

## Cyclopolymerization Protocol for the Synthesis of a Poly(zwitterion-*alt*-sulfur dioxide) to Investigate the Polyzwitterion-to-Poly(anion-zwitterion) Transition

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**ABSTRACT:** The zwitterionic monomer, 3-(*N,N*-diallyl,*N*-carboethoxymethylammonio)propanesulfonate, on cocyclopolymerization with sulfur dioxide in DMSO using azoisobutyronitrile as the initiator afforded the polyzwitterion (PZ) copolymer in excellent yields. The PZ on acidic hydrolysis of the ester groups led to the corresponding polyzwitterionic acid (PZA). The pH-responsive PZA on treatment with sodium hydroxide gave the new poly(electrolyte-zwitterion) (PEZ). The solubility, viscosity behaviors, and solution properties of the salt-tolerant PZ, PZA, and PEZ were studied in detail. Like common PZs, PZ was found to be insoluble in salt-free but soluble in salt-added water. The apparent basicity constants of the carboxyl group in PEZ have been determined. As the name implies, the PEZ possesses dual type of structural feature common to both conventional anionic polyelectrolytes and PZs, and its aqueous solution behavior is found to be similar to that observed for a typical alternating anionic-zwitterionic copolymer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1394–1404, 2013

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### INTRODUCTION

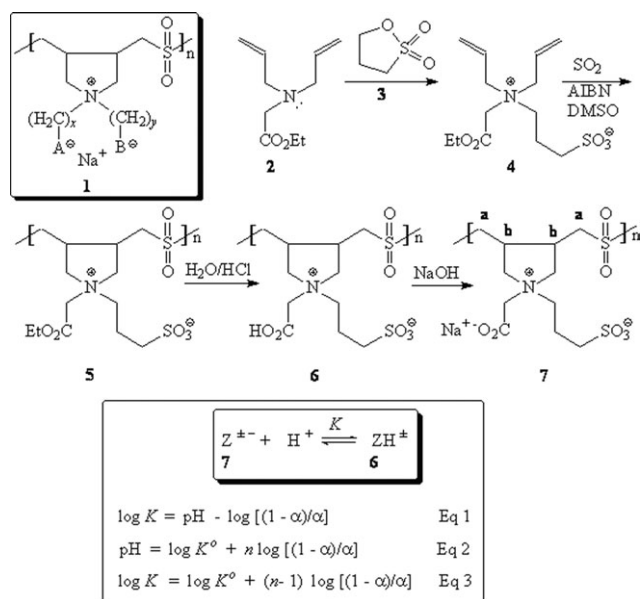
Butler's cyclopolymerization<sup>1–5</sup> as well as cocyclopolymerization of *N,N*-diallyl quaternary ammonium and amine salts with sulfur dioxide<sup>6–9</sup> led to the synthesis of a range of water-soluble cationic polyelectrolytes having quenched and unquenched nitrogen valences, respectively. The cyclopolymers containing the five-membered rings embedded into the polymer backbone are considered to have the eighth major structural feature of synthetic high polymers. These polymers are of significant scientific and technological interest; poly(diallyldimethylammonium chloride) alone has over 1000 patents and publications. Quaternary ammonium polyelectrolytes find manifold application in industrial processes and daily life. The technical applications based on Coulombic attraction between the positively charged macromolecules and negatively charged macro-ions, surfactants, etc., have resulted in different materials including membranes, modified surfaces, coated particles, etc.<sup>4,10,11</sup>

The cyclopolymerization protocol involving zwitterionic diallylammonium monomers has been an interesting avenue for the synthesis of polyzwitterions (PZs) (having charges of both algebraic signs in the same repeating units).<sup>12,13</sup> The unquenched valency of nitrogens in diallylamine salts containing sulfonate and hydrolyzable ester functionalities as pendants led to the

synthesis of a variety of pH-responsive poly sulfo-, carbo-, and polyphosphobetaines (i.e., PZs).<sup>2,3,5</sup> The pH-induced changes in the charge types and their densities in a cyclopolymer backbone have been shown to change a cationic polyelectrolyte to a PZ or a polyampholyte having repeating units containing cationic and anionic charges with or without charge symmetry.<sup>14</sup>

A polysulfobetaine (PSB) having weakly basic sulfonate group remains zwitterionic over a wide range of pH, while a polycarboxybetaine (PCB), because of the weak acid nature of the carboxylic acid group, can be rendered cationic by lowering the pH of the aqueous medium.<sup>3</sup> The pH-responsive PSBs and PCBs having unquenched nitrogens can also be changed to polyanions by neutralization of the ammonio proton.<sup>6–9</sup> The synthesis of copolyzwitterions incorporating 25 mol % carboxybetaine and 75 mol % sulfobetaine and its interesting pH-dependent solution properties have been reported.<sup>15</sup> Nearly monodisperse PZs have been synthesized by group transfer polymerization (GTP) of 2-(dimethylamino)ethyl methacrylate (DMAEMA) followed by quantitatively betainization using 1,3-propanesultone.<sup>16</sup> Well-defined sulfobetaine-based statistical copolymers of DMAEMA with *n*-butyl methacrylate were synthesized via GTP followed by betainization.<sup>17</sup>

PZs have collapsed or globular conformations in salt-free solutions due to the intragroup, intra- and interchain electrostatic



**Scheme 1.** Cyclopolymerization protocol for the synthesis of polyzwitterion and polyanion-zwitterion.

dipole–dipole attractions among the dipolar motifs. They exhibit “antipolyelectrolyte” effect which is globule-to-coil transitions in the salt-added solutions owing to the neutralization of the ionically crosslinked network in a collapsed coil conformation of the polymers.<sup>2,13,18,19</sup> The PZs containing the permanent dipole can thus be tailored for enhancement in solubility and viscosity in the presence of added salt owing to the shielding of the Coulombic (dipole–dipole) attractions.<sup>19–23</sup> The high dipole moment of PZs renders the properties of excellent polar host matrix in which only target ions can migrate.<sup>24,25</sup> The stoichiometric blends of some PZs with alkali metal salts have produced excellent matrices having high ionic conductivity.<sup>26</sup> The pH-responsive PZs, whose structure and behavior seem to mimic biopolymers, have been utilized for the development of anticarcinogenic drugs in combination with fullerenes<sup>27</sup> and improvement of the biocompatibility of various medical<sup>28</sup> and nanotechnology tools.<sup>29</sup> The unique “antipolyelectrolyte” behavior makes PZs attractive candidates for application in enhanced oil recovery, drag reduction, personal care products, cosmetics, and pharmaceuticals.<sup>30–32</sup> Numerous applications also include their uses as fungicides, fire-resistant polymers, lubricating oil additives, emulsifying agents, and bioadherent coatings.<sup>5,33–35</sup> The PZs have been utilized for efficient separations of biomolecules<sup>3</sup> and to develop procedures for DNA assay.<sup>36</sup> They have also drawn attention in the field of ion exchange; their abilities to chelate toxic trace metals (Hg, Cd, Cu, and Ni) have been exploited in wastewater treatment.<sup>2,31</sup> PZs are also used as drilling-mud additives<sup>37</sup> and for the separation of water and oil from water-in-oil emulsions.<sup>38</sup>

In pursuit of pH-responsive polymers, we have recently reported<sup>39</sup> the synthesis and homocyclocopolymerization of a specialty monomer **4** (Scheme 1). We describe herein the cocyclocopolymerization of **4** with SO<sub>2</sub> that would lead to a polymer **7** having zwitterionic and anionic motifs in the same repeating

unit. The cyclopolymerization protocol has so far documented two such (electrolyte-zwitterion)/SO<sub>2</sub> copolymers in the literature; in both cases the anionic motifs in monomer **1** were either sulfonate ( $x = y = 3$ )<sup>40</sup> or carboxylate ( $x = 5, y = 1$ ).<sup>41</sup> The current work involves monomer **4**/SO<sub>2</sub> copolymerization that would lead to poly(electrolyte-zwitterion) (PEZ **7**) (Scheme 1).<sup>40,41</sup> To the best of our knowledge, polymer **7**, obtained via the cyclopolymerization protocol, would represent the first example of this class of PEZ having different anionic motifs (carboxylate and sulfonate) in the same repeating unit as well as a SO<sub>2</sub> spacer in the polymer backbone. The synthesis of the new pH-responsive polymers would provide an opportunity to study PZ **5** to PEZ **7** transition involving polymers having identical degree of polymerization. The effects of backbone stiffening SO<sub>2</sub> spacer on the solution properties of these polymers will be measured and compared with those of the corresponding homocyclocopolymer.<sup>39</sup>

## EXPERIMENTAL

### Physical Methods

Elemental analysis was carried out on a Perkin Elmer Elemental Analyzer Series II Model 2400. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer. The <sup>13</sup>C and <sup>1</sup>H NMR spectra of the polymers have been measured in D<sub>2</sub>O (using HOD signal at 4.65 and dioxane <sup>13</sup>C peak at  $\delta$ 67.4 as internal standards) on a JEOL LA 500 MHz spectrometer. Viscosity measurements have been made by Ubbelohde viscometer (having viscometer constant of 0.005718 cSt/s at all temperatures) using CO<sub>2</sub>-free water under N<sub>2</sub> in order to prevent CO<sub>2</sub> absorption that may affect the viscosity data. For the potentiometric titrations, the pH of the solutions was recorded using a Corning pH Meter 220. Molecular weights of some of the synthesized polymers were determined by gel permeation chromatography (GPC) analysis using Viscotek GPCmax VE 2001. The system was calibrated with nine polyethylene oxide monodispersed standards at 30°C using two Viscotek columns G5000 and G6000 in series.

### Materials

2,2'-Azobisobutyronitrile (AIBN) from Fluka AG (Buchs, Switzerland) was purified by crystallization from a chloroform–ethanol mixture. Dimethylsulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg). For dialysis, a Spectra/Por membrane with a molecular weight cut-off (MWCO) value of 6000–8000 was purchased from Spectrum Laboratories, Rancho Dominguez, CA. All glassware were cleaned with deionized water. Zwitterionic monomer **4** was prepared in 82% yield by heating an equimolar mixture of *N,N*-diallyl-*N*-carboethoxymethylamine (**2**)<sup>42</sup> and 1,3-propanesulfone (**3**) in acetonitrile (130 cm<sup>3</sup> for 0.13 mol amine) at 72°C for 72 h. M.p. (methanol/acetone/diethyl ether) 162–163°C.

### General Procedure for the Copolymerization of the Monomer **4** with SO<sub>2</sub> and Physical Characterization of PZ **5**

All the polymerizations were carried out under the conditions described in Table I. In a typical experiment (entry 4), SO<sub>2</sub> (20 mmol) was absorbed in a solution of monomer **4** (20 mmol) in DMSO (5.8 g). The required amount of the initiator (AIBN) (60 mg) was then added under N<sub>2</sub> and the closed flask was stirred using magnetic stir-bar at 60°C for 24 h. Within 2 h, the

**Table I.** Copolymerization of Monomer 3 with Sulfur Dioxide

| Entry no. | Monomer (mmol) | DMSO (g) | Initiator <sup>a</sup> (mg) | Yield (%) | $[\eta]^b$ (dL g <sup>-1</sup> ) | $\overline{M}_w$   | (PDI) <sup>c</sup> |
|-----------|----------------|----------|-----------------------------|-----------|----------------------------------|--------------------|--------------------|
| 1         | 10             | 2.3      | 30                          | 82        | 0.164                            | –                  | –                  |
| 2         | 10             | 3.6      | 30                          | 95        | 0.186                            | –                  | –                  |
| 3         | 10             | 5.8      | 30                          | 85        | 0.140                            | $1.01 \times 10^5$ | 2.34               |
| 4         | 20             | 5.8      | 60                          | 90        | 0.188                            | $1.33 \times 10^5$ | 2.47               |

Polymerization reactions were carried out in DMSO using equimolar mixture of monomer **4** and SO<sub>2</sub> at 60°C for 24 h.

<sup>a</sup>Azobisisobutyronitrile, <sup>b</sup>Viscosity of 1–0.25% polymer solution in 0.5N NaCl at 30°C was measured with Ubbelohde Viscometer ( $K = 0.005718$ ).

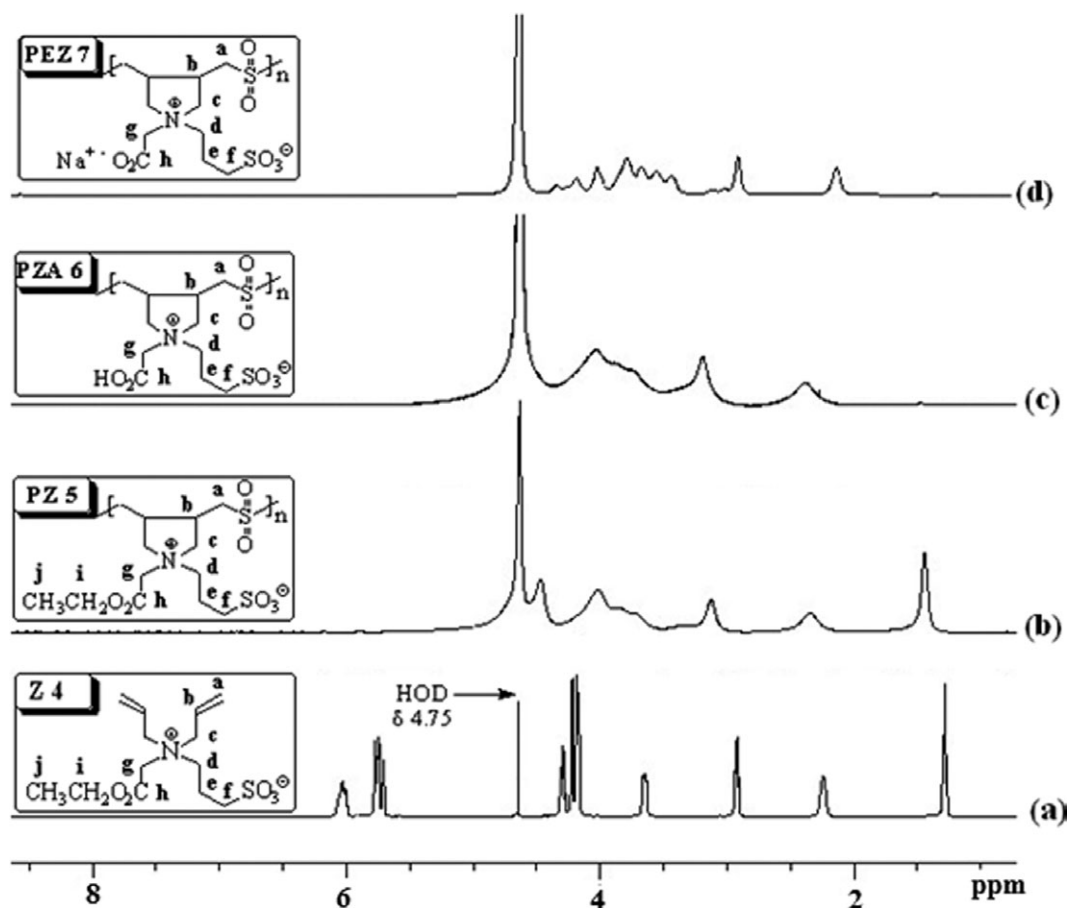
<sup>c</sup>polydispersity index.

magnetic bar stopped stirring, and the initial reaction mixture became a solid mass of white polymer. At the end of the elapsed time, the hard polymeric mass was crushed to powder, soaked in methanol, filtered, and washed with liberal excess of hot (50°C) methanol to ensure the complete removal of the unreacted monomer (as indicated by <sup>1</sup>H NMR). Copolymer **5** was then dried under vacuum at 60°C to a constant weight. The onset of thermal decomposition (closed capillary): the color changed to brown at 255°C and turned to black at 270°C. (Found: C, 42.0; H, 6.5; N, 3.7; S, 16.9%. C<sub>13</sub>H<sub>23</sub>NO<sub>7</sub>S<sub>2</sub> requires C, 42.26; H, 6.27; N, 3.79; S, 17.36%);  $\nu_{\max}$  (KBr): 3755, 3441, 2983, 1744, 1646, 1471, 1417, 1311, 1216, 1127, 1037, 909, 860, 729, 602 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra of PZ **5** are displayed in Figures 1 and 2.

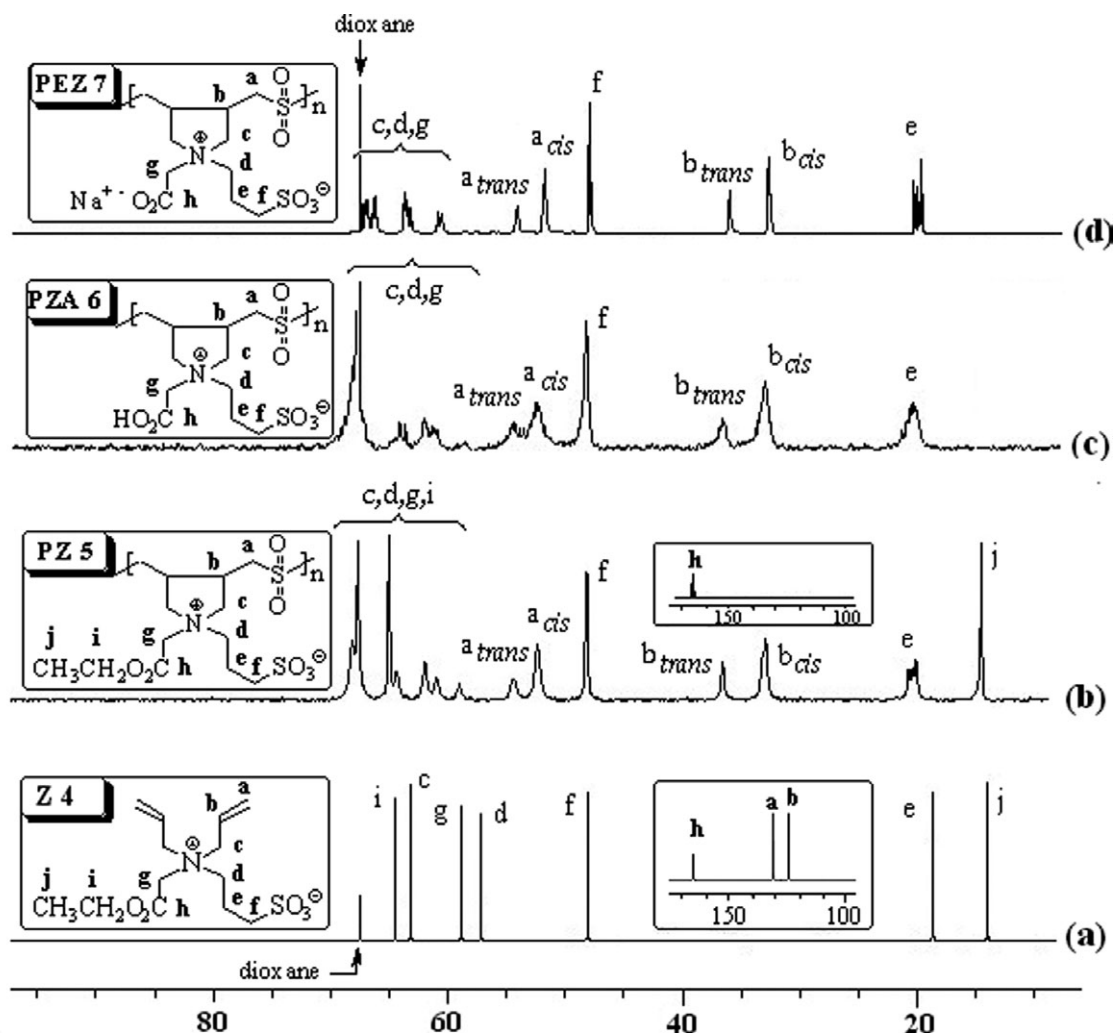
For the determination of molecular weights, the polymer PZ **5** was analyzed using an aqueous solution of 0.5N NaCl as the eluant. Refractive index and viscometer detectors were used to detect polymers. The molecular weight ( $\overline{M}_w$ ) and PDI of some of the polymers are given in Table I.

#### Acid Hydrolysis of PZ **5** to Poly(zwitterion acid) **6** with Aqueous HCl

PZ **4** (3.0 g, 8.12 mmol) (entry 4, Table I) was hydrolyzed in a 6M HCl (60 mL) at 53°C for 48 h. The homogeneous mixture was cooled to room temperature and dialyzed against deionized water (to remove HCl) for 24 h. During dialysis, precipitation of the polymer occurred immediately and its amount increased with time. The resulting mixture containing the solid was freeze dried to obtain



**Figure 1.** <sup>1</sup>H NMR spectrum of (a) **4** in D<sub>2</sub>O, (b) **5** in (D<sub>2</sub>O + NaCl), (c) **6** (D<sub>2</sub>O + NaCl), and (d) **7** in D<sub>2</sub>O.



**Figure 2.**  $^{13}\text{C}$  NMR spectrum of (a) 4 in  $\text{D}_2\text{O}$ , (b) 5 in  $(\text{D}_2\text{O} + \text{NaCl})$ , (c) 6  $(\text{D}_2\text{O} + \text{NaCl})$ , and (d) 7 in  $\text{D}_2\text{O}$ .

poly(zwitterion acid) (PZA 6) as a white solid (2.36 g, 92%). The polymer was found to be insoluble in water but soluble in the presence of HCl. The onset of thermal decomposition (closed capillary): the color changed to dark brown at  $275^\circ\text{C}$  and to black at  $285^\circ\text{C}$ ; (Found: C, 38.4; H, 5.8; N, 3.9; S, 18.5%.  $\text{C}_{11}\text{H}_{19}\text{NO}_7\text{S}_2$  requires C, 38.70; H, 5.61; N, 4.10; S, 18.78%);  $\nu_{\text{max}}$  (KBr): 3620, 3451, 2973, 2930, 2372, 1741, 1643, 1461, 1423, 1310, 1213, 1129, 1034, 700, 729,  $578\text{ cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PZA 6 are displayed in Figures 1 and 2.

#### Basification of PZA 6 to PEZ 7

To a sample of 6 (derived from entry 4, Table I) (0.688 g, 2.02 mmol) was added NaOH (0.163 g, 4.1 mmol) in  $2.5\text{ cm}^3$  deionized water. After stirring for 5 min, PEZ 7 was precipitated in methanol. Filtration and washing with excess methanol gave the white polymer 7 which was dried under vacuum at  $55^\circ\text{C}$  to a constant weight (0.68 g, 93%). The onset of thermal decomposition (closed capillary): the color changed to brown at  $280^\circ\text{C}$  and black at  $305^\circ\text{C}$ . (Found: C, 36.1; H, 5.2; N, 3.7; S, 17.4%.  $\text{C}_{11}\text{H}_{18}\text{NNaO}_7\text{S}_2$  requires C, 36.36; H, 4.99; N, 3.85; S, 17.65%);  $\nu_{\text{max}}$  (KBr): 3446, 3031,

2970, 2921, 1628, 1460, 1405, 1304, 1204, 1131, 1044, 913,  $731\text{ cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PEZ 7 are displayed in Figures 1 and 2.

**Table II.** Solubility<sup>a,b</sup> of PZ 5, PZA 6, and PEZ 7

| Solvent            | $\epsilon$ | PZ 5 | PZA 6 | PZA 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       | -    | -     | -     |

<sup>a</sup>2% (wt/wt) of polymer-water mixture (solution) was made after heating the mixture at  $70^\circ\text{C}$  for 1 h and then cooling to  $23^\circ\text{C}$ .

<sup>b</sup>“+” indicates soluble, “-” indicates insoluble, and “ $\pm$ ” indicates partially soluble.

**Table III.** Critical Salt Concentration for Aqueous Solutions of PZ 5 at 23°C

| Salt               | CSC (M) |
|--------------------|---------|
| LiCl               | 0.32    |
| NaCl               | 0.29    |
| KCl                | 0.31    |
| KBr                | 0.047   |
| KI                 | 0.0060  |
| NH <sub>4</sub> Cl | 0.32    |
| CaCl <sub>2</sub>  | 0.25    |
| HCl                | 0.38    |

### Solubility Measurements and Cloud Point Titration in Aqueous Salt Solutions

A 1% (wt/wt) mixture of PZ 5, PZA 6, and PEZ 7 in a solvent was heated to 70°C for 1 h and then cooled to 23°C. The results of the solubility are shown in Table II.

The critical (minimum) salt concentration (CSC) required to promote water solubility of PZ 5 (entry 4, Table I) at 23°C was measured by titration of a 1% wt/wt polymer solution at sufficiently high salt concentration with deionized water. The accuracy of the CSC values, obtained by visual determination of the first cloud point, was approximately ±2%. The CSC values are reported in Table III.

### Potentiometric Titrations

The potentiometric titrations were carried out as described elsewhere using a solution of certain mmol (Table IV) of PZA 6 in 200 cm<sup>3</sup> of salt-free water or 0.1N NaCl.<sup>7</sup> The log *K* of the carboxyl group is calculated at each pH value by the Henderson–Hasselbalch eq. (2) (Scheme 1) where degree of protonation  $\alpha$  is the ratio  $[ZH^+]_{eq}/[Z]_o$ ,  $[Z]_o$  is the initial concentration of repeating units in PZA 6, and  $[ZH^+]_{eq}$  is the concentration of the protonated species at the equilibrium. The titration with

HCl was carried out in the presence of 1.5–2.5 cm<sup>3</sup> of 0.1036N NaOH to attain the required values of the  $\alpha$ . In this case  $[ZH^+]_{eq} = [Z]_o + C_{H^+} - C_{OH^-} - [H^+] + [OH^-]$ , where  $C_{H^+}$  and  $C_{OH^-}$  are the concentration of the added HCl and NaOH, respectively;  $[H^+]$  and  $[OH^-]$  at equilibrium were calculated from the pH value.<sup>43,44</sup> The polyelectrolytes having apparent basicity constants could be described by the eq. (3) (Scheme 1) where  $\log K^o = \text{pH}$  at  $\alpha = 0.5$  and  $n = 1$  in the case of sharp basicity constants. The linear regression fit of pH vs.  $\log [(1 - \alpha)/\alpha]$  gave  $\log K^o$  and “*n*” as the intercept and slope, respectively. Simultaneous protonation of the two basic sites ( $\text{CO}_2^-$  and  $\text{SO}_3^-$ ) is least likely since the basicity constant for the  $\text{SO}_3^-$  group ( $\log K: \sim -2.1$ ) is less than that of the  $\text{CO}_2^-$  ( $\log K: \sim +3$ ) group by almost five orders of magnitude.

## RESULTS AND DISCUSSIONS

### Synthesis of the Copolymers

Zwitterionic monomer 4/SO<sub>2</sub> underwent cocyclopolymerization in the presence of initiator AIBN to give PZ 5 in excellent yields. The results of the polymerization under various conditions are given in Table I. As evident from the table, changing the amount of solvent DMSO does not have any appreciable effects on the yield or intrinsic viscosity  $[\eta]$  of PZ 5. ( $\pm$ ) PZ 5 upon hydrolysis in 6M HCl afforded ( $\pm$ ) PZA 6 which on treatment with equivalent amount of NaOH gave ( $- \pm$ ) PEZ 7, so named as a result of having both anionic electrolytes as well as zwitterionic motifs in the same repeating unit. Polymers 5–7 were observed to be stable up to around 260°C.

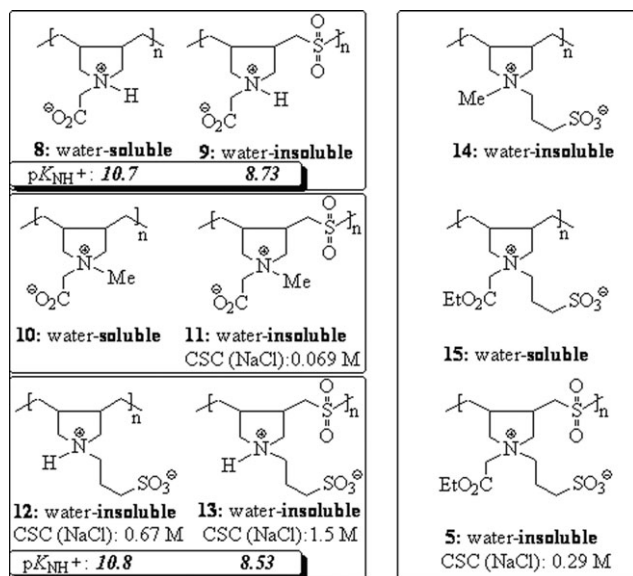
### Infrared and NMR Spectra

The IR spectrum of 5–7 indicates the presence of sulfonate group by its strong characteristic bands at  $\sim 1200 \text{ cm}^{-1}$  and  $\sim 1040 \text{ cm}^{-1}$ . The two strong bands at  $\sim 1300 \text{ cm}^{-1}$  and  $\sim 1130 \text{ cm}^{-1}$  were assigned to the asymmetric and symmetric vibrations of SO<sub>2</sub> unit. Absorption at  $\sim 1740 \text{ cm}^{-1}$  was attributed to C=O stretch of COOEt and COOH of 5 and 6. The symmetric

**Table IV.** Experimental Details for the Protonation of the Polymers PZA 6 (ZH<sup>±</sup>) at 23°C in Salt-Free Water and 0.1 N NaCl

| Run   | ZH <sup>±</sup> (mmol) | C <sub>T</sub> <sup>a</sup> (mol dm <sup>-3</sup> ) | $\alpha$ -range | pH-range  | Points <sup>b</sup> | Log <i>K</i> <sup>c</sup> | <i>n</i> <sup>c</sup> | R <sup>2</sup> <sup>d</sup> |
|---|------------------------|---|-----------------|-----------|---------------------|---------------------------|-----------------------|-----------------------------|
| Polymer in salt-free water <sup>e</sup>   |                        |   |                 |           |                     |                           |                       |                             |
| 1   | 0.3536                 | 0.09930   | 0.17–0.60       | 4.98–3.04 | 24                  | 3.43                      | 2.19                  | 0.9988                      |
| 2   | 0.2910                 | 0.09930   | 0.17–0.53       | 5.01–3.27 | 22                  | 3.46                      | 2.24                  | 0.9959                      |
| 3   | 0.2352                 | 0.09930   | 0.14–0.53       | 5.23–3.28 | 20                  | 3.38                      | 2.29                  | 0.9960                      |
| Average   |                        |   |                 |           |                     | 3.42 (4)                  | 2.24 (5)              |                             |
| log <i>K</i> <sup>f</sup> = 3.42 + 1.24 log [1- $\alpha$ ]/ $\alpha$ For the reaction: z <sup>±</sup> + H <sup>+</sup> $\rightleftharpoons$ zH <sup>±</sup> |                        |   |                 |           |                     |                           |                       |                             |
| Polymer in 0.1N NaCl <sup>e</sup>   |                        |   |                 |           |                     |                           |                       |                             |
| 1   | 0.2847                 | 0.09930   | 0.20–0.51       | 3.74–2.95 | 23                  | 2.95                      | 1.21                  | 0.9887                      |
| 2   | 0.2302                 | 0.09930   | 0.15–0.50       | 3.81–2.91 | 20                  | 2.90                      | 1.20                  | 0.9962                      |
| 3   | 0.1878                 | 0.09930   | 0.14–0.52       | 4.11–3.05 | 22                  | 3.08                      | 1.27                  | 0.9958                      |
| Average   |                        |   |                 |           |                     | 2.98 (9)                  | 1.23 (4)              |                             |
| log <i>K</i> <sup>f</sup> = 2.98 + 0.23 log [1- $\alpha$ ]/ $\alpha$ For the reaction: z <sup>±</sup> + H <sup>+</sup> $\rightleftharpoons$ zH <sup>±</sup> |                        |   |                 |           |                     |                           |                       |                             |

<sup>a</sup>Concentration of titrant HCl, <sup>b</sup>Number of data points from titration curve, <sup>c</sup>Values in the parentheses are standard deviations in the last digit, <sup>d</sup>R = Correlation coefficient, <sup>e</sup>Titration was carried out in the presence of 2.0–3.0 cm<sup>3</sup> of 0.1031 N added NaOH to attain the required values of the  $\alpha$ , <sup>f</sup>log *K*<sub>i</sub> = log *K*<sup>o</sup> + (*n* - 1) log [(1 -  $\alpha$ )/ $\alpha$ ].



**Scheme 2.** Solubility behavior,  $pK_{NH^+}$ , and CSC of several polyzwitterions.

and anti-symmetric stretching of  $COO^-$  in **7** appeared at  $1405\text{ cm}^{-1}$  and  $1628\text{ cm}^{-1}$ , respectively.

The  $^1H$  and  $^{13}C$  NMR spectra of monomer **4** and polymers **5–7** are shown in Figures 1 and 2, respectively. The alkene and carbonyl carbons of **4** and **5** are shown in the insets of Figure 2(a,b). The carbonyl carbon of **6** and **7** appeared at 167.68 and 169.58, respectively [not shown in Figure 2(c,d)]. The absence of any residual alkene proton or carbon signal in the spectra of **5–7** indicated the chain transfer process for the termination reaction involving the macroradical abstracting the labile allylic hydrogen of the monomer.<sup>45–47</sup> The absence of the signals for the methyl protons and carbon of  $OCH_2CH_3$  at  $\sim\delta 1.4$  [Figure 1(c)] and  $\delta 14.5$  [Figure 2(c)], respectively, ascertained the complete hydrolysis of the ester functionality in **5** giving **6**. Integration of the relevant peaks in the  $^{13}C$  NMR spectrum yielded a 75/25 *cis-trans* ratio of the ring substituents at  $C_{b,b}$  (Scheme 1) and is similar to that observed for polymers derived from quarternary ammonium salts.<sup>3,48–50</sup>

### Solubility in Protic and Nonprotic Solvents

All three polymers are found to be insoluble in majority of the protic as well as nonprotic solvents of very high dielectric constants ( $\epsilon$ ) (Table II). However, the polymers are soluble or partially soluble in formamide having a very high dielectric constant of 111. Polymers ( $\pm$ ) **5** and ( $\pm$ ) **6** are insoluble in salt-free water as expected of PZs while the anionic/zwitterionic polymer ( $-\pm$ ) **7** is water-soluble thereby ascertaining its electrolytic nature.

### Polymer Structure Versus Solution Properties

Polybetaines (i.e., PZs) are in general expected to be insoluble in salt-free water, but a considerable number of PCBs and PSBs were reported to be water-soluble.<sup>51–54</sup> A number of PCBs (**8**,<sup>51</sup> **10**<sup>52</sup>) and PSBs (**12**,<sup>55</sup> **14**,<sup>56</sup> **15**<sup>39</sup>) as well as their copolymers with  $SO_2$  (**5**, **9**,<sup>42</sup> **11**,<sup>57</sup> **13**<sup>58</sup>) are listed in Scheme 2. The PCBs **8** and **10** having carboxyl  $pK_a$  of  $> 2$  are reported to be water-soluble, while the corresponding  $SO_2$ -copolymers **9** and **11** are insoluble

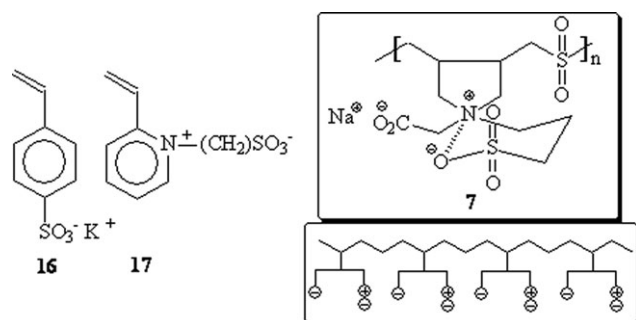
in water. Among the listed PSBs (**5**, **12–15**), all are reported to be insoluble in water except **15**. The difference in the solubility behavior between **14** and **15** has been rationalized in terms of steric factor<sup>13,39,59</sup>; more crowded surroundings around the charges in **15** owing to the presence of bulkier  $CH_2CO_2Et$  group (vs. Me group **14**) do not encourage effective intra- or intermolecular Coulombic interactions.<sup>39</sup> The reported solubility data thus reveals that the presence of  $SO_2$  and  $SO_3^-$  leads to stronger zwitterionic interactions and insolubility (Scheme 2). In a recent article, simulation results show that the negative charges in carboxybetaines interact with water molecules stronger than the sulfobetaines.<sup>60</sup> The respective carboxyl and sulfonyl  $pK_a$  values of  $> 2$  and  $-2.1$  ascertain that the negative charges on the carboxyl moiety are expected to be less dispersed, hence more hydrated<sup>51–53</sup> and as such tend to exhibit weaker Coulombic interactions with the cationic charges on nitrogens<sup>54</sup> thus imparting solubility in salt-free water. The sulfobetaine moiety on the other hand, having more dispersed charges and thus being less hydrated, is able to exert stronger zwitterionic interactions. While a critical NaCl concentration of  $0.67\text{ M}$  is required to shield the zwitterionic interactions and induce solubility of sulfobetaine **12**,<sup>55</sup> a much higher concentration of  $1.5\text{ M}$  NaCl is required to disrupt zwitterionic interactions and promote solubility of PSB **13**<sup>58</sup> having  $SO_2$  moieties on the polymer backbone (Scheme 2). The influence of  $SO_2$  units is manifested by the difference of two orders of magnitude in the  $pK_a$  values of PSBs **12** and **13** (Scheme 2). The presence of electron-withdrawing  $SO_2$  units is expected to disperse the positive charges on nitrogens thus making them less hydrated thereby augmenting the Coulombic interactions with the sulfonate groups. The dipole moment of sulfobetaine moiety (in triethylammonio-propanesulfonate)<sup>61</sup> and carbobetaine (in alanine)<sup>62</sup> has been reported to be 23.0 D and 15.9 D, respectively. The chain collapse may thus be attributed to the greater dipole-dipole intramolecular interactions between the sulfobetaine moieties.

### Critical Salt Concentrations

As discussed above, the presence of  $SO_2$  is responsible for the stronger zwitterionic interactions in PZ **5** which is insoluble in salt-free water while the corresponding homopolymer **15** is water-soluble. The PZ **5** is found to be soluble in aqueous solutions of HCl and in the presence of variety of salts including divalent  $Ca^{2+}$  which is known to precipitate polyelectrolytes. For various salts, the critical minimum CSCs required to promote water solubility of PZ **5** at  $23^\circ\text{C}$  are shown in Table III. For a common anion,  $Cl^-$ , the cations do not show any appreciable effect on the solubility power; this is expected since the fairly large hydration shell of the cations due to their large charge/radius ratio cannot approach close enough to neutralize the highly dispersed charge on the sulfonate group.<sup>23</sup> The anions, on the other hand, are known to play a more dominant role in deciding the solubility behavior by effectively shielding the cationic charges on the nitrogens; for a common cation,  $K^+$ , the sequence of increasing solubilizing power was found to be:



The concentration of KCl required to promote water solubility was found to be 6.6 and 52 times more than that of KBr and



Scheme 3. Conformation of an (anion-zwitterion) motif.

KI, respectively. The increased solubilizing power of KI is attributed to the most polarizable (soft) iodide anion's ability to effectively neutralize the ionic crosslinks. Note that the CSC (NaCl) required for promoting solubility of PZ 5 and 13 were found to be 0.29 and 1.5M, respectively; the considerable difference is attributed to the less crowded cationic charges in the later (Scheme 2).

PZA 6 is found to be insoluble in salt-free water; a 1 wt % mixture remained insoluble at 23°C even after stirring overnight. However it was soluble while stirring in the presence of 0.025N NaCl. It is worth mentioning that the CSC of PZA 6 cannot be determined since dilution of its solution in 0.025N NaCl with salt-free water did not produce any turbidity while the turbidity returned by adding a few drops of 6M HCl. The interesting solubility behavior of PZA 6 may be attributed to the presence of zwitterionic moiety and the undissociated CO<sub>2</sub>H in the solid state. Once the polymer is dissolved in the presence of the added salt (NaCl), dissociation of the carboxyl groups introduces the anionic motifs and keeps it in the solution state as the (±) PZA 6 moves towards (− ±) PEZ 7 (i.e., [(..N<sup>±</sup>...CO<sub>2</sub>H (6) ⇌ ..N<sup>±</sup>...CO<sub>2</sub><sup>−</sup> (7) + H<sup>+</sup>]). Dilution with salt-free water further increases the CO<sub>2</sub>H dissociation and solubility. The addition of HCl, however, shifts the equilibrium from soluble (− ±) PEZ 7 toward insoluble (±) PZA 6.

The sulfonyl moiety in PEZ 7 is expected to be involved in zwitterionic interactions as depicted in Scheme 3 leaving out the carboxyl moiety to impart anionic character and solubility.

### Viscosity Measurements

Viscosity data for the polymers 5–7, having almost identical degree of polymerization, were evaluated by the Huggins equation:  $\eta_{sp}/C = [\eta] + k [\eta]^2 C$ . The dependency of viscosity of (±) PZ 5, (±) PZA 6, and (− ±) PZA 7 in aqueous solution containing various concentration of NaCl are shown in Figure 3(a–c), respectively. An increase in the intrinsic viscosity with increasing NaCl concentration explains antipolyelectrolyte behavior of PZ 5 [Figure 3(a)]. The increasing dissociation of the CO<sub>2</sub>H groups in (±) PZA 6 with dilution keeps the viscosity curve concave upwards [Figure 3(b)]. Based on the carboxyl pK<sub>a</sub> value of 2.98 in 0.1N NaCl (*vide infra*), its percent dissociation in 1, 0.5, 0.25, and 0.125 g/dL solutions has been calculated to be 17, 23, 31, and 41, respectively. Therefore, increasing introduction of CO<sub>2</sub><sup>−</sup> anionic motifs would expand the polymer backbone hence increase the viscosity values with dilution.

Note that the viscosity values of (±) PZA 6 remain almost similar with further increase in the salt concentration to 0.5N and 1N NaCl [Figure 3(b)]. The carboxyl pK<sub>a</sub> in PZA 6 has been determined to be 3.42 and 2.98 in salt-free and 0.1N NaCl, respectively (*vide infra*); percent dissociation of CO<sub>2</sub>H groups is thus expected to increase with the increase in the ionic strength of the medium. The near constancy of the viscosity values with the salt concentrations may be attributed to the opposite effect of increasing dissociation to CO<sub>2</sub><sup>−</sup> and increased shielding of the charges on the viscosity values; while the dissociation increases the viscosity, shielding decreases it.

Figure 3(c) displays the viscosity behavior of PEZ (− ±) 7 in salt-free water and various concentrations of NaCl. In salt-free water, the viscosity plot is typical of a polyelectrolyte, i.e. concave upwards. The presence of an extra negative charge per repeating unit in anionic-zwitterionic (− ±) PEZ 7 makes its viscosity behavior as typical of an anionic polyelectrolyte. The viscosity behavior of PZ 5, PZA 6, and PEZ 7 having identical degree of polymerization are compared in Figure 3(d) in 1.0N NaCl. Polymer (− ±) 7 having completely dissociated CO<sub>2</sub><sup>−</sup> anions has higher viscosity values than that of (±) 6 having partially dissociated CO<sub>2</sub>H groups. Note that under extreme dilution the viscosity values of both the polymers are expected to be identical.

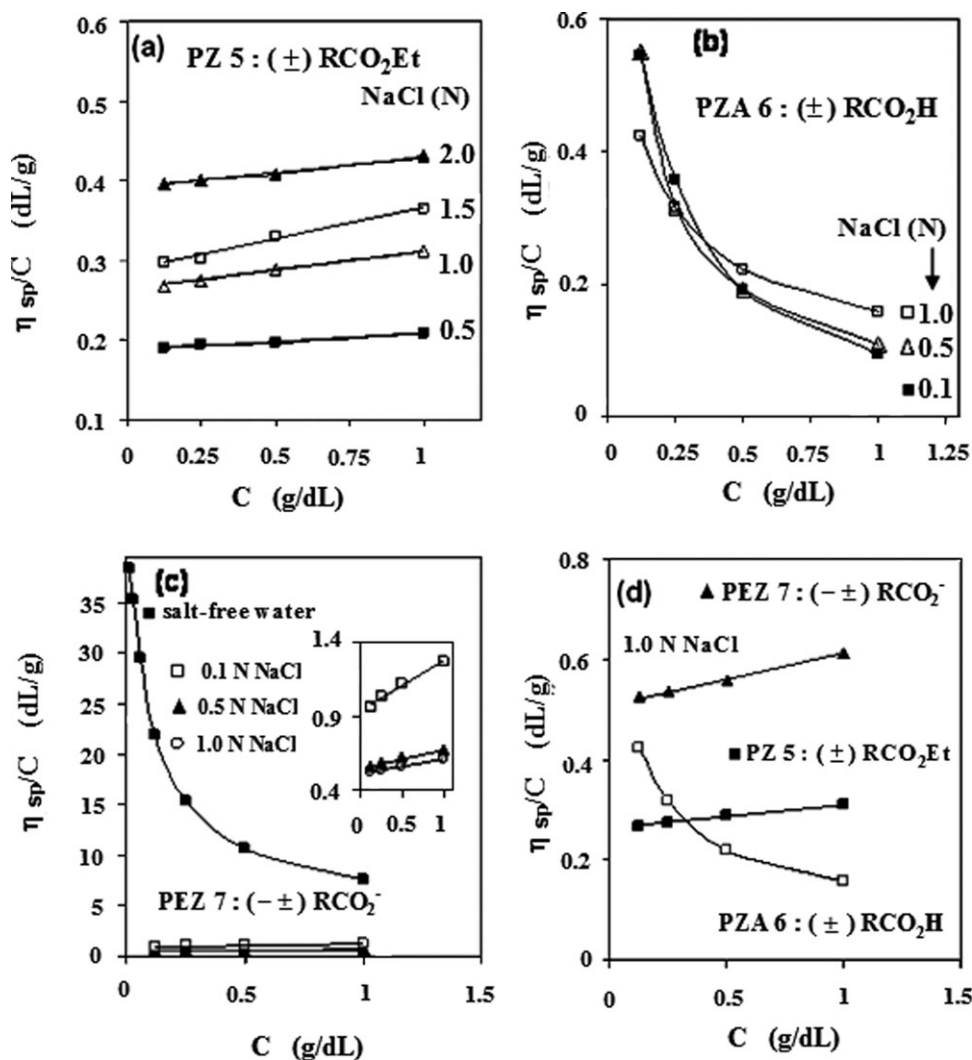
The dependency of viscosity of PEZ (− ±) 6 in aqueous solution containing various concentration of NaOH in 0.1N NaCl is shown in Figure 4(a). The viscosity increases with increasing amount of NaOH which gradually transforms (±) PEZ 6 to (− ±) PEZ 7.

The intrinsic viscosity  $[\eta]$  of (− ±) PEZ 7 in 0.1N NaCl, KCl, KBr, KI at 30°C was determined to be 0.935, 0.956, 0.965, and 0.980 dL/g, respectively [Figure 4(b)]. It is known that the intrinsic viscosity of polybetaines or polyampholytes in 0.1N aqueous salt solution decreases in the order KI > KBr > KCl.<sup>23,51,55,57</sup> However, the presence of salt has an equal and opposite influence on the anionic (−) and zwitterionic (±) motifs; it helps the anionic portion to coil up and the zwitterionic part to expand. Since the viscosity of anionic polyelectrolytes is mostly independent of the effect of anions (like Cl<sup>−</sup>, Br<sup>−</sup>, etc.), more polarizable (soft) iodide anion is expected to effectively neutralize the cationic charges thereby forcing the expansion of the macromolecule so as to minimize repulsion among the more exposed negatives charges CO<sub>2</sub><sup>−</sup> and SO<sub>3</sub><sup>−</sup>.<sup>63</sup> However, this is found not to be case; the salt effect on intrinsic viscosity is found to be minimal as a result of shielding of the anionic motifs as well in a sea of cations [Figure 4(b)]. The aqueous solution behavior of PEZ 7 is found to be similar to that observed for an alternating anionic-zwitterionic copolymer derived from monomers 16 and 17 (Scheme 3).<sup>64</sup> The current PEZ 7 may also be described as an alternate anionic-zwitterionic polymer as depicted in the Scheme.

The solution behavior of polyampholytes with or without charge symmetry has been described mathematically<sup>19,65–67</sup> in terms of:

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

where  $v^*$  is the electrostatic excluded volume,  $I_B$  is the Bjerrum length,  $f$  is the total fraction of charged monomers,  $\Delta f$  is the



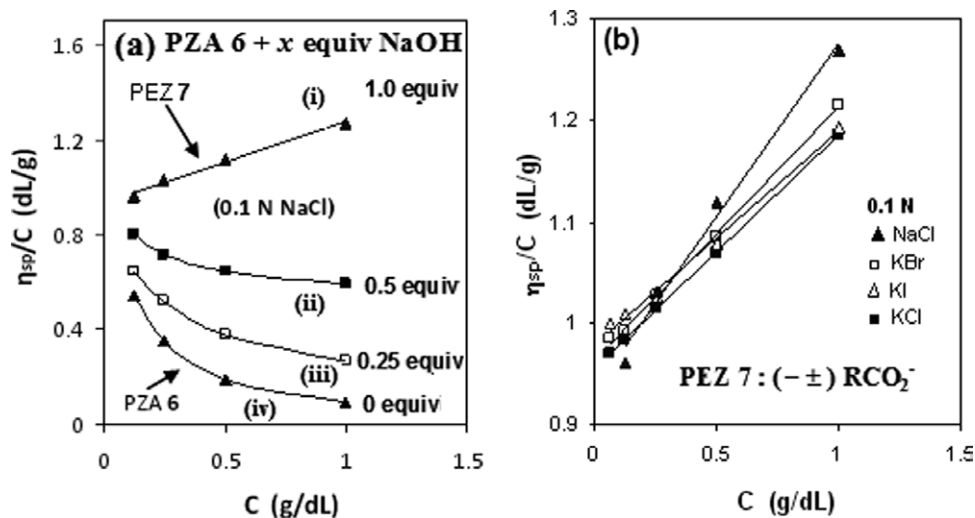
**Figure 3.** Using an Ubbelohde Viscometer at 30°C, variation of viscosity of (a) PZ 5 (from entry 4, Table I), (b) PZA 6 (derived from entry 4, Table I), and (c) PEZ 7 (derived from entry 4, Table I) with salt (NaCl) concentration. The viscosity behavior of (d) PZ 5, PZA 6, and PEZ 7 (from or derived from entry 4, Table I) in 1.0N NaCl.

charge imbalance, and  $\kappa_S$  is the Debye–Huckel screening parameter. The screening of the attractive polyampholytic and Coulombic repulsive interactions are described by the first and second term of eq. (4), respectively. Solution behavior of the electroneutral ( $\pm$ ) PZ 5 must then be described by the screening of the attractive polyampholytic interactions only since the second term of eq. (4) becomes zero as a result of  $\Delta f = 0$ . The negative electrostatic excluded volume indicates contraction to a collapsed polymer chain. In the presence of added salt NaCl, the electroneutrality of ( $\pm$ ) PZ 5 cannot be maintained since the cationic nitrogens are more effectively screened by  $\text{Cl}^-$  ions, while  $\text{Na}^+$  with its larger hydration shell cannot shield the  $\text{SO}_3^-$  to the same extent.<sup>23</sup> As a result, PZ 5 will acquire an overall anionic charge thus helping expansion of the polymer coil by making  $\nu^*$  less negative than in the absence of NaCl.

For ( $\pm$ ) PZA 6 and ( $-\pm$ ) PEZ 7,  $\Delta f \neq 0$ ; the charge imbalance is maximum for the PEZ ( $\Delta f = 0.33$ ), while it depends on the extent of dissociation in the case of the PZA. Since the

percent dissociation of  $\text{CO}_2\text{H}$  (i.e.,  $\text{RCO}_2\text{H} \rightleftharpoons \text{RCO}_2^- + \text{H}^+$ ) in 0.1N NaCl for 1, 0.5, 0.25, and 0.125 g/dL solutions of PZA 6 has been determined to be 17, 23, 31, and 41, respectively, the corresponding  $\Delta f$  values are calculated as 0.078, 0.10, 0.13, and 0.17. The increasing importance of the second term in eq. (4) with decreasing polymer concentration thus leads to the expansion of polymer coil. This correlates directly with the viscosity data in Figure 3(b) i.e., the increase of viscosity values with the decrease in polymer concentration. The polymer has a higher ampholytic character at a concentration of 1 g/dL than at 0.125 g/dL. Indeed, this is corroborated by the experimental observation; a closer look at Figure 3(b) reveals that the viscosity value increases with the increase in NaCl concentration at the higher end of the polymer concentration (i.e., 1 g/dL), while it decreases at the lower end (i.e., 0.125 g/dL). At the higher end, there is an overall expansion; the expansion due to screening of the ampholytic motifs is greater than the contraction due to screening of the anionic motifs.





**Figure 4.** Using an Ubbelohde Viscometer at 30°C, variation of viscosity of (a) PZ 6 (derived from entry 4, Table I) with NaOH concentration and (b) PEZ 7 (derived from entry 4, Table I) with various 0.1N salts.

At the higher concentrations of salt (0.5N or more), the viscosity values of  $(-\pm)$  PEZ 7 remain constant as a result of the near completion of screening of both the ampholytic and anionic motifs [Figure 3(d): inset]; the electrostatic contribution to the polymer size becomes insignificant as a result of minimized importance of both terms in eq. (4) as a result of complete shielding of all electrostatic effects.

#### Basicity Constants

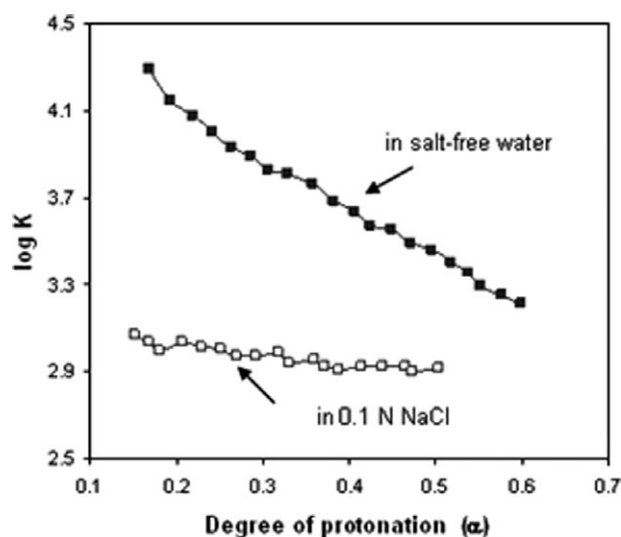
An  $n$  values of  $>1$  ascertain the decrease of basicity constant ( $K$ ) with the degree of protonation ( $\alpha$ ) of the  $\text{CO}_2^-$  in PEZ 7 thus reflecting the “apparent”<sup>68</sup> nature of  $K$  (Figure 5, Scheme 1, Table IV). The  $n$  values of 2.24 and 1.27 in salt-free water and 0.1N NaCl, respectively, reflect a stronger polyelectrolyte effect in the former medium (Table IV). After each protonation, the anionic/zwitterionic motif  $(-\pm)$  in PEZ 7 is progressively transformed to electroneutral motif  $(\pm)$  in PEZ 6; the decrease in the overall negative charge density per each repeating unit in partially protonated  $(-\pm)$  PEZ 7 thus leads to a progressive decrease in the electrostatic field force that encourages protonation. It is worth mentioning that the  $n$  value for the protonation of basic  $\text{CO}_2^-$ , which is in the  $\alpha$ -position with respect to the positive nitrogens as in **8** and **10**, is found to be  $< 1$ .<sup>28,29</sup> The  $n$  value of  $< 1$  in **8** or **10** is diagnostic of a tightly compact zwitterionic  $(\pm)$  conformation which uncoils during protonation (leading to cationic motifs) thereby allowing the protons to have easier access to the  $\text{CO}_2^-$  anions with the increase in the  $\alpha$ .<sup>69</sup> To our knowledge, this is the second example in which the  $\log K$  of the  $\text{CO}_2^-$  in an  $\alpha$ -position with respect to the positive nitrogens in an anionic/zwitterionic motif has been determined and found to be  $>1$ .

The neutralization process, which transforms the anionic motifs in  $(-\pm)$  PEZ 7 to zwitterionic motifs in  $(\pm)$  PZA 6, may be described by the viscometric transformation of Figure 4(a) (i) to 4(a) (iv) in 0.1N NaCl. Even though the corresponding transformation of  $(-\pm)$  PEZ 7 from salt-free water [Figure 3(c)] to  $(\pm)$  PZA 6 in salt-free-water cannot be achieved owing to the

insolubility of the later, it can be assumed that the magnitude of the viscosity change would be much larger than in 0.1N NaCl. Since PEZ 7 in salt-free water [Figure 3(c)] is the most expanded hence more hydrated, the greater number of water molecules are released as a result of each protonation in salt-free water than in 0.1N NaCl thereby leading to an entropy-driven<sup>70</sup> higher basicity constant and  $n$  in the former medium (Table III). The basicity constant ( $\log K^\circ$ ) of the carboxyl group was found to be 3.42 and 2.98 in salt-free water and 0.1N NaCl, respectively. Note that the carboxyl basicity constant ( $\log K^\circ$ ) in PEZ 7 is the  $\text{p}K_a$  value for the corresponding conjugate acid PZA 6.

#### CONCLUSIONS

Zwitterionic monomer **4**, synthesized by a simple reaction, underwent cocyclopolymerization with sulfur dioxide to provide the first synthetic example of a poly{(electrolyte-zwitterion)-



**Figure 5.** Plot for the apparent  $\log K$  versus degree of protonation ( $\alpha$ ) for PZA 6 in salt-free water and 0.1N NaCl.

alt-SO<sub>2</sub>} 7 having carboxylate and sulfonate pendants. The presence of SO<sub>2</sub> in the polymer backbone has been shown to have a profound effect on the solution properties of the polymer. The apparent basicity constants of the carboxyl group in 7 have been determined. The study describes a simple way to convert a PZ to a PEZ and hence gives an opportunity for the direct comparison of the solution properties of these ionic polymers having the same degree of polymerization. The solution behavior of PEZ 7 has been found to be similar to a typical alternate anionic-zwitterionic polymer.

Only a few PEZs 7, including the one presented in this work, have been documented so far in the literature. This new class of materials awaits potential applications in various fields to exploit the properties of the unique structural motifs (anionic and zwitterionic). The current challenge in the field of polymers is the construction of stimuli responsive advanced materials that have high added-value applications in drug delivery systems, separation materials, sensors, catalysts, etc. The PEZs' effectiveness in various such applications has to be tested. Currently, work is underway in our laboratory to synthesize crosslinked resins via cyclopolymerization of 4 and suitable crosslinkers so as to study the adsorption efficacy of the resulting resin that can be transformed to crosslinked polymer containing the anionic-zwitterionic functionalities.

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