Polyzwitterion-to-Polyampholyte Transition Using pH-Responsive Cycloterpolymers of Diallyldimethylammonium Chloride, (*N,N*-diallylammonio)methanecarboxylate and Sulfur Dioxide

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ABSTRACT: The cycloterpolymerizations of varying proportions of diallyldimethylammonium chloride (I) and *N,N*-Diallyl-*N*-carboethoxymethylammonium chloride (II) in the presence of sulfur dioxide afforded a series of cationic (+) polyelectrolytes (CPEs) (III) in excellent yields. CPEs, upon acidic hydrolysis of the ester functionalities of the repeating units of II, resulted in the formation of cationic/zwitterionic (+/±) polymers (IV). pH-responsive zwitterionic units of ammonioethanoate ($NH^+CH_2CO_2^-$) (having unquenched valency of nitrogen) in IV was converted to its anionic counterparts ($NCH_2CO_2^-$) by treating with equivalent amount of NaOH to give cationic/anionic i.e., ampholytic (+/−) polymers (V) with a charge symmetry or asymmetry arising out of either excess of cationic or anionic centers. The transformations of III to IV to V have thus provided an opportunity to study the effects of the polyelectrolyte-to-polyzwitterion-to-polyampholyte transitions on the solution properties of these polymers. Basicity constants of the carboxylate group ($NH^+CH_2CO_2^-$) in IV as well as the amine group ($NCH_2CO_2^-$) in V were found to be "apparent" and as such follow the modified Henderson–Hasselbalch equation. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1959–1969, 2012

Key words: water-soluble polymers; polyelectrolytes; polyampholytes; polyzwitterions; pH-responsive polymers; ionic polymers; diallylammonium monomers

INTRODUCTION

The polyampholytes (PA) have charges of both algebraic signs (+/−) distributed in the same polymer chain with or without charge symmetry, while the polyzwitterions (PZ) contain both charges (±) on the same repeating unit. PAs and PZs, which seem to mimic biopolymers like life-mediating proteins or DNA, have offered many new applications in industries dealing with textiles, medical products, and charge dispersing agents, colloids, and related materials.[1] While the polymerization of acrylamide- and acrylate-based zwitterionic monomers forms the basis of synthetic PZs, Butler's cyclopolymerization reaction of zwitterionic diallylammonium monomers or their copolymerizations with sulfur dioxide has also been an attractive method for the synthesis of PZs.[2–9] The cationic and anionic polyelectrolytes show polyelectrolytic behavior i.e., reduction in viscosity in the presence of added electrolytes (e.g., NaCl). The PAs and PZs, on the other hand, can exhibit "antipolyelectrolyte behavior"[9–13] i.e., enhancement in viscosity and solubility in the presence of added electrolytes because of the neutralization of the ionically cross-linked network in a collapsed coil conformation of the polymers.

The conformation and hydrodynamic volume of the polymers having pH-responsive functional groups in their repeating units are very sensitive to added salt and pH. In pursuit of tailoring pH-responsive polymers, we continue to cycloterpolymerize diallyldimethylammonium chloride (**1**) and *N,N*-diallyl-*N*-carboethoxymethylammonium chloride (**2**) in varying proportions with sulfur dioxide to obtain a series of cationic polyelectrolytes (CPEs) (**3**) (Scheme 1). The copolymer of **2** with SO_2[14] or its homopolymer[15] leads to CPEs, which can only be transformed to PZs. However, the incorporation of monomer **1** in the terpolymer **3** would indeed provide an avenue to transform the CPEs **3** to PA in addition to PZs. Thus, transformation of CPEs **3** to pH-responsive CPE/PZ **4** and PA **5** having unquenched nitrogen valency would allow us to study polyelectrolyte-to-polyzwitterion-to-polyampholyte transitions by changing the type of dominant charges and their densities in the terpolymer backbone.

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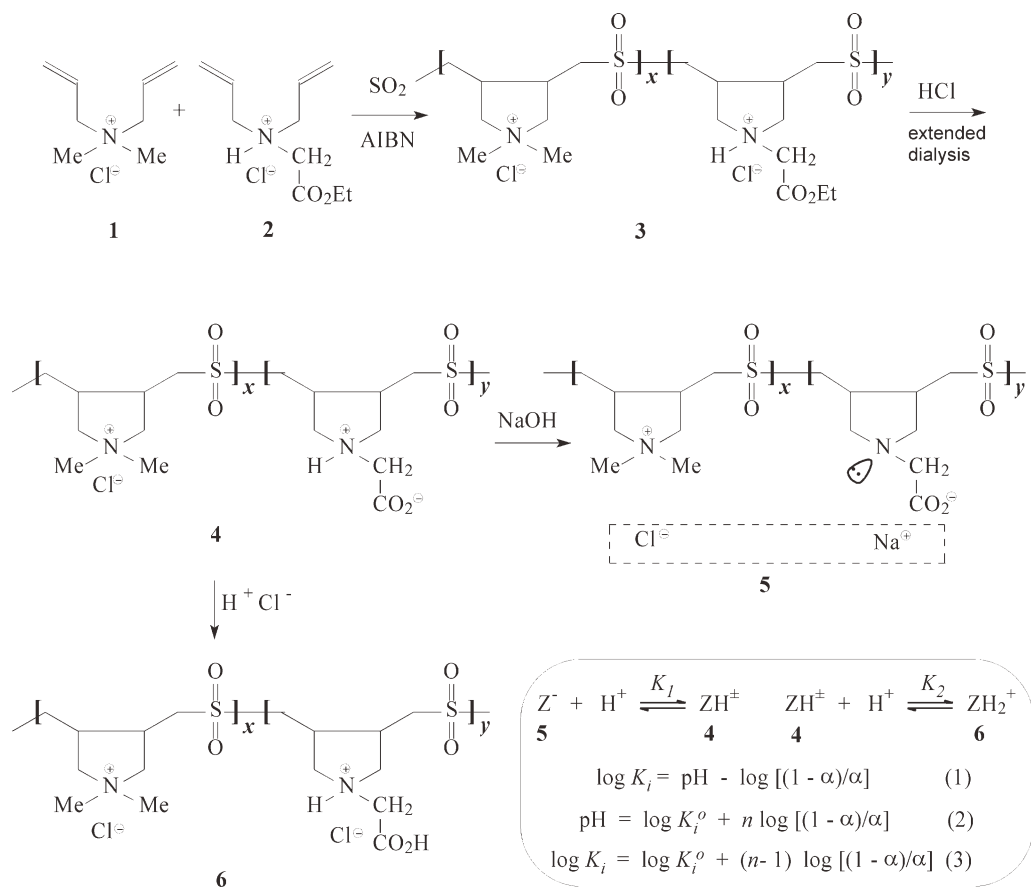
Scheme 1 Cycloterpolymerizations of diallyldimethylammonium chloride (**1**), N,N-diallyl-N-carboethoxymethylammonium chloride (**2**) and sulfur dioxide.

EXPERIMENTAL

Materials

2,2′-Azobisisobutyronitrile (AIBN) from Fluka Chemie 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). All glassware was cleaned using deionized water. For dialysis, Spectra/Por membrane with molecular weight cut-off (MWCO) of 6000–8000 was purchased from Spectrum Laboratories Inc. Diallyldimethylammonium chloride (**1**) (65 wt % in water), obtained from Aldrich, was freeze-dried and crystallized (acetone/methanol). N,N-Diallyl-N-carboethoxymethylammonium chloride (**2**) was prepared as described in a previous report.[14]

Physical methods

Melting points were recorded in a calibrated Electrothermal-IA9100- Digital Melting Point Apparatus. Elemental analysis was carried out on a *EuroVector* Elemental Analyzer Model EA3000. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer.

^{1}H spectra of the polymers were measured in D_2O on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made by an Ubbelohode viscometer (having Viscometer Constant of 0.005718 cSt/s at all temperatures) using CO_2-free water under N_2 in order to avoid CO_2 absorption that may affect the viscosity data. A gentle stream of N_2 was passed through distilled deionized water at 90°C for 15 min in order to remove dissolved gases. This water was used for viscosity measurements in salt-free and salt (NaCl, 99.9% purity) solutions.

General procedure for the polymerization reactions

All the polymerizations were carried out using conditions as described in the Table I. In a typical experiment, SO_2 was absorbed in a mixture of the monomer **1** (M_1), and **2** (M_2) in DMSO. The required amount of the initiator (AIBN) was then added under N_2 and the closed flask was stirred using magnetic stir-bar at 60°C. At this time, a sample of the polymerization mixture was analyzed by ^{1}H NMR to determine the actual feed composition. The polymerizations presented in Table I were carried out for duration of 10–15 min in order to keep the

TABLE I
Polymerization[a] of Monomers 1 (M_1)/2 (M_2)/SO_2

Entry no.	Sample[b]	M_1	M_2	Polymers quenched after $\sim$ 10–15 min			Polymers quenched after 24 h	
				Polymer[c] $M_1 : M_2$	Yield (%)	Intrinsic viscosity[d] (dL g^{-1})	Yield (%)	Intrinsic viscosity[d] (dL g^{-1})
1	**3**-M_2-0	20	0	100 : 0	6.8	0.645	77	0.645
2	**3**-M_2-25	15.0	5.0	74.8 : 25.2	8.1	0.532	93	0.554
3	**3**-M_2-32	13.6	6.4	68.9 : 31.1	7.7	0.573	82	0.592
4	**3**-M_2-38	12.5	7.5	61.8 : 38.2	7.2	0.601	75	0.622
5	**3**-M_2-50	10	10	49.5 : 50.5	7.1	0.462	79	0.472
6	**3**-M_2-60	7.5	12.5	37.3 : 62.7	5.9	0.392	76	0.380
7	**3**-M_2-75	5.0	15.0	24.8 : 75.2	6.8	0.512	96	0.532
8	**3**-M_1-0	0	20	0 : 100	5.3	0.723	76	0.723

[a] Polymerization reactions were carried out in DMSO (4.5 g) containing 20 mmol each of ($M_1 + M_2$) and SO_2 in the presence of AIBN (100 mg) at 60°C. For the polymer samples at low conversions ($\sim$ 5–8%), the polymerization was terminated usually after 10–15 min of polymerization by adding onto acetone.

[b] mol % in the feed as determined by gravimetry and corroborated by ^{1}H NMR at zero time before adding the initiator.

[c] mol % in the polymer (as determined by ^{1}H NMR).

[d] Viscosity of 0.5–0.0625 g/dL polymer solution of **3**-M_2 in 0.1N NaCl at 30°C was measured with a Ubbelohde Viscometer ($K = 0.005718$).

conversion below 10% so as to avoid any compositional drifts. The polymerizations were terminated by adding onto acetone. Table I also represents the polymerizations run for 24 h at 60°C. Within hours, the magnetic bar stopped stirring, and initial reaction mixture (slurry) became a solid mass of white polymer. At the end of the elapsed time, the polymerization was terminated by adding onto acetone. The hard polymeric mass was crushed to a powder, soaked in acetone, and filtered to obtain CPEs **3**, which were then dried under vacuum at 60°C to constant weights and stored in a desiccator.

Acidic hydrolysis of the cationic polyelectrolytes 3

A solution of the cationic polyelectrolyte e.g., **3**-M_2-50 (10.57 g, Entry 5, Table I, 24 h run) in 6M HCl (70 cm^3) was stirred at 50°C for 60 h (or until the hydrolysis of the ester group was complete as indicated by the absence of the methoxy proton signals in the ^{1}H NMR spectrum). The solution of the polymer was then dialyzed against deionized water for the removal of HCl. The polymer solution, when placed in the dialysis tube, showed immediate precipitation; however, within 1 h it showed some solubility, and in 2 h, the solution became transparent indicating complete solubility. After complete removal of HCl (monitored by AgNO$_3$ test), the resulting solution was then freeze dried to obtain **4**-M_2-50 (8.5 g, 85.3%). Hydrolysis of the polymer **3**-M_2-25 using procedure as described earlier, followed by dialysis and freeze drying, afforded **4**-M_2-25 in 87% yield.

The acid hydrolysis product of **3**-M_2-75 was insoluble in the reaction mixture. After dialysis, the suspension of the polymer was freeze dried to give **4**-M_2-75 (88%). The polymer was not soluble in salt-free water, gave a cloudy solution in 0.6N NaCl, and clear solution in 1N NaCl.

Basification of 4

To a solution of the **4**-M_2-50 (4.00 g) in 1N NaCl (20 mL), a solution of 1N NaOH (18 mL) was added in small portions. The basified solution was immediately dialyzed for 28 h. The resulting solution was freeze dried to give **5**-M_2-50 (3.30 g, 97%). The polymers **4**-M_2-25 and **4**-M_2-75 were basified as follows: a calculated amount ($\sim$ 3 mmol) of each polymer was added with stirring to 2 mL H$_2$O containing excess NaOH (about 2 equivalents of the M_2 repeating units). The homogenous solution was added to a stirring methanol. The solid polymers **5**-M_2-25 and **5**-M_2-75 were separated by filtration and repeatedly washed with methanol. Finally, the polymers were dried under vacuum at 60°C to constant weights.

Infrared spectra, thermal decomposition, and elemental analyses of the polymers

Infrared spectra

The polymer M_2-50 displayed the presence of the following absorption bands in the IR spectrum:

3-M_2-50 (Entry 5, Table I): ν_{max} (KBr) 3415, 2968, 2638, 1743, 1636, 1476, 1384, 1309, 1240, 1129, 1017, 848, 750, and 509 cm^{-1}.

4-M_2-50: ν_{max} (KBr) 3414, 3023, 2961, 1628, 1473, 1399, 1305, 1127, 644, and 513 cm^{-1}.

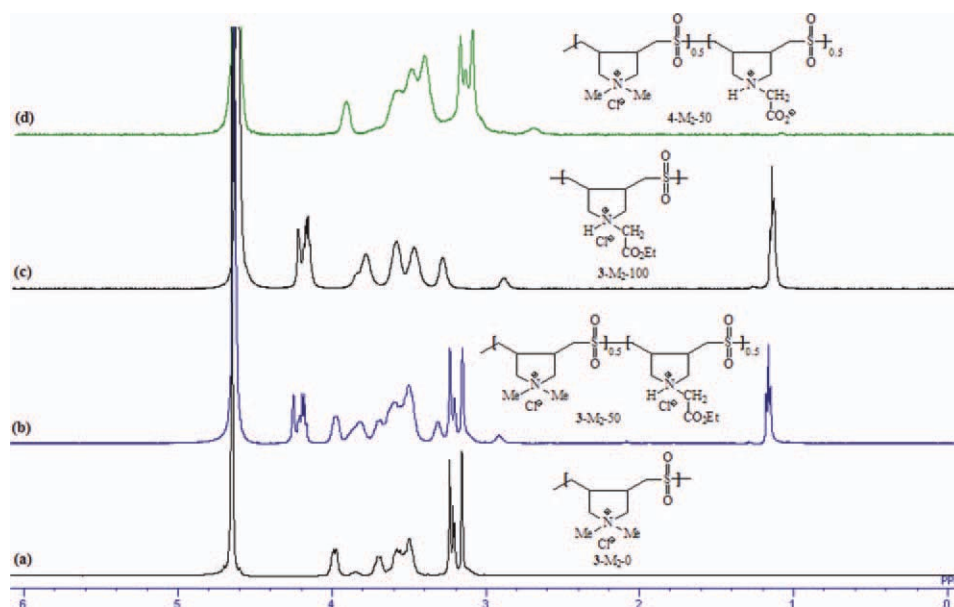**5**-M_2-50: ν_{max} (KBr) 3414, 3039, 2973, 2915, 1606, 1474, 1392, 1302, 1126, 1040, 664, and 514 cm^{-1}.

Figure 1 ^{1}H NMR spectrum of (**a**) **3**-M$_2$-0, (**b**) **3**-M$_2$-50, (**c**) **3**-M$_2$-100, and (**d**) **4**-M$_2$-50 in D$_2$O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal decomposition

The onset of thermal decomposition for the polymers (Closed capillary):

3-M$_2$-0: the color changed to light brown at 260°C, brown at 265°C and black (with volume expansion) at 293°C.

3-M$_2$-50: the color changed to light brown at 230°C, brown (with volume expansion) at 238°C, and black at 265°C.

3-M$_2$-100: 232–250°C (decomposed, turned brown).[14]

4-M$_2$-50: the color changed to light brown at 225°C, and brown at 235°C, volume expanded at 255°C, and it turned black at 278°C.

5-M$_2$-50: the color changed to light brown at 218°C, brown (with volume expansion) at 255°C, and black at 285°C.

5-M$_2$-100: 240–250°C (decomposed, turned brown, charred at 280°C).[14]

Elemental analyses

The elemental analyses ascertained the mole ratio of $(M_1 + M_2)$: (SO$_2$) as 1 : 1. The elemental analyses supported the compositions of the copolymers as determined by ^{1}H NMR spectroscopy (*vide infra*). The analyses for M$_2$-50 samples of **3** [(C$_8$H$_{16}$ClNO$_2$S)$_{0.5}$(C$_{10}$H$_{18}$ClNO$_4$S)$_{0.5}$], **4** [(C$_8$H$_{16}$ClNO$_2$S)$_{0.5}$(C$_8$H$_{13}$NO$_4$S)$_{0.5}$], and **5** [(C$_8$H$_{16}$NO$_2$S)$_{0.5}$(C$_8$H$_{12}$NO$_4$S)$_{0.5}$] were as follows (the numbers in parentheses represent calculated values): **3** M$_2$-50: C, 41.8% (42.45%); H, 6.9% (6.77%); N, 5.4% (5.57%); S, 12.3 % (12.75%). **4**-M$_2$-50: C, 42.8% (43.20%); H, 6.7% (6.56%); N, 6.1% (6.30%); S, 14.0 % (14.41%). **5**-M$_2$-50:

C, 46.9% (47.27%); H, 7.3% (7.01%); N, 6.7% (6.89%); S, 15.1% (15.77%). The other polymers also gave appropriate elemental analyses.

Terpolymer compositions

The terpolymers were synthesized by varying the feed ratio of **1** and **2**. Figure 1 (a–d) displays the ^{1}H NMR spectra of **3**-M$_2$-0, **3**-M$_2$-50, **3**-M$_2$-100, and **4**-M$_2$-50. The incorporation of the monomers was calculated using integration of ^{1}H NMR signals. The signal at δ 1.17 ppm, having an integrated area of A, was assigned to the 3 methyl protons of the carboethoxymethylammonium chloride unit (M_2). The remaining 14 protons of the M_2 and the entire 16 protons of the other monomeric unit M_1 appeared in the range δ 2.8–4.2 ppm having an area of B. Subtracting the contribution of the 14 protons belonging to M_2 (i.e., $14 \times A/3$) from the integration B, and dividing by 16 gives the integration area (C) corresponding to a single proton of M_1.

$$C = \frac{B - (14 \times A/3)}{16}$$

The compositions of the polymers were determined using:

$$\text{mol\% } M_1 = \frac{C}{C + A/3} \times 100$$

where C is the area of a single proton of M_1, while $(C + A/3)$ represents the combined areas for a single proton of M_1 and M_2.

TABLE II
Solubility Behavior[a]

Entry no.	Sample	Water-solubility		
		3	4	5
1	M_2-0	+	NA[b]	NA[b]
2	M_2-25	+	+	+
5	M_2-50	+	+	+
7	M_2-75	+	−	+
8	M_2-100	+	−	+

[a] One percent polymer mixture in water heated to 70°C for 30 min then cooling to room temperature. '+' indicates soluble,' – ' indicates insoluble.
[b] Not applicable since it does not have the carboxyl units.

Solubility in aqueous solutions

The solubility behavior of **3**, **4**, and **5** is reported in Table II. The **4**-M_2-75 was found to be insoluble in salt-free water; however it was soluble in the presence of NaCl. The critical (minimum) salt concentration (CSC) of NaCl required for promoting water-solubility of polymer **4**-M_2-75 at 23°C was determined to be 0.6N.

Potentiometric titrations

The potentiometric titrations were carried out at 25°C. A gentle stream of N_2 was passed through distilled deionized water at 90°C for 15 min for the removal of dissolved gases. This water was used for titration in salt-free and salt (NaCl, 99.9% purity) solutions and viscosity measurements. For each titration, 200 cm^3 of 0.1N NaCl solution containing a weighed amount (usually ca. 0.24–0.57 mmol) of CPE/PZ **4**-M_2-50 was used. The solution was titrated at 25°C with either 0.1157N NaOH or 0.1015N HCl delivered by a burette under N_2. After each addition of the titrant (0.1–0.25 cm^3), the solution was stirred briefly with a magnetic stir bar under N_2. The pH of the solution was recorded with a Corning 220 pH meter.

The protonation constants of the amine nitrogen (log K_1) and CO_2^- (log K_2) were calculated at each pH value by the well-known Henderson–Hasselbalch Equation 1 (Scheme 1) where degree of protonation (α) is the ratio $[ZH^\pm]_{eq}/[Z]_o$. The detailed procedure for the determination of basicity constants is reported elsewhere.[15] The typical electrolytes having apparent basicity constants could be described by the eq. (2) (Scheme 1) where log K^o = pH at α = 0.5, and $n = 1$ in the case of sharp basicity constants. The linear regression fit of pH versus log $[(1 - \alpha)/\alpha)]$ gave log K^o and "n" as the intercept and slope, respectively. Simultaneous protonation of the two basic sites is least likely since the basicity constant for the COO^- group is less than that of the amine group by at least six orders of magnitude.

The experimental details of the potentiometric titrations are summarized in the Table III. Inserting the value of pH from eq. (2) into eq. (1) leads to a modified Henderson–Hasselbalch equation [eq. (3)][16,17] (Scheme 1) where $(n - 1)$ gives a measure of the deviation of the studied polymers from the behavior of small molecules showing sharp basicity constants (for molecules having sharp basicity constants, n becomes 1).

TABLE III
Experimental Details for the Protonation of Polymer 4 ($ZH^\pm$) at 25°C in 0.1N NaCl

Run	$ZH^{\pm a}$ (mmol)	C_T [b] (mol dm^{-3})	α−range	pH−range	Points[c]	Log K_i^{od}	n_i [d]	R^{2}, [e]
Polymers 4 ($ZH^\pm$) in 0.1N NaCl								
1	0.3459 ($ZH^\pm$)	− 0.1045	0.85−0.40	7.25−8.29	17	8.41	1.61	0.9875
2	0.5730 ($ZH^\pm$)	− 0.1045	0.86−0.36	7.20−8.80	19	8.36	1.52	0.9883
3	0.2401 ($ZH^\pm$)	− 0.1045	0.83−0.31	7.35−8.90	16	8.28	1.57	0.9815
Average						8.35 (7)	1.57 (5)	
		Log K_1 [f] = 8.35 + 0.57 log $[(1 − \alpha)/\alpha]$		For the reaction : $Z^- + H^+ \rightleftharpoons ZH^\pm$				
Polymers 4 ($ZH^\pm$) in 0.1N NaCl								
1	0.2373 ($ZH^\pm$)	+0.0993	0.12−0.56	2.47−2.27	12	2.31	0.19	0.9837
2	0.3344 ($ZH^\pm$)	+0.0993	0.14−0.63	2.50−2.20	14	2.37	0.23	0.9893
Average[f]						2.34 (3)	0.21 (2)	
		Log K_2 [f] = 2.34 − 0.79 log $[(1 − \alpha)/\alpha]$		For the reaction : $ZH^\pm + H^+ \rightleftharpoons ZH_2^+$				

[a] mmol repeating units of the polymer is divided by 2 to obtain the mmol repeating unit of the pH-responsive M_2.
[b] Titrant concentration (negative and positive values indicate titrations with NaOH and HCl, respectively).
[c] Number of data points from titration curve.
[d] Values in the parentheses are standard deviations in the last digit.
[e] R = Correlation coefficient.
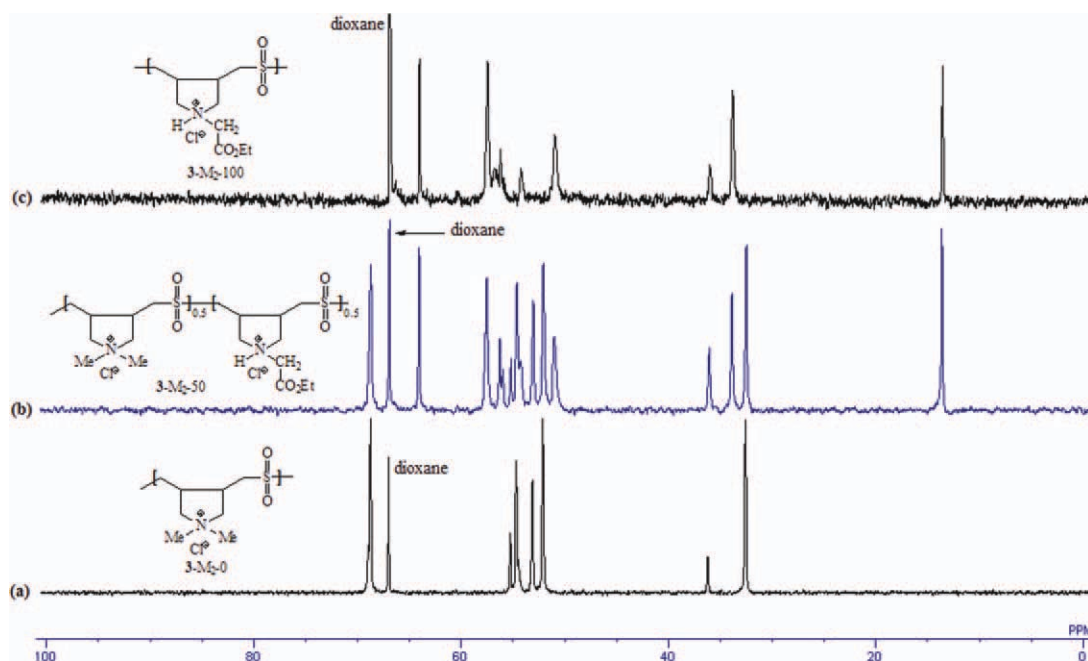[f] log K_i = log K_i^0 + (n − 1) log$[(1−\alpha)/\alpha]$.

Figure 2 ^{1}H decoupled ^{13}C NMR spectrum of (a) 3-M$_2$-0, (b) 3-M$_2$-50, and (c) 3-M$_2$-100 in D$_2$O. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Synthesis and physical characterization of the polymers

Cyclopolymerization of **1/2**/SO$_2$ in DMSO using AIBN as the initiator for 24 h gave polymer **3** in excellent yields (Scheme 1, Table I). The reactions presented in Table I also contained data for termination at <10% conversion to minimize the composition drift. Reactivity ratios "r_1" and "r_2" for the monomers **1** (M_1) and **2** (M_2) were determined by using the copolymerization eq. (4) where n and x represent the molar ratio M_1/M_2 in the polymer at <10% conversion and feed, respectively. Using the data at low-conversions in Table I, the copolymerization plot (Fig. 2) gave the values of r_1 and r_2 as 0.99 and 0.91 for the monomer pair M_1 and M_2, respectively. The reactivity ratios being similar and close to 1 ascertained the monomers to be equally reactive, and thus led to a random polymer.

$$n = \frac{r_1 x + 1}{(r_2/x) + 1} \tag{4}$$

Copolymer **3**-M$_2$-38 (entry 4, Table I), for instance, describes the polymer that contained 38.2 mol % of monomeric unit **2** (M_2)**,** while the corresponding feed was 38 mol %. In all the examples, the monomer ratios in the feed closely resemble the ratios in the polymer, thereby corroborating the results obtained from the reactivity ratio experiment. The polymer composition was determined by ^{1}H NMR spectroscopic analysis (*vide supra*).

Polymerizations given in Table I were also allowed to run for longer duration. Monomer incorporations were found to match closely with the feed ratio as expected since the polymers were obtained at high conversions ($\sim$ 90%). The sulfur analyses ascertained the mole ratio of ($M_1 + M_2$):SO$_2$ as 1 : 1 in all the polymers.

Most of the polymers (24 h samples) presented in Table I, on hydrolysis by HCl/H$_2$O followed by extended dialysis, afforded the polymers **4** having cationic (+) and zwitterionic ($\pm$) motifs of different compositions in the polymer backbone (Scheme 1). Polymers **4** on treatment with NaOH led to the formation of **5**, an interesting polymer having ampholytic; cationic and anionic motifs in the same polymer chain. Note that in the case of $x > y$, the polymer backbone will have y pair of ampholytic motifs and ($x - y$) cationic charges, while for $x < y$ would lead to x pair of ampholytic motifs and ($y - x$) anionic charges.

Infrared and NMR spectra

The IR spectrum of **3**-M$_2$-50 (Table I, entry 5) indicates the presence of the ester group by its characteristic bands at 1743 cm^{-1}. The two strong bands at 1309 and $\sim$ 1129 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO$_2$ unit. The ^{1}H spectra of **3**-M$_2$-0, **3**-M$_2$-50, **3**-M$_2$-100, and **4**-M$_2$-50, are displayed in Figure 1. The ^{13}C spectra of **3**-M$_2$-0, **3**-M$_2$-50, and **3**-M$_2$-100 are displayed in Figure 3. The absence of any residual alkene proton or carbon signal in the spectra suggested the chain transfer process[18] and/or coupling for the termination
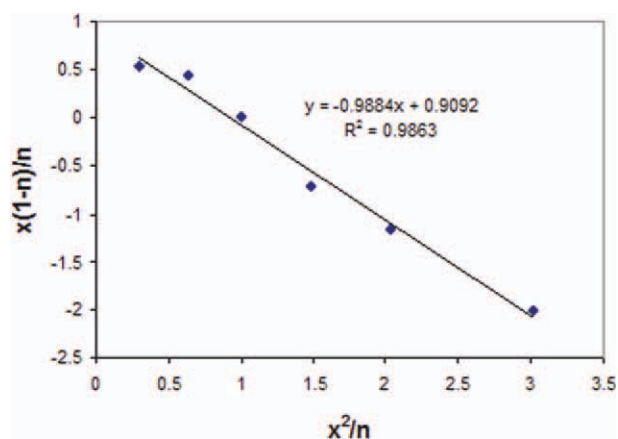
$$y = -0.9884x + 0.9092$$
$$R^2 = 0.9863$$

Figure 3 Terpolymerization reactivity plot for the monomers **1**, **2**, and SO_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction. The five-membered cyclic structure of the polymers is based on precedent literature[7,14,19–21] on cyclopolymerization reactions involving various diallyl quaternary ammonium salts. The ^{13}C spectra of **3**-M_2-0[19] and **3**-M_2-100[14] are reported in the literature. Inspection of ^{13}C signals in Figure 3(b), representing **3**-M_2-50, revealed the presence of the repeating units of both M_1 [Fig. 3(a)] and M_2 [Fig. 3(c)].

Solubility and critical salt concentrations

Intra- and inter-chain interactions in zwitterionic polymers induce the polymer backbone to adapt a globule-like collapsed coil conformation, and most often to insolubility in pure water.[22] The smaller ions of a low-molecular weight added electrolyte (e.g., NaCl) can enter and partially neutralize a portion of the inter- and intra-chain interactions, thereby allowing the collapsed coil to expand and the PZs to be soluble.[11,22] The net charge in the polymer backbone of **4** depends on the composition of M_1 and M_2; while M_2-100 is a fully zwitterionic ($\pm$) polymer whereas M_2-0 is fully cationic ($+$). The extent of the charge imbalance ($\pm$ versus $+$) dictates the overall solution properties of the polymer. For instance, the predominance of cationic **1** and zwitterionic **2** motifs in the polymers is expected to exhibit properties of a cationic polyelectrolyes and PZs, respectively. Changing the zwitterionic motifs in **4** to anionic units by treatment with y equivalent of NaOH would result in the conversion to **5** having randomly placed polyampholytic motifs in addition to excess cationic ($x > y$) or anionic charges ($x < y$) (Scheme 1). The extent of the charge asymmetry will depend on the magnitude of "x" and "y." Equal amount of cationic **1** and anionic **2** in the polymer molecule **5** is expected to give an ideal pure polyampholyte. The solubility behaviors of the polymers in water are shown in Table II. As expected, all the CPEs **3** were soluble in water, while polymers having higher proportion of zwitterionic monomer M_2 as in **4**-M_2-75 and M_2-100 were found to be insoluble in salt-free water.

Viscosity behavior

Viscosity behavior of polymers **3**-M_2-25, **4**-M_2-25, and **5**-M_2-25 in salt-free water at 30°C is presented in Figure 4. As expected, the plots became concave upwards typical of a polyelectrolyte. The polyelectrolyte effect is highly pronounced in the case of **3**-M_2-25, while it is the least in the case of **5**-M_2-25. The rationale behind these observations is attributed to the effect of charge densities and their types on the polymer backbone (Scheme 2). The **3**-M_2-25 contains 100% cationic repeating units, while **4**-M_2-25 has 75% cationic and 25% zwitterionic units. Polymer **5**-M_2-25, on the other hand, contained 50% each of polyampholyte and cationic units. As the zwitterionic or polyampholytic motifs increases, their anti-polyelectrolyte effects tend to counterbalance the polyelectrolytic effects of cationic or anionic units.

The effect of salt concentrations on the viscosity behavior of polymers **3**-M_2-25, **4**-M_2-25, and **5**-M_2-25 is shown in Figure 5. A look into Scheme 2 reveals that **3**, **4-**, and **5**-M_2-25 contain 100% cationic, 75 : 25 cationic/zwitterionic and 50 : 50 cationic/ampholytic repeating units, respectively. As expected, cationic **3**-
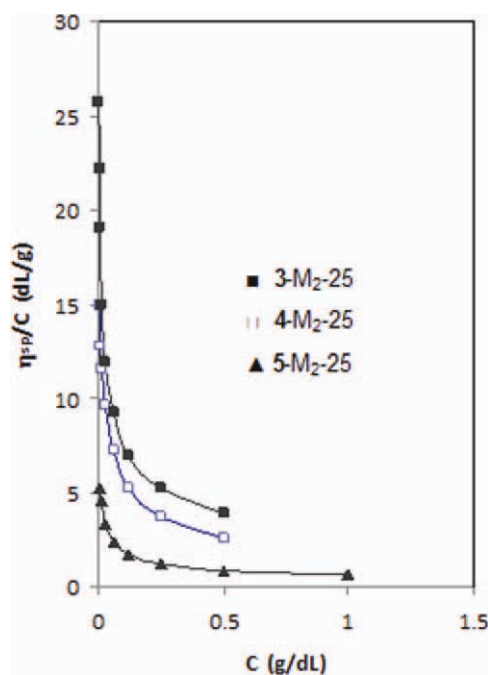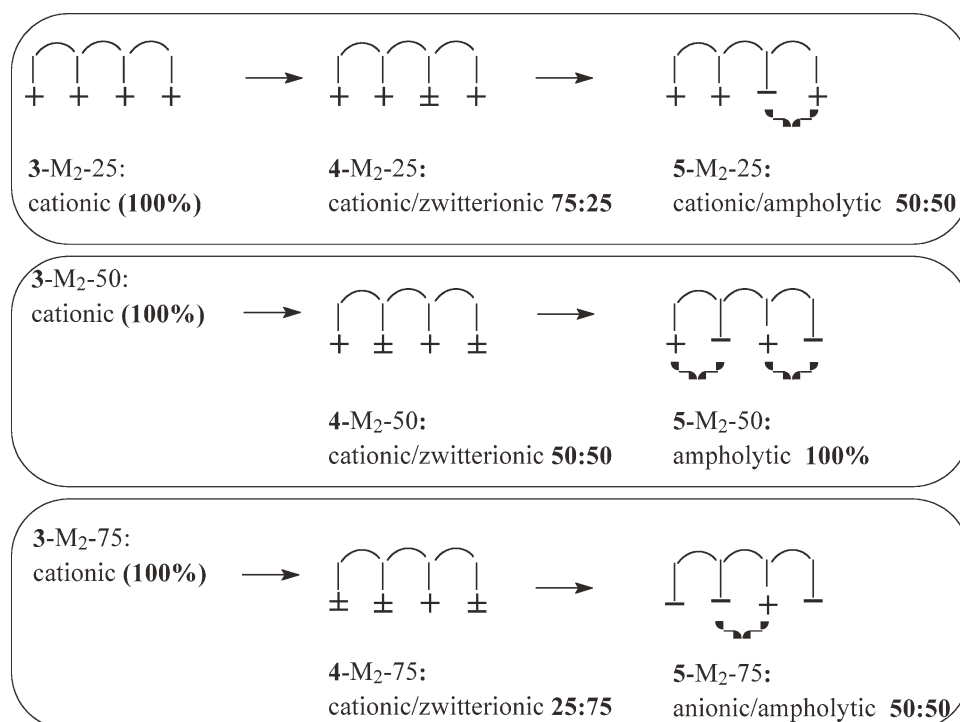

Figure 4 Viscosity behavior of polymers **3**-M_2-25, **4**-M_2-25, and **5**-M_2-25 in salt-free water at 30°C using an Ubbelohode viscometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2 Transformations of polyelectrolytes-to-polyzwitterions-to-polyampholytes.

M_2-25 as well as 75 : 25 cationic/zwitterionic **4**-M_2-25 displayed marked polyelectrolytic effect as evidenced by a decrease in the viscosity at a higher salt concentration of 0.5N NaCl. As expected, completely cationic **3**-M_2-25 has higher viscosity values than **4**-M_2-25. For the **5**-M_2-25, increase of salt concentration has a minimal effect on the viscosity values; this is attributed to the nearly equal opposing effects of

equal proportion of cationic and ampholytic motifs on the viscosity.

Figure 6 displays the viscosity behavior of polymers **3**-M_2-50, **4**-M_2-50, and **5**-M_2-50 in salt-free water. While the CPE **3**-M_2-50 showed polyelectrolyte effect (increase of reduced viscosities with the decrease of polymer concentration), the corresponding CPE/PZ **4**-M_2-50 also displayed polyelectrolyte effect; however, to a lesser degree since it has only 50% repeating units in the cationic while the rest is in the zwitterionic form. As anticipated, the **5**-M_2-50
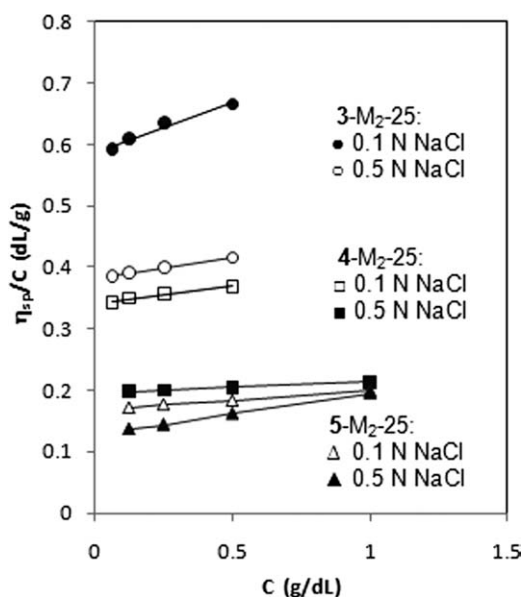

Figure 5 Viscosity behavior of polymers **3**-M_2-25, **4**-M_2-25, and **5**-M_2-25 in different concentrations of NaCl solution at 30°C using an Ubbelohode viscometer.

Figure 6 Viscosity behavior of polymers **3**-M_2-50, **4**-M_2-50, and **5**-M_2-50 in salt-free water at 30°C using an Ubbelohode viscometer.

Figure 7 Viscosity behavior of polymers 3-M_2-50, 4-M_2-50, and 5-M_2-50 in different concentrations of NaCl solution at 30°C using an Ubbelohode viscometer.
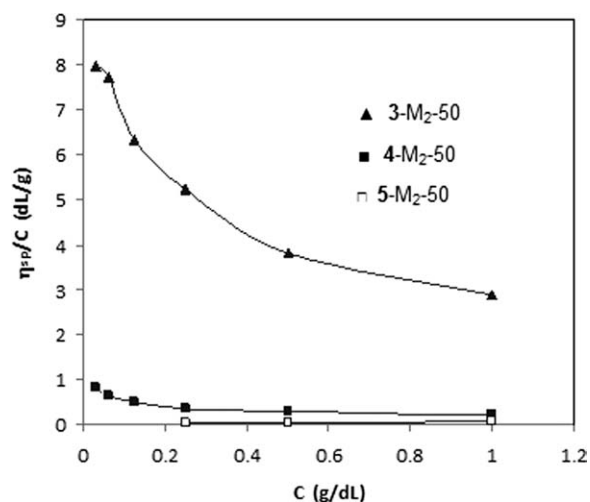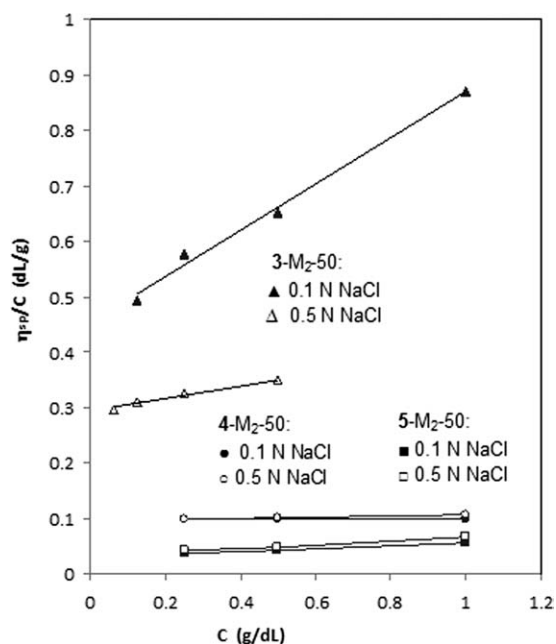
displayed linear viscosity plot akin to that of a polyampholyte since the polymer chain contains equal number of cationic and anionic centers.

The effect of salt concentrations on the viscosity behavior of polymers 3-M_2-50, 4-M_2-50, and 5-M_2-50 is shown in Figure 7. A look into Scheme 2 reveals that 3, 4-, and 5-M_2-50 contain 100% cationic, 50 : 50 cationic/zwitterionic and 100% polyampholytic repeating units, respectively. As expected, cationic 3-M_2-50 displayed marked polyelectrolytic effect as evidenced by a decrease in the viscosity at a higher salt concentration of 0.5N NaCl. For the 4-M_2-50, increase of salt concentration has a minimal effect on the viscosity values; this is attributed to the opposing effects of equal proportion of cationic and zwitterionic motifs on the viscosity.

Viscosity data in salt-free water for 3-M_2-75 and 5-M_2-75 are included in Figure 8; the data for 4-M_2-75 could not be obtained since the polymer was insoluble in salt-free water. As the polymer 3-M_2-75 is fully cationic, it showed higher viscosity values than its corresponding 5-M_2-75, which has 50% anionic and 50% ampholytic motifs in the polymer chain. The effect of salt on the viscosity values are displayed in Figure 9. Polymer 4-M_2-75, which contained 25% cationic and 75% zwitterionic motifs, was determined to have a CSC value of 0.6N NaCl (concentration of salt required to promote solubility). The polymer displayed antipolyelectrolyte effect as its viscosity was found to increase with the increase of NaCl concentration. The salt effect is minimal in 5-M_2-75 as the equal proportion of anionic and
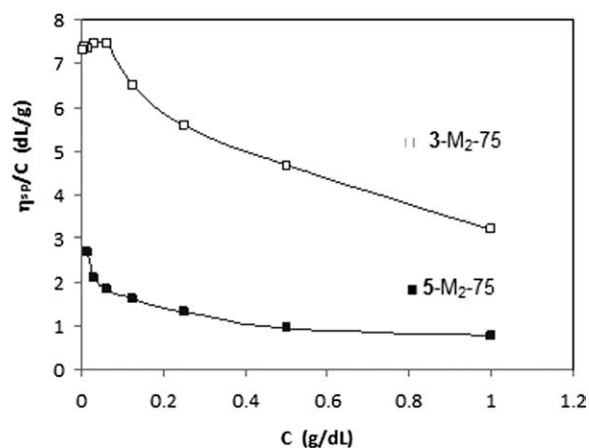

Figure 8 Viscosity behavior of polymers 3-M_2-75 and 5-M_2-75 in salt-free water at 30°C using an Ubbelohode viscometer.

ampholytic fractions have opposing effects on the viscosity.

The terpolymers prepared under similar polymerization conditions are expected to have similar molecular weights. The intrinsic viscosity values were found to be very similar (Table I), thereby ascertaining the similarity in their molecular weights. These similar molecular weights may permit approximate comparison among the polymers having variable compositions. In this context, various viscosity plots for M_2-25, M_2-50, and M_2-75 are displayed in Figure 10, which does allow meaningful assessments of the effects of charge densities and their types on the viscosity values. While the viscosity values for the anionic/
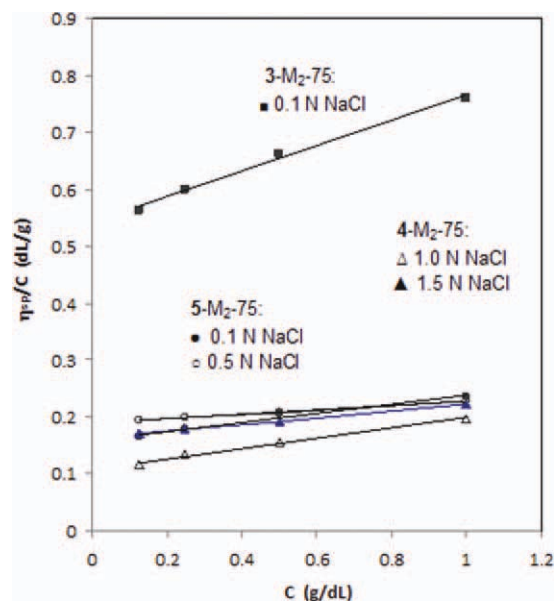

Figure 9 Viscosity behavior of polymers 3-M_2-75, 4-M_2-75, and 5-M_2-75 in different concentrations of NaCl solution at 30°C using an Ubbelohode viscometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ampholytic and cationic/ampholytic polymers each with a 50 : 50 ratio for the charge motifs were found to be very similar, the 50 : 50 cationic/zwitterionic polymer has lower viscosity value. The zwitterionic motifs thus impart more intra- and inter-chain associations to reduce the hydrodynamic volumes than the ampholytic motifs. Polymers with 100% ampholyte motif were measured to have the lowest viscosity.

Basicity constants

To gain further information on the conformational transitions, we have determined the basicity constants, K_i^o, and the corresponding n_i values relative to the protonation of the tertiary amine in polymer **5** and carboxylate in the polymer **4** in 0.1N NaCl solution. Basicity constants and the corresponding n_i values as well as the experimental details of the potentiometric titrations, are given in Table III.

The basicity constant (log K_1^o) and n_1 values of the amine group were determined to be 8.35 and 1.57, respectively, whereas the respective values for the log K_2^o and n_2 of the carboxylate (CO_2^-) were 2.34 and 0.21. Both the basicity constants K_1 and K_2 were thus found to be "apparent"[16,17,23,24] since their n values are greater than and less than 1, respectively. The K_1 and K_2 values thus decreases and increases, respectively, with the degree of protonation (α). The variation of K with the degree of protonation α is known as polyelectrolyte effect, the strength of
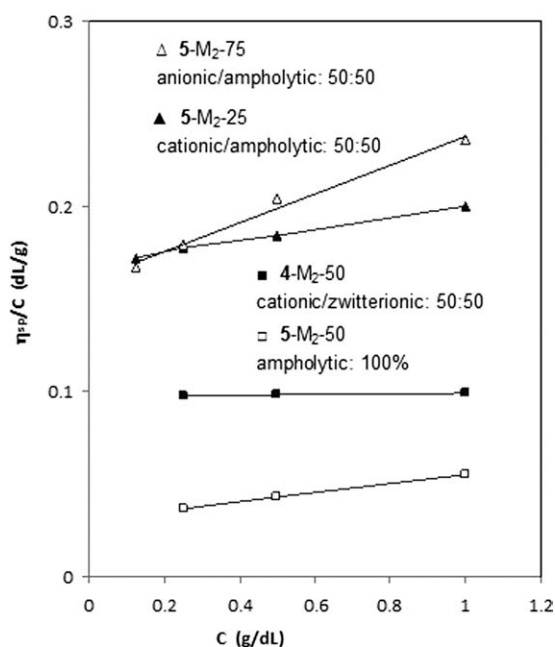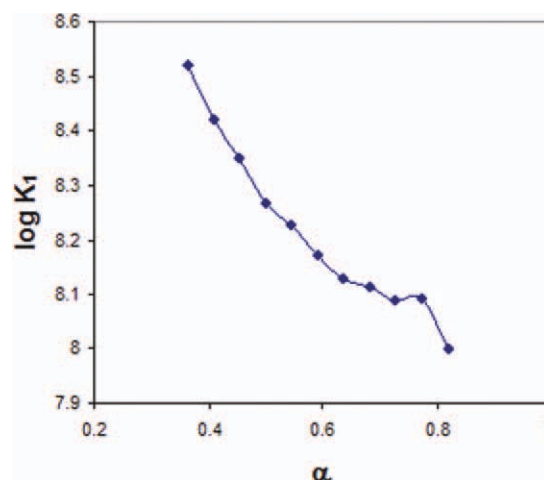
Figure 11 Plot for the apparent log K versus α for **4**-M$_2$-50 in 0.1N NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is reflected by the magnitude of n. The decrease in log K_1 values can be attributed to a decrease in the electrostatic field force as a result of decreasing overall negative charge density in the macromolecule (Fig. 11). The increase of log K_2 with the degree of protonation α, on the other hand indicates that a decrease in the number of zwitterionic groups with a consequent increase in the size of the macromolecular coil exposes the COO^- groups for easier access to protonation.

CONCLUSION

The pH-responsive repeating unit of M_2 alongside the cationic repeating unit of M_1 in **4** provided us with the latitude of varying charge types and their densities in the polymer backbone. A convenient route to **4** thus led to the synthesis of a series of new ionic polymers whose conformational behaviors are strongly influenced by the nature and the net charge on the chain. The M_2 as a sole repeating unit can lead to cationic, zwitterionic, and anionic polyelectrolyte; however, inclusion of cationic M_1 has provided an additional avenue to transform the polymer backbone to that of a polyampholyte. The work has thus provided an opportunity to compare the solution properties of the different type of interconvertible polymers (**3** → **4** → **5**) having similar degree of polymerization. The pH-induced changes in the charge types and densities in the terpolymer backbone of **4** have permitted us to study the polyelectrolyte-to-polyzwitterion-to-polyampholyte transitions.

For polymers having 50 : 50 ratio for the cationic/zwitterionic, cationic/ampholytic, or anionic/ampholytic motifs, viscosity values remained unchanged with the increase of added salt (NaCl) owing to opposing effects of cationic and ampholytic

Figure 10 Viscosity plots displaying the effect of charge types and their densities in behavior of polymers **4**-M$_2$-50, **5**-M$_2$-25, **5**-M$_2$-50, and **5**-M$_2$-75 in 0.1N NaCl solution at 30°C using an Ubbelohode viscometer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

motifs. This salt tolerance would indeed be helpful in industry where viscosification of water is of prime interest. Further studies on the use of these polymers in the construction of aqueous two-phase systems[25] as well as their potential in protein separation are currently under investigation in our laboratory. pH-Induced conformational changes would be helpful in controlling hydrodynamic volumes that may permit selective and preferred interaction with specific biomolecules thus leading to their separations.

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