalant behavior of PZA **7** and a commercial antiscalant (PERMATREAT® PC-191 Nalco Company, IL) used in our University desalination plant were evaluated in supersaturated CaSO₄ solution containing 2600 and 6300 ppm of Ca²⁺ (from CaCl₂) and SO₄²⁻ (from Na₂SO₄), respectively. This is three times the concentration in 1 CB (one concentrated brine) of reject brine procured from a Reverse Osmosis plant.³¹ A pre-heated (40°C) solution of sodium sulfate (6 CB, 60 mL) was added quickly to a solution of calcium chloride (6 CB, 60 mL) containing PZA **7** (20 ppm) at 40°C ± 1°C stirred at 300 rpm using a magnetic stir-bar. Conductivity measurements of the resultant solution containing 10 ppm of PZA **7** were made at



Scheme 2. The monomer in different forms and protonation constants.

an initial interval of every 10 min. A drop in conductivity indicated the precipitation of CaSO₄. Any turbidity from precipitation was inspected visually.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ionic Polymers

The substitution reaction between tertiary amine **2** and bromide **3** gave the salt R₂R₂N⁺Br⁻ (i.e. Br⁻ counterpart of salt **4**) which was treated with large excess of HCl and NaCl in aqueous solution (twice) to replace the Br⁻ with Cl⁻. The exchange is necessary since the Br⁻ salts are known to give polymers in low yields owing to oxidation of Br⁻ to Br₂.¹ Cationic monomer **4** underwent cyclopolymerization to afford cationic polyelectrolyte (CPE) **5** in reasonable yields bearing in mind the difficulty in putting four rather bulky substituents on a five-membered ring (Scheme 1, Table I). Note that the isolated yields are lower than the yields determined by the NMR analysis of the crude reaction mixture. A considerable portion of the polymer chains escapes the dialysis bag having a MWCO of 6000–8000. The involvement of the ethoxy groups in the chain transfer is one of the causes that lead to the lower yields and intrinsic viscosity [η] values (Table I).³² The average molar mass \overline{M}_w and polydispersity index of the polymer sample from entry 5, Table I were determined to be 26,500 g mol⁻¹ and 2.1, respectively.

The CPE (+) **5** was hydrolyzed in 6.7M HCl to give water-soluble cationic polyacid (CPA) (+) **6**, which on extended dialysis gave water-insoluble PZA (\pm) **7**. Note that cationic acid monomer (+) **11**, obtained via hydrolysis of **4**, upon polymer-

ization also afforded (\pm) PZA **7** (entry 6, Table I, Scheme 2). Neutralization of **7** with 1 or 2 or 3 equivalents of NaOH is expected to generate polyzwitterion-monoanion (PZMAN) ($\pm-$) **8**, polyzwitterion-dianion (PZDAN) ($\pm=$) **9** and polyzwitterion-trianion (PZTAN) ($\pm\equiv$) **10**, respectively. Likewise, neutralization of **11** would lead to zwitterion acid (\pm) **12**, zwitterion-anion ($\pm-$) **13**, zwitterion-dianion ($\pm=$) **14** and zwitterion-trianion ($\pm\equiv$) **15**.

While CPE (+) **5** was soluble in all the tested solvents, PZA (\pm) **7** was partially soluble in formamide, and soluble in formic acid, but notably insoluble in water (Table II). This is expected since (\pm) polyzwitterions are usually insoluble in salt-free water due to the strong electrostatic attractive interactions between the charges of opposite algebraic signs as well as intragroup, intra- and interchain associations promoted by dipolar interactions.² Water-insoluble PZA (\pm) **7** has been shown to be water-soluble in the presence of NaCl with a minimum critical salt concentration (CSC) of 0.71M, which screens the zwitterionic charges thus permitting expansion of the polymer backbone and globule-to-coil transition.^{33,34} However, upon addition of deionized water into the polymer solution in 0.71M NaCl, it remained soluble below CSC as a result of its progressive dissociation to PZMAN ($\pm-$) **8** in which the anionic portion encourages the water-solubility. Solubility of PZA (\pm) **7** in formic acid could be attributed to its protonation to water-soluble CPA (+) **6**. This was supported by an observation during the dialysis: the polymer remained soluble in 6.7M HCl owing to the presence of protonated form CPA (+) **6** while after 1 h of

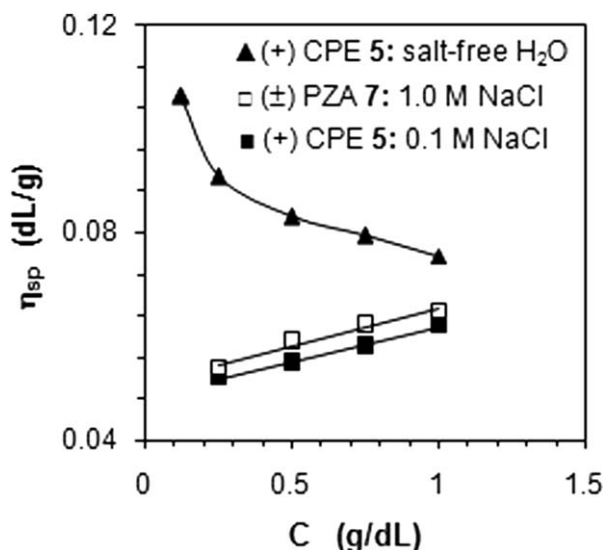


Figure 3. The viscosity behavior of (+) CPE 5 in ▲ salt-free water, □ (±) PZA 7 in 1M NaCl, ■ (+) CPE 5 in 0.1M NaCl, using an Ubbelohde Viscometer at 30°C. (All polymers used are derived from entry 5, Table I).

dialysis PZA (±) 7 started to precipitate as a result of the depletion of HCl (Scheme 1).

NMR Spectra

The ^1H and ^{13}C NMR spectra of 4, 5, and 7 are displayed in Figures 1 and 2, respectively. The absence of the OCH_2CH_3 signals in the spectra of 7 indicates its removal by hydrolysis [Figures 1(c) and 2(c)]. Polymer 5 or 7 even after extended dialysis contains $\approx 4\%$ residual alkene presumably as a result of some chain propagation without cyclization.² The integration of the ^{13}C [Figure 2(b,c)] as well as ^{31}P peaks of CPE 5 (see Experimental) revealed a 75/25 *cis-trans* ratio of the configurational isomers of pyrrolidinium ring at $C_{b,b}$ which is similar to the earlier findings (Scheme 1).^{5,6}

Viscosity Measurements

Equation (1) was developed to give a mathematical expression to rationalize the solution behavior of symmetrically or asymmetrically charged ionic polymers.^{35–38}

$$\nu^* = -\frac{\pi(fI_B)^2}{\kappa_S} + \frac{4\pi I_B \Delta f^2}{\kappa_S^2} \quad (1)$$

where f is the total fraction of charged monomers, Δf is the charge imbalance, I_B is the Bjerrum length, and κ_S is the Debye-Huckel screening parameter, and ν^* is the excluded volume: a negative or a positive value of which indicates chain contraction or expansion, respectively. For symmetrically charged polymers i.e. polymers having equal number of charges of both algebraic signs, the second term in eq. (1) is eliminated by virtue of $\Delta f=0$; hence a negative excluded volume (ν^*) indicates contraction to a collapsed coil. In the event of charge imbalance (i.e. $\Delta f \neq 0$), the second term in eq. (1), which describes the shielding of the Coulombic repulsive interactions, would play a role and in case of its domination over the first term may lead to the expansion of the polymer chain to a semicoil owing to a positive ν^* value.

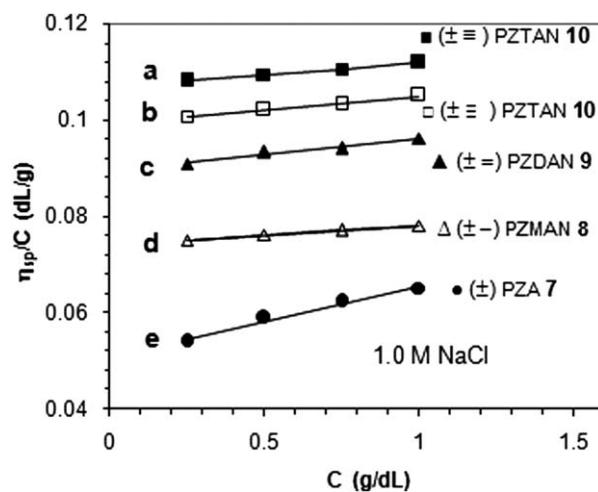


Figure 4. The viscosity behavior in 1M NaCl of: (a) ■ (± ≡) PZTAN 10 (PZA 7 + four equivalents NaOH), (b) □ (± ≡) PZTAN 10 (PZA 7 + three equivalents NaOH), (c) ▲ (± =) PZDAN 9, (d) △ (± -) PZMAN 8 and (e) ● (±) PZA 7, using an Ubbelohde Viscometer at 30°C. (All polymers are derived from entry 5, Table I).

Figure 3 shows the viscosity behavior of 5 and 7 in salt-free and salt-added water. The viscosity plot of CPE (+) 5 resembles that of a polyelectrolyte i.e. concave upwards in salt-free water and linear in 0.1M NaCl. The viscosity plot of PZA (±) 7 in 1M NaCl remains linear and it has higher viscosity values than the CPE (+) 5 in 0.1M NaCl.

Figures 4 and 5 demonstrate the pH-responsiveness of the polymers 7–10. The pHs are increased upon addition of NaOH as a result of the following transformations: (±) 7 (PO_3H_2)(PO_3H^{1-}) \rightarrow (±-) 8 (PO_3H^{1-})(PO_3H^{1-}) \rightarrow (±=) 9 (PO_3H^{1-})(PO_3^{2-}) \rightarrow (±≡) 10 (PO_3^{2-})(PO_3^{2-}). The pH of a $\approx 0.0015\text{M}$ polymer solutions of 7, 8, 9, and 10 were found to be 3.21, 7.10, 9.04, and 10.88, respectively. With the successive increase in the pH values, the increase in size, as demonstrated by the increased viscosities, is caused by the

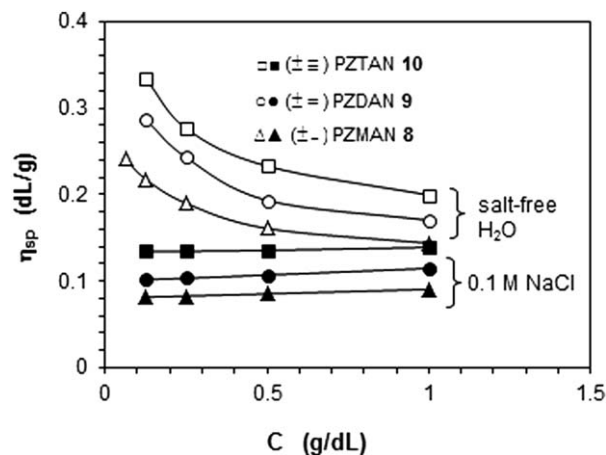


Figure 5. The viscosity behavior in salt-free water and 0.1M NaCl of: □■ (± ≡) PZTAN 10, ○● (± =) PZDAN 9, and ▲▲ (± -) PZMAN 8 (e) ● (±) PZA 7, using an Ubbelohde Viscometer at 30°C. (All polymers are derived from entry 5, Table I).

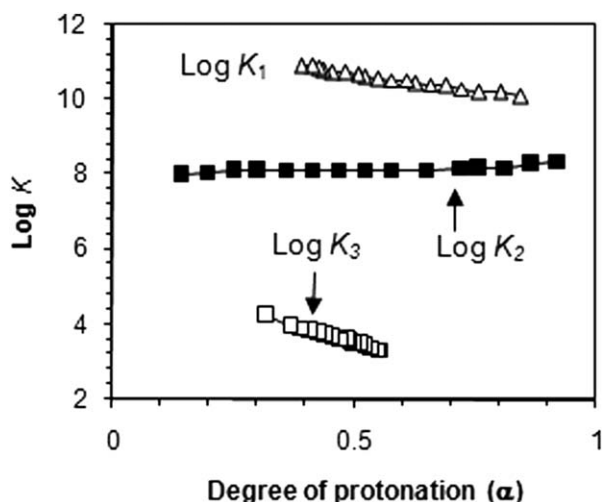


Figure 6. Plot for the apparent $\log K_1$, $\log K_2$, and $\log K_3$ versus degree of protonation (α) (entries 3, 3 and 3, Table III) for $(\pm\equiv)$ PZTAN 10.

repulsion among the excess negative charges in the polymer chain (Figure 4). A meaningful comparison of the viscosity values is made since all the polymers are derived from the same polymer sample (entry 5, Table I). Note that (\pm) 7 collapses into a water-insoluble polymer which is soluble only in the presence of added salt (NaCl) (*vide supra*). The viscosity values increase in the order: (\pm) 7 < $(\pm -)$ 8 < $(\pm =)$ 9 < $(\pm \equiv)$ 10. This is in line with the increase in charge imbalance in going from 7 to 10 which in turn makes ν^* progressively less negative (or more positive) owing to the contribution of the second term in eq. (1) resulting in the expansion of the polymer chains. The higher viscosity values for $(\pm\equiv)$ PZTAN 10 in the presence of 1 equivalent NaOH [Figure 4(a)] than in its absence [Figure 4(b)] can be rationalized in terms of the equilibrium: $[10 (Z^{\pm\equiv}) + H_2O \rightleftharpoons 9 (ZH^{\pm =}) + OH^-]$; in the presence of OH^- the equilibrium is shifted towards left thereby increasing the proportion of $(\pm\equiv)$ 10, overall charge imbalance, ν^* value, and viscosity.

For pure electroneutral zwitterions (\pm) , the viscosity plots are known to be linear either in salt-free or salt-added solutions. Unlike (\pm) PZs, the viscosity plots of $(\pm -)$ 8, $(\pm =)$ 9 and $(\pm \equiv)$ 10, like cationic or anionic polyelectrolytes, remain concave upwards in salt-free water and linear in 0.1M NaCl (Figure 5). The viscosity behaviors of these polymers are thus controlled by the anionic portions of the polymers; with the increase in the charge imbalance, the viscosity values increase in the order: $8 < 9 < 10$.

Basicity Constants

Equation 3 (Scheme 2) describes the apparent basicity constants of anionic centers where $\log K_i^o = \text{pH}$ at $\alpha = 0.5$ and $n_i = 1$ in the case of sharp basicity constants. The " n_i " and $\log K_i^o$ as the respective slope and intercept were determined from the linear regression fit of pH versus $\log [(1 - \alpha)/\alpha]$. We were able to determine the basicity constants $\log K_1$ (10.74), $\log K_2$ (8.12), and $\log K_3$ (3.51) for the respective protonation of $^{2-}O_3P-X^+-PO_3^{2-}$ in $(\pm\equiv)$ (10), $^{2-}O_3P-X^+-PO_3H^-$ in $(\pm =)$ 9 and $^-HO_3P-X^+-PO_3H^-$ in $(\pm -)$ 8 (Table III). The $\log K_4$ for the protonation of $H_2O_3P-X^+-PO_3H^-$ in (\pm) PZA

7 could not be determined owing to its proximity to the value of $\log K_3$ (see Experimental). Note that basicity constant $\log K$ of any base B is the $\text{p}K_a$ of its conjugate acid BH^+ .

The $\log K_1$, $\log K_2$, and $\log K_4$ for the monomer ($\pm \equiv$) 15 were determined to be 9.78, 7.43, and 2.30, respectively (Table IV). $\log K_3$ of the monomer cannot be determined for the reason given in the experimental. The polymer's basicity constants are found to be higher than those of the monomer; the influence of the negative charges on the neighboring units increases the overall electrostatic force that encourages protonation in polymer. The basicity constants $\log K_1$ and $\log K_3$ are of "apparent"³⁹ nature ($n > 1$) as demonstrated in Figure 6 which reveals a decrease in $\log K$ with the increase in degree of protonation (α) as a direct consequence of a gradual decrease in the electrostatic field force that encourages protonation. Note that $\log K_2$ associated with the transformation of $^{2-}O_3P-X^+-PO_3H^-$ [$(\pm =)$ 9] to $^-HO_3P-X^+-PO_3H^-$ [$(\pm -)$ 8] remained almost constant ($n = 0.88$) with the change in α (Figure 6). We cannot, at this stage, offer any rationale for this observation.

Note that the highest polyelectrolyte index i.e. the highest n value of 3.06 belongs to n_3 associated with the transformation of polyzwitterion/anion $(\pm -)$ 8 to electroneutral polyzwitterions (\pm) 7 during protonation (Table III). This is a remarkable demonstration of the beneficial entropy effects⁴⁰ associated with the release of a greater number of hydrated water molecules from the repeating unit of more hydrated $(\pm -)$ 8 to the least hydrated collapsed coil conformation of (\pm) 7.

Effectiveness of PZA 7 as an Antiscalant

Smooth functioning of a desalination process is often plagued by precipitation (scale formation) of $CaCO_3$, $CaSO_4$, $Mg(OH)_2$, etc. Inhibition of the growth rate of crystal formation by anionic antiscalants like poly(phosphate)s, organophosphates, and polyelectrolytes^{41,42} is associated with their effectiveness in sequestering cations and altering the crystal morphology at the time of nucleation.^{43,44}

The reject brine in the Reverse Osmosis (RO) process has dissolved salts which precipitate in the event of exceeding their solubility limits. Antiscalant behavior of a supersaturated solution of $CaSO_4$ containing three times the concentration of the Ca^{2+} and SO_4^{2-} ions of a reject brine from a RO plant³¹ was investigated in the absence and presence of 10 ppm of PZA 7 and a commercial antiscalant (PERMATREAT® PC-191) (Figure 7). To our great satisfaction, conductivity did not decrease for about 4280 min (71.3 h), thus registering an amazing $\approx 100\%$ scale inhibition in the presence of a meager 10 ppm of PZA 7 [Figure 7(a)]. The newly developed antiscalant PZA 7 may continue to inhibit precipitation even for longer duration; however the test was abandoned after 71.3 h. Note that precipitation started immediately in the absence of antiscalant [Figure 7(c); Blank]. The commercial antiscalant maintained $\approx 100\%$ scale inhibition efficiency up to 100 min, thereafter the conductivity started to decrease gradually [Figure 7(b)]. It is worth mentioning that the residence time of reject brine in an osmosis chamber of a desalination plant is for duration of ≈ 30 min only. The optimistic result thus certifies that the additive PZA 7 is very much suitable in inhibiting calcium sulfate scale formation in RO plants. The presence of multi

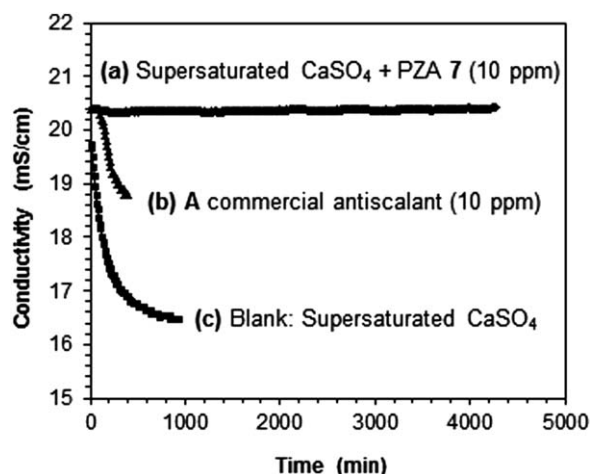


Figure 7. Precipitation behavior of supersaturated solution (3 CB) of CaSO_4 in the presence (10 ppm) and absence of PZA 7 and a commercial antiscalant.

adsorption sites on the *bis*-phosphonate motifs in PZA 7 effectively sequesters the Ca^{2+} ions to inhibit nucleation as well as crystal growth. Note that neither monomers **4** and **11** nor polymer **5** gave any effective inhibition; screening experiments based on visual inspection revealed that under the same conditions the system becomes cloudy within 1 h.

CONCLUSIONS

The work describes the synthesis and polymerization of a new cationic monomer **4**. Polymer CPE **5** represents the first example of a Butler's symmetric cyclopolymer containing two identical phosphopropyl pendants in the same repeating unit. The hydrolysis of the phosphonate ester groups resulted in the pH-responsive CPA (+) **6** which permitted to study the interesting solution properties (including solubility behavior) that involved its conversion to (\pm) PZA **7**, (\pm -) PZMAN **8**, (\pm =) PZDAN **9**, and (\pm \equiv) PZTAN **10** all having identical degree of polymerization. The solution properties were correlated to the type of charges and their densities on the polymer chain. Several apparent basicity constants of (\pm \equiv) PZTAN **10** and monomer (\pm \equiv) ZTAN **15** have been determined. PZA **7** at a meager concentration 10 ppm imparted excellent inhibition of calcium sulfate scale formation, and as such, it can be used as an effective antiscalant in Reverse Osmosis plants.

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