

The pH-Responsive Cycloterpolymers of Diallyldimethylammonium Chloride, 3-(*N,N*-diallylammonio)propanesulfonate, and Sulfur Dioxide

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ABSTRACT: The cycloterpolymerizations of diallyldimethylammonium chloride, 3-(*N,N*-diallylammonio)propanesulfonate, and sulfur dioxide afforded a series of pH-responsive cycloterpolymers in excellent yields. The solution properties of these ionic polymers were controlled by the composition of the monomeric units; exhibiting dominance either in polyzwitterionic or cationic character. The unquenched valency of nitrogen in the monomeric units of the sulfobetaine zwitterions has permitted these cationic/zwitterionic polymers to be converted into a series of polyampholytes with a charge asymmetry arising out of excess of either the cationic or anionic centers. The water-solubility of these polymers, upon low- and high-salt (NaCl) additions has been investigated to provide

critical solution concentrations to promote water-insolubility and -solubility. A series of associating polymers of the above two monomers and SO₂ with a hydrophobic incorporation of 3–7 mol % of diallyloctadecylammonium chloride has also been synthesized. The solubility and viscosity of the hydrophobically modified polymers in the polyampholytic form were increased considerably in the presence of anionic surfactant sodium dodecyl sulfate. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3662–3672, 2011

Key words: water-soluble polymers; cyclopolymerization; polyampholytes; polyzwitterions; diallylammonium monomers; polysulfobetaines

INTRODUCTION

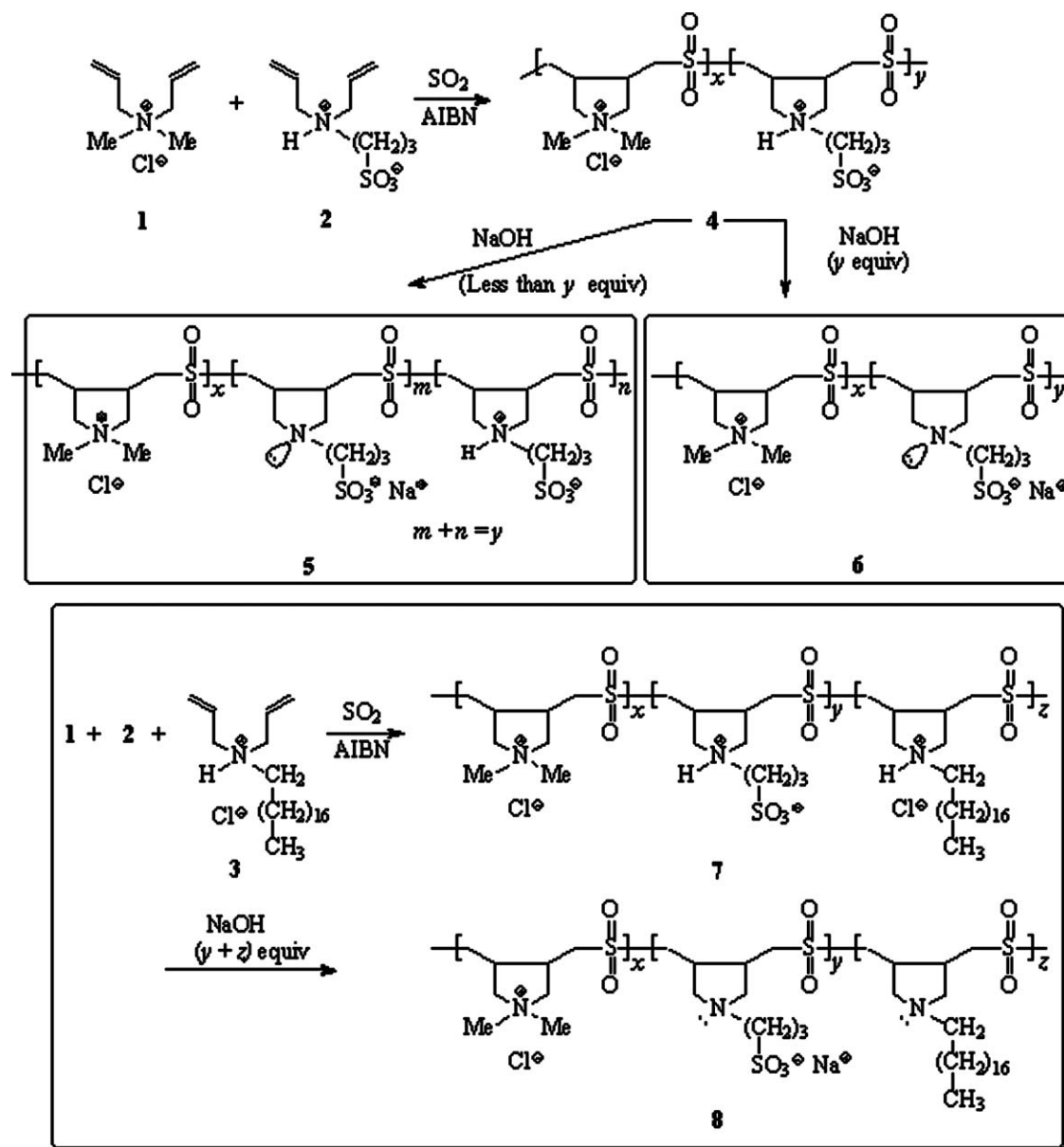
While the polymerization reaction of cationic (M^+) and anionic monomers (M^-) lead, respectively, to the cationic and anionic polyelectrolytes, the incorporation of zwitterionic monomer (M^{\pm}) having charges of both algebraic signs in the same molecular framework would provide polyzwitterions. The presence of both M^+ and M^- in the same polymer chain would, however, leads to polyampholytes with or without charge symmetry. While biopolymers like proteins or DNA mediate life processes, commercial polyampholytes and polyzwitterions, which seem to mimic biopolymers, have offered many new applications. The polymers derived from acrylamide- and acrylate-based zwitterionic monomers have been widely used in industries dealing with textiles, medical products, and charge dispersing agents, colloids, and related materials.¹ Butler's cyclopolymerization reaction of zwitterionic diallylammonium monomers or their copoly-

merizations with sulfur dioxide has been an attractive method for the synthesis of polyzwitterions.^{2–10} Polyampholytes and polyzwitterions, unlike polyelectrolytes, can exhibit "antipolyelectrolyte behavior"^{5,10–14} i.e., enhancement in viscosity and solubility in the presence of added electrolytes (e.g., NaCl) owing to the disruption of the ionically crosslinked network in a collapsed coil conformation of the polymers. The conformation of these polymers in aqueous solution is very sensitive to ionic strength, type of added salt, and pH. The methods of synthesis of acrylamide-based polyampholytes and polybetaines, and their solution behaviors are highlighted in two review articles.^{15,16} A comparative study of acrylamide-based polyampholyte terpolymers and polybetaine copolymers of low charge densities (5–10 mol %) has been reported.¹⁷ The pH- and salt-responsive viscosity behavior of the polymers has been examined to evaluate the effects of the polymer architecture and composition on the solution properties. The polyampholyte terpolymers have been shown to exhibit greater solution viscosities than the polybetaine copolymers because of their stronger intramolecular interactions and increased chain stiffness.

In pursuit of tailoring stimuli-responsive polymers, we continue to synthesize a series of cycloterpolymers 4 of cationic diallyldimethylammonium chloride (**1**), zwitterionic 3-(*N,N*-diallylammonio)propanesulfonate

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Scheme 1

(2), and sulfur dioxide (Scheme 1). We have also studied the effects of incorporation of a hydrophobic monomer, diallyloctadecylammonium chloride (3) into the polymer backbone of the hydrophilic monomers 1 and 2 in polymers 7. The unquenched nitrogen valency in the pH-responsive sulfobetaine 2 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.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization (chloroform-ethanol). Dimethylsulfoxide (DMSO),

dried overnight over calcium hydride, was distilled under reduced pressure, bp 64–65°C (4 mmHg). Sulfur dioxide (>99% purity) cylinder was purchased from Fluka (Buchs, Switzerland). Diallyldimethylammonium chloride (1) (M₁), (65 wt % in water), obtained from Aldrich, was freeze-dried and crystallized (acetone/methanol). 3-(N,N-diallylammonio)propanesulfonate (2) (M₂)¹⁸ and monomer 3 (M₃)¹⁹ were prepared as described in the literature. Sodium chloride of 99.9% purity was used to study the salt effects. All glassware were cleaned using deionized water.

Physical methods

Melting points are recorded in a calibrated Electrothermal-IA9100-Digital Melting Point Apparatus.

TABLE I
Polymerization of Monomers 1 (M₁)/2 (M₂)/3 (M₃)/SO₂

Entry No.	Sample ^a	Feed ^b M ₁ :M ₂ :M ₃	Yield (%)	Intrinsic viscosity ^c (dL g ⁻¹)
1	4-M ₂ -28	81 : 19 : 0	9.5	0.180
2	4-M ₂ -35	77 : 23 : 0	8.5	0.185
3	4-M ₂ -37	75 : 25 : 0	9.9	0.190
4	4-M ₂ -46	68 : 32 : 0	9.2	0.248 ^d
5	4-M ₂ -61	52 : 48 : 0	9.3	0.345
6	4-M ₂ -63	46 : 54 : 0	8.3	0.390
7	4-M ₂ -83	24 : 76 : 0	8.7	0.450
8	7-M ₂ /M ₃ -45 : 3.2	62 : 31 : 7	8.0	0.0568

^a mol % in the polymer (as determined by ¹H NMR).

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

^c Viscosity of 1.0–0.125 g dL⁻¹ polymer solution of 6-M₂ (i.e. 4-M₂ in the presence of 1 equivalent of NaOH) in 1.0N NaCl at 30°C was measured with a Ubbelohde Viscometer (Viscometer Constant, K = 0.005718).

^d [η] in 0.6N NaCl is 0.0863 dL g⁻¹.

Elemental analysis was carried out on a EuroVector Elemental Analyzer Model EA3000. IR spectra were recorded on a Perkin–Elmer 16F PC FTIR spectrometer. ¹H spectra of the polymers were measured in D₂O on a JEOL LA 500 MHz spectrometer. The CO₂-free water used for viscosity measurements was prepared by passing a gentle stream of N₂ through distilled deionized water at 90°C for 15. Viscosity measurements were made by an Ubbelohde viscometer using the CO₂-free water under N₂ to avoid CO₂ absorption that may affect the viscosity data. A Brookfield digital rotational viscometer with a UL adaptor or SC4-18 spindle accessories was used to measure apparent viscosities at various shear rates.

Molecular weight of some synthesized polymers was determined by GPC analysis using Viscotek GPCmax VE 2001. The system was calibrated with nine polyethylene oxide monodispersed standards, having M_ws in the range 3500–1,040,000, at 30°C using two Viscotek columns G5000 and G6000 in series.

General procedure for the terpolymerization of the monomers 1, 2, and 3 with SO₂

All the polymerizations in Tables I and II were carried out in DMSO (10.5 g) containing 30 mmol each of (M₁+M₂+M₃) and SO₂ in the presence of AIBN (150 mg) at 60°C. In a typical experiment, SO₂ was absorbed in a mixture of the monomer 1 (M₁), 2 (M₂), and 3 (M₃) in DMSO. The initiator was then added under N₂, and the mixture in the closed flask was stirred using magnetic stir-bar at 60°C. The polymerizations presented in Table I were carried out for duration of 15–20 min to keep the conversion

below 10%. However, Table II represents the polymerizations run for 24 h. At the end of the elapsed time, the hard polymeric mass was crushed to a powder, soaked in 1 : 1 acetone/methanol, filtered, and washed with liberal excess of hot (50°C) 1 : 1 acetone/methanol. The polymers 4 and 7 were then dried under vacuum at 60°C to constant weights and stored in a desiccator.

Infrared spectra, thermal decomposition, elemental analyses of the polymers, molecular weights (M_w) and polydispersity index (PDI)

A sample of polymer 4-M₂-50 (entry 3, Table II) displayed the presence of the following absorption bands in the IR spectrum: ν_{max} (KBr) 3440, 3023, 2961, 2927, 2695, 1646, 1472, 1418, 1306, 1198, 1129, 1037, 856, 786, and 736 cm⁻¹.

The onset of thermal decomposition for the polymers (Closed capillary): the color changed to brown at 235°C and black at 260°C.

The elemental analyses ascertained the mole ratio of (M₁ + M₂ + M₃):(SO₂) as 1 : 1, and also supported the compositions of the copolymers as determined by ¹H NMR spectroscopy (*vide infra*). The analyses for a few samples of 4 [(C₈H₁₆CINO₂S)_x(C₉H₁₇NO₅S₂)_{1-x}] and 7 [(C₈H₁₆CINO₂S)_x(C₉H₁₇NO₅S₂)_y(C₂₄H₄₈CINO₂S)_{1-x-y}] were as follows (the numbers in parentheses represent calculated values where x < 1 or (x+y)<1): 4 M₂-50: C, 40.1% (40.36%); H, 6.8% (6.60%); N, 5.4% (5.57%); S, 18.0% (18.42%).

TABLE II
Polymerization of Monomers 1 (M₁)/2 (M₂)/3 (M₃)/SO₂

Entry No.	Sample ^a	Feed ^b M ₁ : M ₂ : M ₃	Yield (%)	Intrinsic viscosity ^c (dL g ⁻¹)
1	4-M ₂ -25	75 : 25 : 0	92	0.0392
2	4-M ₂ -37	63 : 37 : 0	85	0.131
3	4-M ₂ -50	50 : 50 : 0	89	0.207 ^d
4	4-M ₂ -63	37 : 63 : 0	89	0.237
5	4-M ₂ -75	25 : 75 : 0	85	0.254 ^e
6	7-M ₂ /M ₃ -73 : 3	24 : 73 : 3	89	0.105 ^f
7	7-M ₂ /M ₃ -71 : 5	24 : 71 : 5	84	ND ^g
8	7-M ₂ /M ₃ -70 : 7	23 : 70 : 7	85	ND ^g

^a mol % in the polymer (as determined by ¹H NMR).

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

^c Viscosity of 1.0–0.125 g dL⁻¹ polymer solution of 6-M₂ (i.e. 4-M₂ in the presence of 1 equivalent of NaOH) in 1.0N NaCl at 30°C was measured with a Ubbelohde Viscometer (Viscometer Constant, K = 0.005718).

^d [η] in 0.6N and 0.8N NaCl are 0.0794 and 0.105 g dL⁻¹, respectively.

^e [η] in 0.1N and 0.5N NaCl are 0.371 and 0.265 g dL⁻¹, respectively.

^f Cloudy in 1.0N NaCl.

^g Not determined due to insolubility in 1.0N NaCl.

TABLE III
Molecular Weight (\bar{M}_w)^a and Polydispersity Index (PDI)
of Some of the Polymers

Polymer	Source (table, entry no)	\bar{M}_w	PDI
4-M ₂ -28	1, 1	2.01×10^5	1.57
6-M ₂ -63	1, 6	1.87×10^5	1.66
4-M ₂ -25	2, 1	1.46×10^5	1.62
6-M ₂ -63	2, 4	1.67×10^5	1.74
6-M ₂ -75	2, 5	1.99×10^5	1.40

^a Given values are Polyethylene oxide equivalents.

4-M₂-63: C, 39.5% (39.79%); H, 6.6% (6.45%); N, 5.2% (5.41%); S, 19.2% (19.51%). 4-M₂-37: C, 40.6% (40.93%); H, 6.9% (6.74%); N, 5.5% (5.73%); S, 16.9% (17.32%). 7-M₂/M₃-45 : 3.2: C, 40.9% (41.27%); H, 6.9% (6.77%); N, 5.3% (5.53%); S, 17.4% (17.77%).

For the molecular weight determination, deionized water was used as the eluant for the polymer samples 4-M₂-28 (Table I, Entry 1) and 4-M₂-25 (Table II, Entry 1). Since the polymer samples 4-M₂-63 (Table I, Entry 6), 4-M₂-75 (Table II, Entry 5), and 4-M₂-63 (Table II, Entry 2), were insoluble in water, their corresponding polymers **6**, prepared by treatment with equivalent amounts of NaOH, were then analyzed using an aqueous solution of 0.1N NaNO₃ as the eluant. Refractive Index and viscometer detectors were used to detect polymers. The molecular weight (\bar{M}_w) and PDI of some of the polymers are given in Table III.

Copolymer composition

The copolymers were synthesized by varying the feed ratio of 1/2/3. Figure 1(a–d) displays the ¹H-NMR spectra of (a) 4-M₂-0 (i.e., 100 mol % M₁), 4-M₁-0 (i.e., 100 mol % M₂), 4-M₂-35, 7-M₂/M₃-45 : 3.2. The signal at δ 2.26 ppm, having an integrated area of **A**, was assigned to the 2 protons marked “a” at C² of the sulfobetaine unit (M₂) [Fig. 1(b,c)]. The remaining 14 protons of the M₂ and the entire 16 protons of the other monomeric unit M₁ appeared in the range δ 2.8–4.1 ppm having an area of **T**. The compositions of the polymer were determined using:

$$\text{mol\% } M_2 = \frac{A}{2} \times \frac{16}{(A + T)} \times 100$$

where (A/2) is the area of a single proton of M₂, while (A + T)/16 represents the combined area for a single proton of M₁ and M₂.

Likewise, the compositions of the polymers containing the hydrophobes were calculated by the following method of calculation. The nonoverlapping signals in the range δ 0.7–1.5 ppm were attributed to the (CH₂)₁₆ (marked **b**) and CH₃ (marked **c**) protons of the alkyl chain (Fig. 1 day). The integrated area

(**B**) thus belonged to the above 35 protons. Area of a single proton belonging to the hydrophobe thus becomes (**B**/35). The signal at δ 2.26 ppm, having an integrated area of “**A**”, was assigned to the 2 protons marked “a” at C² of the sulfobetaine unit (M₂) and as such the area for a single proton of M₂ became (A/2). The signals in the range δ 2.8–4.1 ppm having an area of “**T**” belonged to the remaining 14 and 12 protons of the M₂ and M₃, respectively, as well as the entire 16 protons of the other monomeric unit M₁. The area for a single proton of each monomeric unit and mol % of the monomers were calculated using following equations.

$$\text{Area for 1 proton of } M_2 = \frac{A}{2}$$

$$\text{Area for 1 proton of } M_3 = \frac{B}{35}$$

$$\text{Area for 1 proton of } M_1 = \left[T - \frac{14A}{2} - \frac{12B}{35} \right] / 16 = D$$

$$\text{mol\% } M_2 = \frac{A/2}{A/2 + B/35 + D} \times 100$$

$$\text{mol\% } M_3 = \frac{B/35}{A/2 + B/35 + D} \times 100$$

Cloud point titration in aqueous salt solutions

The critical (minimum) salt concentration (CSC_S) required for promoting water solubility of polymers **4** and **7** and their corresponding polymers **6** and **8** (obtained by treating **4** and **7** with equivalent amounts of NaOH) was measured at 23°C by titration of a 1% w/w polymer solution (10 cm³) at sufficiently high salt concentrations (2M and 1M, respectively) with deionized water. The accuracy of the CSC_S values, obtained by visual determination of the first cloud point, was approximately \pm 1–2%. The CSC_S values are reported in Table IV.

The critical (minimum) salt concentration (CSC_{IN}) required for promoting water-insolubility of polymers **4** and **7** at 23°C was measured by adding solid NaCl (~1 mg at a time) to a 1% w/w polymer solution (10 cm³). The accuracy of the CSC_{IN} values, obtained by visual determination of the first cloud point, was approximately \pm 2–3%. The CSC_{in} values are reported in Table IV.

RESULTS AND DISCUSSION

Synthesis and physical characterization of the polymers

Cyclopolymerization of 1/2/SO₂ and 1/2/3/SO₂ in DMSO using AIBN as the initiator gave polymers **4** and **7**, respectively, in excellent yields (Scheme 1)

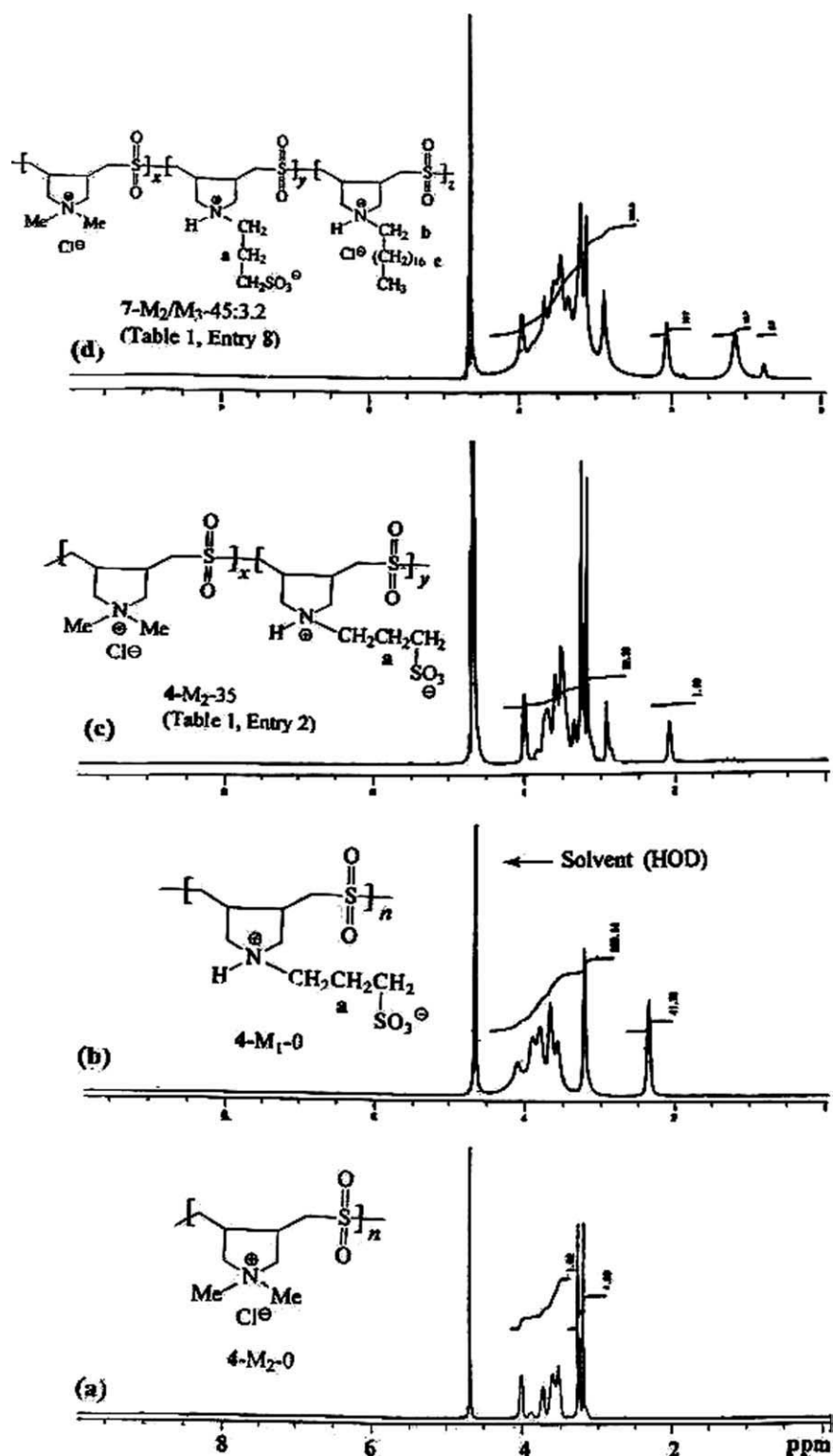


Figure 1 ^1H NMR spectrum of (a) $4\text{-M}_2\text{-0}$, (b) $4\text{-M}_1\text{-0}$ (in $\text{D}_2\text{O}\text{-NaCl}$), (c) $4\text{-M}_2\text{-35}$, and (d) $4\text{M}_2/\text{M}_3\text{-45:3.2}$ in D_2O .

(Table II). Feed ratios of the monomers in Tables I and II were so chosen to have each type of the repeating unit an appreciable say in the copolymer properties. The monomer incorporation was kept in the approximate range 25–75 mol %. The properties of copolymers having monomer incorporation too

much outside this range will either be dictated by 1 or 2. The reactions presented in Table I were terminated 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 equation 1 which was

TABLE IV
Critical Salt (NaCl) Concentrations for Promoting Water-Insolubility (CSC_{IN}^a) and -Solubility (CSC_S^b) of the Polymers 4 and 7, and Their Corresponding "NaOH-neutralized" Polymers 6 and 8

Sample	Source (table, entry no.)	Salt-free water ^c	CSC_{IN}^a NaCl (M)	CSC_S^b NaCl (M)	4/7 + NaOH ^d → 6/8	CSC_S^e NaCl (M)
4-M ₂ -28	(1,1)	+	0.15	1.48	–	0.55
4-M ₂ -35	(1,2)	+	0.12	1.63	–	0.75
4-M ₂ -37	(1,3)	+	0.10	1.56	–	0.73
4-M ₂ -46	(1,4)	+	0.029	1.70	–	0.63
4-M ₂ -61	(1,5)	–	NA	1.73	+	NA ^f
4-M ₂ -63	(1,6)	–	NA	1.69	+	NA ^f
7-M ₂ /M ₃ -45 : 3.2	(1,8)	+	0.037	1.69	–	0.45
4-M ₂ -25	(2,1)	+	0.17	1.62	–	0.73
4-M ₂ -37	(2,2)	+	0.029	1.65	–	0.80
4-M ₂ -50	(2,3)	+	0.011	1.77	–	0.57
4-M ₂ -63	(2,4)	–	NA ^f	1.82	+	NA ^f
4-M ₂ -75	(2,5)	–	NA ^f	1.73	+	NA ^f
7-M ₂ /M ₃ -73 : 3	(2,6)	–	NA ^f	Insol ^g	Insol ^g	NA ^f
7-M ₂ /M ₃ -71 : 5	(2,7)	–	NA ^f	Insol ^g	Insol ^g	NA ^f
7-M ₂ /M ₃ -70 : 7	(2,8)	–	NA ^f	Insol ^g	Insol ^g	NA ^f

^a Critical salt concentration (CSC_{IN}) for promoting insolubility of 4/7 (1 wt %) at 23°C.

^b Critical salt concentration (CSC_S) for promoting solubility of 4/7 (1 wt %) at 23°C.

^c "+" indicates soluble; "–" indicates insoluble.

^d Solubility of polymers 6/8 (1 wt %) in salt-free water (i.e., 4/7 in the presence of 1 equivalent of NaOH).

^e Critical salt concentration (CSC_S) for promoting solubility of 6/8 at 23°C.

^f Not applicable.

^g Insoluble in 0–2N (or higher) NaCl.

rearranged to give Eq. (2) where n and x represent the molar ratio M_1/M_2 in the polymer and feed, respectively. Using the data in Table I, the copolymerization plot (Fig. 2) gave the values of r_1 and r_2 as 0.53 and 1.53 for the monomers M_1 and M_2 ,

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

$$\frac{x(1-n)}{n} = \frac{-r_1 x^2}{n} + r_2 \quad (2)$$

respectively. The Sulfobetaine monomer **2** was thus found to have a greater easiness with which it is incorporated into the growing chains. The more crowded steric environment around the N in **1** than **2** presumably leads to the decreased reactivity of the monomer **1**. Terpolymer 4-M₂-37 (Entry 3, Table I), for instance, describes the polymer that contained 37 mol % of monomeric unit **2** (M_2); the corresponding feed, however, contained 25 mol % of monomer **2**. The polymer composition was determined by ¹H NMR spectroscopic analysis (*vide supra*). The polymer 7-M₂/M₃-45 : 3.2 (Entry 8, Table I) describes a hydrophobically modified polymer containing 51.8 mol % of **1** (M_1), 45 mol % of **2** (M_2) and 3.2 mol % of **3** (M_3) obtained from a feed having 62, 31 and 7 mol % of **1**, **2** and **3**, respectively. The analysis of the mol % data reveals that hydrophobic monomer **3** has the least easiness with which it is incorporated into the growing chains. This could be attributed to the steric encumbrance of the long alkyl chain. Since

the polymerizations are terminated at <10% conversion, the polymer samples are expected to be homogeneous having a random placements of the monomers. The r_1 , r_2 and $r_1 r_2$ values of 0.53, 1.53, and 0.81 ascertain that the polymers are neither blocky nor alternating in nature.

Polymerizations given in Table II were allowed to run for longer duration. Monomer incorporations were found to match closely with the feed ratio. This is expected since the polymers were obtained at high conversions (~90%). The Entries 6–8 (Table II) describe the incorporation of the octadecyl monomer M_3 in the mol % range 3–7. The M_1/M_2 ratio were kept similar (~1 : 3) to that in entry 5. The terpolymer 7-M₂/M₃-71 : 5 (Entry 7), for instance, indicates the incorporation of 5 mol % of hydrophobic

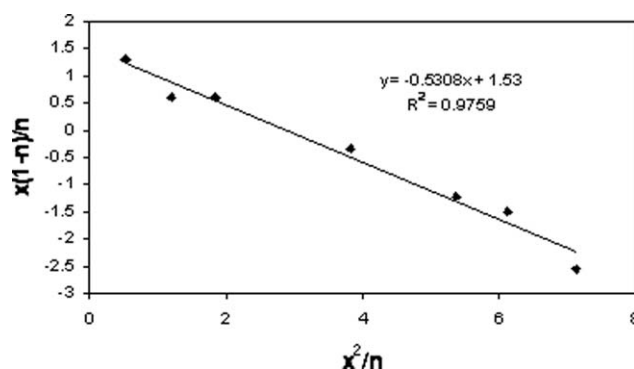


Figure 2 Terpolymerization reactivity plot for the monomers **1**, **2**, and SO_2 .

octadecyl monomer **3**. Since the polymerizations are terminated at high conversions, the polymer samples are expected to be heterogeneous; at the beginning and towards the end, the dead polymer chains would be richer in M_2 and M_1 , respectively, with reference to the composition of the feed.

To have a meaningful assessment of the solution behavior of the polymers, it is important to have their degree of polymerizations similar. Since the polymerizations were run under similar conditions (with the variation in the composition of the feed only), the polymers are expected to have similar molar masses. It is evident from Table III that the \bar{M}_w of several polymer samples do vary in a relatively narrow range. Therefore it is safe to assume that the molar masses could be considered as invariant in the discussion of the solution properties of the polymers (*vide infra*).

Infrared and NMR spectra

The IR spectrum of 4- M_2 -50 (Table II, entry 3) indicates the presence of the sulfonate group by its characteristic bands at ~ 1200 and ~ 1040 cm^{-1} . The two strong bands at ~ 1300 and ~ 1120 cm^{-1} were assigned to the asymmetric and symmetric vibrations of SO_2 unit. The ^1H spectra of 4- M_2 -0, 4- M_1 -0, 4- M_2 -35, and 7- M_2 / M_3 -45/3.2 are displayed in Figure 1. The absence of any residual alkene proton or carbon (not shown) signal in the spectra suggested the chain transfer process²⁰ or coupling reaction for the termination reaction. The above statement should be taken with caution since the presence of a double bond at the end of a long polymer chain (in the case of termination by disproportionation) would probably remain outside the detection limit of the IR and NMR instruments.

Solubility and critical salt concentrations (CSC)

Internal neutralization of the charges in zwitterionic polymers, like polysulfobetaines, is known to lead the polymer backbone to adapt a collapsed coil conformation as a result of intra- and interchain interactions.²¹ When the net charge of an ionic polymer approaches zero, attraction between the oppositely charged units leads to a globule-like conformation, and most often to insolubility in pure water. The low molecular weight anions and cations of the added electrolyte (e.g., NaCl) enter and partially neutralize a portion of the inter- and intrachain interactions, thus allowing the collapsed coil in pure water to expand.²¹ A charge asymmetry exists in the polymer backbone of **4**; the extent of charge imbalance 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 polyelectrolyte and a polyzwitterion, respectively.

The solution properties of the terpolymers are pH-responsive. Note that cationic motifs **1** incorporated in **4** have the valency quenched for the nitrogens, while zwitterionic motifs **2** have the valency unquenched. Therefore, the pH-responsiveness arises owing to the presence of the zwitterionic motifs whose concentration is pH-dependent. With the increase of pH, the zwitterionic motifs could be partially or completely converted to anionic motifs in **5** or **6**, respectively. It is worth mentioning that decreasing the pH by adding HCl will not be efficient in changing the zwitterionic motifs to cationic since the extremely acidic SO_3H groups will remain dissociated as SO_3^- . Changing the zwitterionic motifs in **4** to anionic units by treatment with y equivalent of NaOH would result in its conversion to **6** 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 **6** is expected to give an ideal pure polyampholyte. The solubility behaviors of the polymers in water are shown in Table IV. While polymers **4** having $< 50\%$ incorporation of the zwitterionic motifs (M_2) were found to be soluble in salt-free water, the corresponding polymers **6** were insoluble. The opposite trend is observed for the polymers **4** and **6** having $> 50\%$ incorporation of the zwitterionic motifs; while the former were insoluble in salt-free water, the latter were soluble. Surprisingly, the salt-free water-soluble polymers **4** showed interesting solubility behavior; addition of a small amount of NaCl led to their insolubility. Upon further addition of NaCl, the polymers became soluble again. Therefore salt-free water-soluble polymers **4** were found to be insoluble in a certain range of NaCl concentration. For instance, the polymer 4- M_2 -35 (Table III) was found to be insoluble in water in the presence of 0.12–1.63N NaCl; outside this range the polymer became soluble. The lower end of the NaCl concentration was given the name critical salt concentration (CSC_{IN}) required for promoting insolubility in water, while the higher end is called critical salt concentration (CSC_s) required for promoting water solubility. The CSC_s value for the zwitterionic polymer 4- M_1 -0 is reported²² to be 1.5N NaCl, while the current polymers were found to have slightly higher values of $\sim 1.7\text{N}$ NaCl. One would have expected a lower CSC_s value for the current polymers as these are not pure polyzwitterions as a result of the presence of a considerable portion of the cationic units (M_1). One reason could be that the efficient screening of the attractions of the $-\text{NH}^+$ part of the zwitterionic dipole with Cl^- is not the end of the road; the

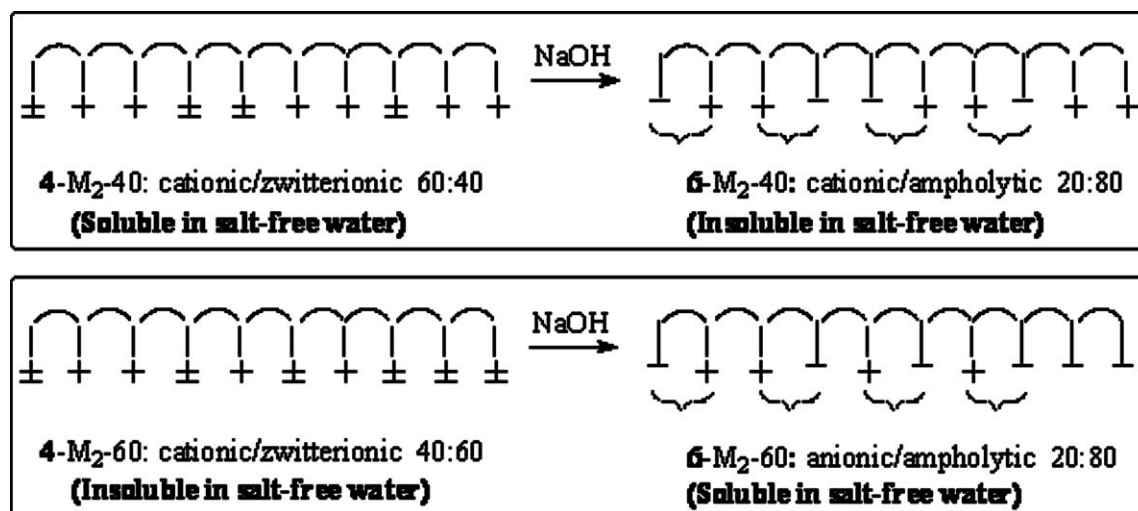


Figure 3 Conversion of pH-responsive polyzwitterions to polyampholytes.

exposed $-\text{SO}_3^-$ group has now the freedom of teaming up with the quaternary nitrogen of 1 (M_1) to act as an ampholytic pair, thereby requiring further addition of NaCl to break up the new liaison. Note that the polymers having zwitterionic M_2 of < 50 mol % were found to be soluble in salt-free water and thereby gave both the CSC_{IN} and CSC_5 values, whereas those having > 50 mol % M_2 were insoluble in salt-free water, hence, provided CSC_5 values only.

The interesting solubility behaviors are explained using Figure 3 in which two theoretical examples involving 4-M₂-40 and 4-M₂-60 are presented. The salt-free water solubility of 4-M₂-40, having 60% cationic (M_1) and 40% zwitterionic motifs (M_2), is promoted owing to the repulsive contribution of the dominant positive charges making the hydrodynamic volume greater hence contributing to the greater hydration of the polymer chains. In an excellent article, Bendejacq et al.²³ have reconciled the low- and high-salt solution behavior of sulfobetaine polyzwitterions in term of zeta potential of the polymers. In our examples, the polymer 4-M₂-40 is expected to have a positive ζ -potential as a result of excess cationic charges. However, the charge asymmetry is reduced upon addition of small amount of NaCl as the Cl^- effectively neutralizes the positive charges by strongly binding with the quaternary nitrogens of the repeating units of 1 (M_1). Note that the small salt additions do not disturb the special attraction enjoyed by the $-\text{SO}_3^-$ and NH^+ groups in zwitterionic M_2 ; according to Nesterenko and Haddad²⁴ a $-\text{SO}_3^-$ group interacts more preferably with a N^+ than a Cl^- does. Eventually, at a certain concentration of NaCl, the ζ -potential will be approaching zero; the polymer becomes a pure polyzwitterions with no charge asymmetry, thus resulting in their precipitations. One would expect that greater the charge asymmetry, larger the amount of NaCl will

be required to approach zero ζ -potential. This is in line with the experimental values of CSC_{IN} as reported in Table IV; for instance, 4-M₂-28 with a greater charge asymmetry than 4-M₂-35 has shown a greater value of CSC_{IN} . Upon higher salt additions, the Coulombic attraction between ammonium and sulfonate groups of the zwitterionic dipoles will be screened resulting in the solubility of the polymer at a salt concentration of CSC_5 . Obviously, in the second case involving 4-M₂-60, zwitterionic motifs dominate so much that the polymer remains insoluble in salt-free water (Fig. 3). Neutralization of the cationic/zwitterionic 4-M₂-40 and 4-M₂-60 with NaOH, causes the transition to cationic/polyampholytic 6-M₂-40 and anionic/polyampholytic 6-M₂-60, respectively. While ampholytic motifs (80 mol %) dominate in both the resulting polymers, a charge asymmetry of equal magnitude (20 mol %) results from the excess cationic and anionic charges in 6-M₂-40 and 6-M₂-60, respectively. Note that the polymers 6 having excess cationic and anionic charges were found to be soluble and insoluble in salt-free water, respectively. The rationale behind the opposite solubility behaviors of these two polyampholytes could be attributed to the difference in the binding ability of the Cl^- and Na^+ , counterions of the ammonium and sulfonate moieties of the polymer backbone, respectively. While the chloride counterions are more effective in binding strongly thus neutralizing the excess cationic charges in 6-M₂-40, the large hydration shell of Na^+ may not be able to approach close enough to neutralize the more dispersed excess anionic charges of the sulfonate moieties in 6-M₂-60.¹⁰ As a consequence of this difference, 6-M₂-40 is expected to be more ampholytic in nature, hence less soluble, than 6-M₂-60.

The dependence of the CSC_5 values of the pH-responsive polymers was determined with the

TABLE V
Critical NaCl Concentrations (CSC_S) for Solubility of the Polymers 4-M₂-46 (Table I, Entry No. 4)

NaOH Equiv	CSC _S (M)
0	1.70
0.25	1.32
0.50	0.96
0.75	0.72
1.0	0.63

variation of the amount of NaOH added to the system. The values for polymer 5-M₂-46 [obtained from 4-M₂-46 (Table I, Entry no. 4) in the presence of different concentration of NaOH] are given in Table V; as expected, the CSC_S values were found to be decreasing with the increase in the added equivalent of NaOH. With every increase in the amount of NaOH, the percent of zwitterionic motifs decreases, while that of the polyampholyte motifs increases. The study indicates that the zwitterionic motifs show stronger inter- and intermolecular attractions than the ampholytic motifs since the former requires a higher concentration of the added salt to break up the interactions.

Polymer 7-M₂/M₃-45 : 3.2, containing 3.2 mol % of hydrophobes was found to be soluble in salt-free water as expected, while its corresponding NaOH treated polymer remained insoluble. The hydrophobically modified polymers 7-M₂/M₃-73 : 3, 7-M₂/M₃-71 : 5 and 7-M₂/M₃-70 : 7 containing ~ 70 mol % zwitterionic monomer M₂ were found to be insoluble in the presence or absence of added salt. The amount of salt required to break the zwitterionic interactions is simply too much and makes the system hostile to the hydrophobic octadecyl chains. Thus, it leads to the salting-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreases, the polymer chains are unable to manifest effective intermolecular associations and tend to precipitate.

Note that the CSC_S values of ~ 0.7M for the polyampholytes 6 (obtained via treating 4 with NaOH) were found to be considerably less than the value of ~ 1.7M obtained for the corresponding zwitterionic polymers 4. This clearly demonstrates the greater attractive interactions manifested by the zwitterionic dipoles than the randomly placed polyampholytic motifs. This is reasonable since the distance between the opposite charges centers in a randomly placed polyampholyte may not be close enough to exert maximum Coulombic attractions. The previous study¹⁷ involved mainly acrylamide-based polymers where a comparison is made between the low charge density (5–10 mol %) polyampholytes and polyzwitterions having different molecular architectures. The positive charges rested on the nitrogens with a quenched valency and negative charges on the carboxyl groups. The polymers have 90–95 mol

% neutral acrylamide units. The polybetaines were found to be more soluble than the polyampholytes of similar charge density. The greater salt response of the polyampholytes indicated that the intramolecular forces are much greater in the polyampholytes than in the polybetaines, which have been shown to demonstrate only weak antipolyelectrolyte effects. However, the current study involved a pH-responsive polyzwitterionic-to-polyampholyte transition owing to the presence of nitrogen having an unquenched valency. Therefore a more meaningful comparison between the two types of polymers is possible in our case since both contain similar polymer architecture and degree of polymerization. Also note that the negative charges in the current polymers lie with the sulfonate instead of carboxylate functionality.

Viscosity measurements

It is evident from Tables I and II that the intrinsic viscosities of 6-M₂, obtained via neutralization of the zwitterionic units in 4-M₂ with 1 equivalent of NaOH, in 1N NaCl increases with the increase in the anionic repeating unit of monomer 2. The rationale behind the observed trend in the viscosity values could be attributed to the efficient binding of the cationic motifs in M₁ by Cl⁻, while the SO₃⁻ motifs remains unshielded by the inefficient Na⁺ ions

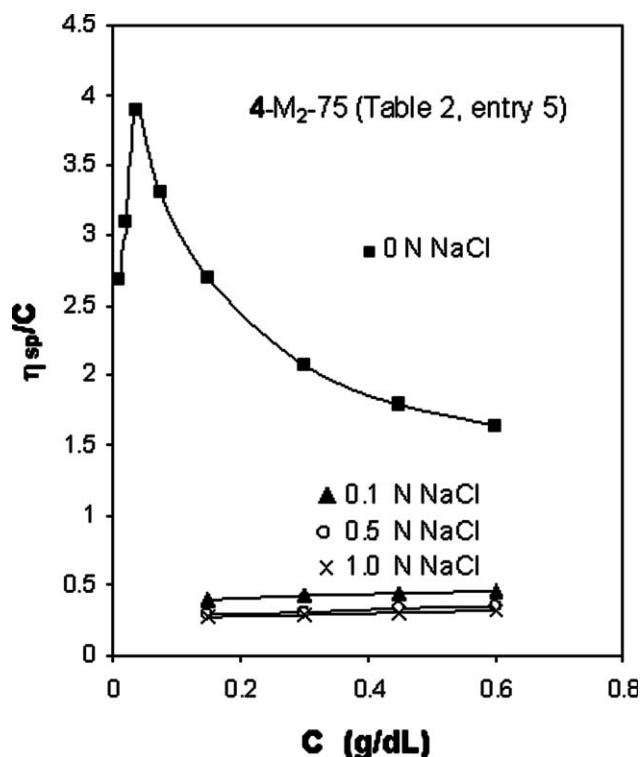


Figure 4 Effect of added salt (NaCl) on the viscosity behavior of polymer 6-M₂-75 [obtained by treating 4-M₂-75 (Table II, Entry 5) with NaOH].

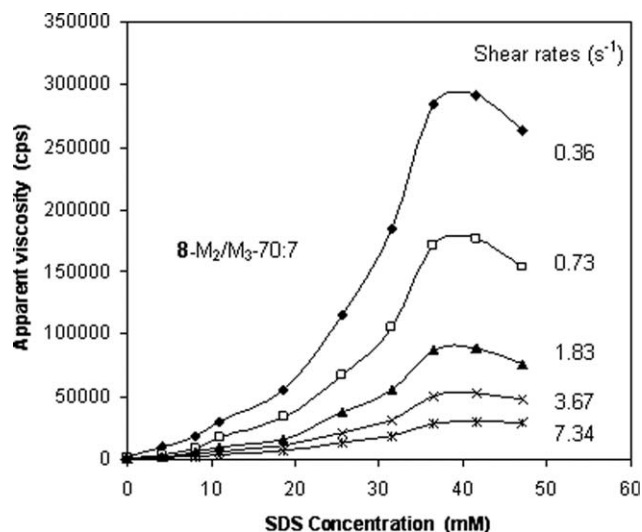


Figure 5 Variation of viscosity with SDS concentrations of a 3 g dL⁻¹ solution of 7-M₃-7 at different shear rates at 30°C in salt-free water.

having larger hydration shells. The repulsions among the negative charges thereby lead to an increase in the viscosity value. Viscosity data for 6-M₂-75, obtained by treating the polymer 4-M₂-75 (Entry 5, Table II) with 1 equiv of NaOH is presented in Figure 4. With reference to Figure 3, 6-M₂-75 is calculated to have 50 mol % each of ampholytic motifs and anionic centers. In the absence of added salt (NaCl), the plot is typical for a polyelectrolyte i.e., concave upward. However, at higher dilution, the reduced viscosity tends to fall off owing to the formation of the zwitterionic species by partial protonation of the basic amine nitrogen in the polymer 6-M₂-75 (i.e., $6 + \text{H}_2\text{O} \leftrightarrow 5 + \text{OH}^-$, Scheme 1). The relative proportions of the zwitterions in 5 as well as the compactness of the polymer chains are expected to increase with dilution. It is interesting to note that the viscosity values for polymer 6-M₂-75 decreased

in the presence of added salt NaCl thereby ascertaining its polyelectrolytic nature; the randomly placed polyampholytic motifs having densities equal to that of the anionic motifs failed to dictate the solution behavior (Fig. 4). The addition of salt did not, however, have a drastic effect in reducing the intrinsic viscosities. The $[\eta]$ values of 0.371, 0.265, and 0.254 dL g⁻¹ in 0.1N, 0.5N, and 1.0N NaCl demonstrate the opposing effects of polyelectrolytes of excess anionic charges (-) and antipolyelectrolytic effects of polyampholytes (+ -) in 6-M₂-75.

The intrinsic viscosity of polymer 6-M₂-46 was determined to be 0.0863 and 0.248 dL/g in 0.6N and 1.0N NaCl, respectively, (footnote^e, Table I, entry 4). An increase in the intrinsic viscosity with increasing NaCl concentration is a demonstration of the "antipolyelectrolyte behavior" of the polymer. The polymer 6-M₂-46 with reference to Figure 3 is calculated to comprise of polyampholytic motifs (92%) and excess positive charges of 8%. Thus, as expected, the polymer has demonstrated the predominant polyampholytic behavior. Likewise, the intrinsic viscosity of polymer 6-M₂-50, derived from 4-M₂-50, was determined to be 0.0794, 0.105, and 0.207 dL/g in 0.6N, 0.8N, and 1N NaCl, respectively, (footnote^e Table II, Entry 3), thereby demonstrating the polyampholytic behavior of the polymer.

Polymer surfactant interactions

An interesting feature of amphiphilic polyelectrolytes with poor water solubility is that redissolution is greatly facilitated by addition of surfactants, which indicates the existence of surfactant/polymer interactions such that surfactant micelles provide the solubilization of the hydrophobic moieties of the amphiphilic polyelectrolyte. The interactions are driven by electrostatic attraction and/or association of the hydrophobic groups on the polymers and those of the surfactant molecules.^{25,26} The polymer surfactant

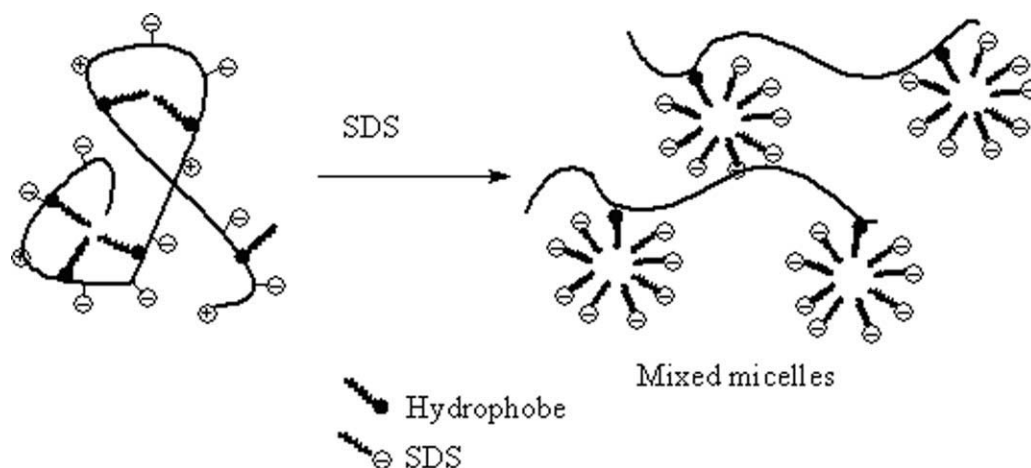


Figure 6 Effect of SDS on the interchain hydrophobic association of 7-M₂/M₃-70 : 7.

interaction was examined using viscometric measurements on polymer 8-M₂/M₃-70 : 7 [derived by treating 7-M₂/M₃-70 : 7 (Entry 8, Table II) with 1 equivalent of NaOH] in the presence of anionic surfactant sodium dodecyl sulfate (SDS). It is worth mentioning that the viscosity is not increased in the presence cationic surfactant CTAB; the polymer was salted out instead. Figure 5 illustrates the viscosity behavior of a 3 g dL⁻¹ solution of 8-M₂/M₃-70 : 7 in the presence of anionic surfactant SDS at various shear rates. Note that the polymer is partially soluble at this concentration, and gave a hazy mixture. However, upon the addition of SDS, the mixture became increasingly clear. A concentration of 3 g dL⁻¹ of 8-M₂/M₃-70 : 7 corresponds to a concentration of 7.46 mM octadecyl pendants. Upon the addition of SDS above its critical micelle concentration (CMC) of 8.2 mM, the solution of 8-M₂/M₃-70 : 7 became more viscous which indicates the existence of surfactant/polymer interactions. The polymer is sufficiently hydrophobic to overcome competitive ionic repulsion effects, promoting the bridging micelle formation. This interaction of anionic polyelectrolyte with surfactant of like charge (SDS) is rather unusual, but it is not unique. An interaction in aqueous solutions of hydrophobically modified polyelectrolytes with surfactants of the same charges has been reported.²⁷ Upon further increase in the SDS concentration, the viscosity continues to increase, suggesting gradual polymer restructuring and formation of mixed micelle domains which contain hydrophobic groups belonging to two or more distinct polymer chains. The viscosity attains its maximum value at a SDS concentration of ~ 40 mM, which corresponds to ~ 5 SDS molecules per octadecyl pendent of the polymer. At a shear rate of 0.36 s⁻¹, the polymer 7-M₂/M₃-70 : 7 was found to have apparent viscosity values of 2000 and 290,000 cps in the absence and presence of 40 mM SDS, respectively. Note that the viscosity is sharply decreased at higher shear rates—a typical shear thinning behavior owing to the disruptions of hydrophobic associations. This observation is similar to that frequently observed for hydrophobically modified associative polymers. The addition of surfactants to hydrophobically modified polymers solutions can increase the viscosity of polymer solutions, provided comicellization between the polymer and surfactant provides bridging between the polymer chains (Fig. 6). Further increase in concentration of SDS leads to the formation of more micelles and the number of micelles per polymer bound hydrophobe increases and this eventually disfavors comicellar bridge.

CONCLUSION

The unquenched valency of nitrogens in the zwitterionic units has made the polymers 4 and 7 pH-respon-

sive. The interconvertible polymers (4 → 5 → 6; and 7 → 8) have thus offered an opportunity to assess their comparative solution properties. The solution behavior of these polymers, in low- and high-salt domains, has indeed corroborated the recent findings on this new topic.²³ The addition of small amounts of SDS to a solution of 7-M₂/M₃-70 : 7 makes the solution more viscous indicating polymer-surfactant interactions. The pH-induced changes in the charge types and densities in the terpolymer backbone have permitted us to study the polyelectrolyte-to-polyzwitterion-to-polyampholyte transitions. The polymers in this report have shown interesting solution properties that imparted a choice of using these polymers under certain ionic strengths, pH, and recycling them by precipitation by changing those parameters.

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