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The effects of charge densities on the associative properties of a pH-responsive hydrophobically modified sulfobetaine/sulfur dioxide terpolymer

Yunusa Umar[a], B.F. Abu-Sharkh[b], Sk. Asrof Ali[a,*]

[a] *Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*
[b] *Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

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Abstract

Sulfur dioxide, zwitterionic monomer, 3-(*N*,*N*-diallylammonio)propanesulfonate and a hydrophobic monomer *N*,*N*-diallyl-*N*-octadecylammonium chloride were cycloterpolymerized in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator to afford water-insoluble polysulfobetaines (PSB) in excellent yields. The PSBs were converted into the corresponding anionic polyelectrolyte (APE) by treatment with 1 equiv. of sodium hydroxide. Treating the pH-responsive PSB polymers with different equivalents of NaOH varied the zwitterionic and anionic charge densities in the polymer chain. The polymer chains with zwitterionic fraction greater than 0.5 were found to be insoluble in water. The solution properties of the APE and PSB/APE systems containing varying amount of the hydrophobic monomers in the range 0–10 mol% were investigated by viscometric techniques. It was found that PSB/APE polymer with a ratio of 33:67 for the zwitterionic and anionic fractions in the polymer chains, respectively, gave the highest viscosity value. The polymer concentration (C^*_{HA}) of around 1 g/dl was required for the manifestation of significant hydrophobic associations. The polymer solutions exhibited sharp increase in viscosity with increasing polymer concentrations in salt (NaCl)-free as well as salt-added solutions. The presence of sodium chloride is shown to enhance intermolecular associations in polymers having hydrophobes in the lower mol% range, whereas, intramolecular associations were manifested in polymers containing higher proportions of the hydrophobes.

Keywords: Associating ionic polymers; Cyclopolymerization; Polysulfobetaines

1. Introduction

The polymers derived from acrylamide and acrylate based zwitterionic monomers have been widely used in industries dealing with textiles, medical products, charge dispersing agents, colloids, and related materials [1]. In recent years the uses of structurally modified monomers have provided entries into zwitterionic polymers [2–7] via Butler's cyclopolymerization reactions [8]. The polyzwitterions are electrolyte-tolerant and they can exhibit enhancement in viscosity and solubility in the presence of added electrolytes. This behavior renders these systems useful in water treatment, drag reduction, petroleum recovery, viscosification, coatings and cosmetics.

Quaternary ammonium salts (**1**, R≠H)-derived polycarboxybetains or their copolymer with SO_2 (e.g., **3**) [2–7] with an anionic pendant have the capacity to show pH-responsive solution behavior due to incorporation of the pH-triggerable CO_2^- functionality (Scheme 1). However, amine salts (**1**, R=H) containing an N–H moiety and having carboxy group in the pendant show pH-responsive solution behavior over a wider spectrum of the pH scale due to the incorporation of two pH-triggerable functionalities (CO_2^- and the amine nitrogen) [9–11]. Even though several groups have reported the synthesis of polysulfobetaines (PSB), an important class of cyclopolymers, from monomer **2** (R≠H) [12–14], these polymers do not have much scope of showing pH-responsive solution behaviors. The very low pK_a value of the SO_3H group renders these polysulfobetaines unable to respond to the changes in pH values; it remains dissociated almost completely as SO_3^-. The use of monomer **2** (R=H) [15,16] on the other hand makes the corresponding polysulfobetaines pH-responsive as a result of the presence of N–H moiety. In our continuing studies of zwitterionic polymers, we now report

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* Corresponding author. Tel.: +966 3 860 3830; fax: +966 3 860 4277.
E-mail address: shaikh@kfupm.edu.sa (S. Asrof Ali).

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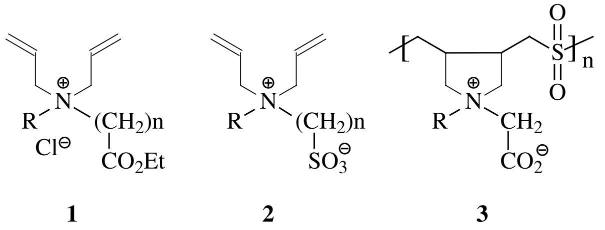


Scheme 1.

the synthesis and comparative solution properties of a series of hydrophobically associating pH-responsive polysulfobetaine (PSB) **6** containing various proportions of the hydrophobe (Scheme 2). The effects of zwitterionic and anionic charge densities on the associative properties of the polymers has been studied using the intermediate polymer **7** containing varying proportions of zwitterionic, anionic and hydrophobic moieties in a ratio of *x*:*z*:*y*, respectively.

2. Experimental

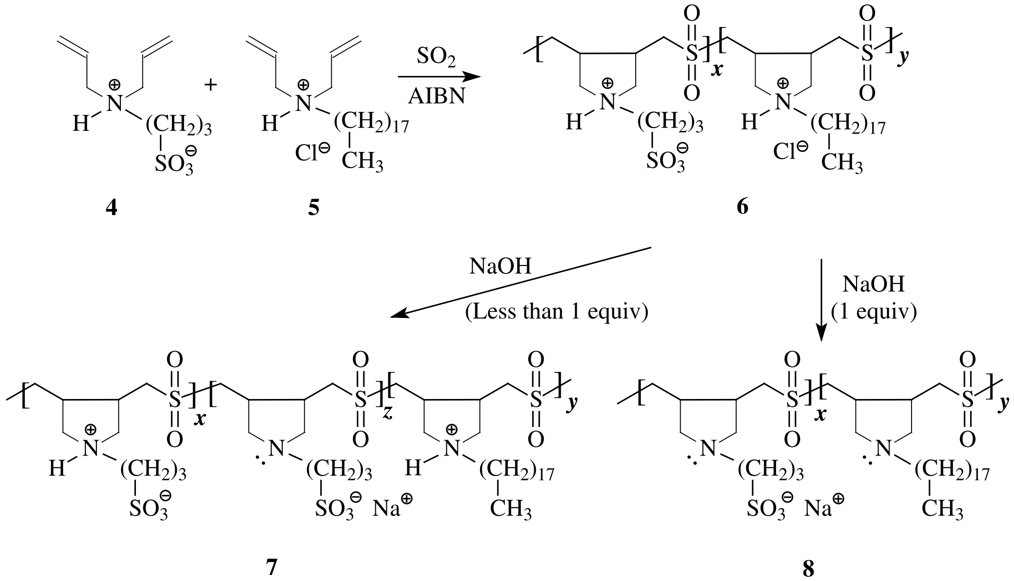
2.1. Physical methods

Melting points are recorded in a calibrated Electrothermal-IA9100-Digital Melting Point Apparatus using heating rates of 1 °C/min in the vicinity of the melting points. Elemental analyses were carried out in a Carlo-Erba elemental analyzer Model 1102. 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 Ubbelohde 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 in the viscometric titrations in salt-free and salt-added solutions. Digital Brookfield rotational viscometer with UL adaptor accessories or SC4-18 spindle accessories was used to measure apparent viscosities at various shear rates. The pH of the polymer solutions was recorded using a Corning pH Meter 220 at 25 °C.

Molecular weights of the polymer samples were determined by light scattering experiments at 21 °C. Solutions of the PSB **6** and APE **8** (polymer concentration range: 0.03 to 0.1 g/dl) were prepared in 1.5 and 0.5 N NaCl, respectively; the presence of salt allows the screening of the charges in order to minimize ionic interactions and allow the polymer chains to form random coils. Methanol, which is helpful in disrupting hydrophobic associations, was not used as a solvent owing to the insolubility of the polymers in this solvent. Millipore disposable filters of pore size 0.02 μm were used to remove dust particle from the aqueous solutions of polymers. Corrections were made for the concentration of the polymer solution after filtration to account for screened polymer by the filtration media. Measurements were performed on each solution immediately after filtration. Static light scattering (SLS) experiments were performed using DAWN EOS light-scattering instrument (Wyatt Technology Corporation, CA). The system light source was a linearly polarized gallium arsenide (GaAs) laser. The laser is positioned so that the incident beam was vertically polarized. A RFM-340 Refractometer (Bellingham&Stanley, UK) was used to measure the differential refractive indices (d*n*/d*c*) of different polymer solutions. Molecular weight determination of the hydrophobically modified polymers was complicated owing to hydrophobic associations. As a result we can expect that the light scattering measurements lead to an apparent weight, $\overline{M}_{w,app}$ rather than true molecular weight.

2.2. Materials

2,2′-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from



Scheme 2.

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 mm Hg). All glassware were cleaned using deionized water. 3-(*N*,*N*-Diallylammonio)propanesulfonate (**4**) was prepared as described in a previous report [15]. *N*,*N*-Diallyl-*N*-octadecylammonium chloride (**5**) was prepared as before [17].

2.3. General procedure for the terpolymerization of the monomers **4** and **5** with SO_2

All the polymerizations were carried out using conditions as described in the Table 1. In a typical experiment, SO_2 was absorbed in a solution of the monomer **4** (M_1) and **5** (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 59 °C for 24 h. 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 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 ^{1}H NMR). The copolymer was then dried to a constant weight at 60 °C under vacuum. The white polymers, PSB **6**, were stored in a desiccator.

The elemental analyses ascertained the mole ratio of $(M_1+M_2):M_3(SO_2)$ as 1:1. The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M_2-0 as reported [16]. The ^{1}H NMR spectra were used to determine the ratio of the M_1 and M_2 incorporated in the polymer as described (vide infra).

The onset of thermal decomposition (closed capillary for the polymer sample of entry 3, Table 1): the color changed to brown at 260 °C and black at 280 °C. The other terpolymers also revealed the thermal decomposition at similar temperatures.

2.4. Conversion of PSB **6** to PSB/APE **7** and APE **8** by basification and its use in viscosity measurements

The PSB terpolymer **6**-M_2-5 was converted to the corresponding PSB/APE **7** ($x=0.28$, $z=0.67$, $y=0.05$) by adding 0.67 equiv. of aqueous NaOH. Thus a sample of 0.500 g (1.714 mmol) was treated with 1.714×0.67, i.e., 1.148 mmol of NaOH [10.10 cm^3 of 0.1137 N NaOH was used for the purpose]. The solution was then diluted to 25.0 cm^3 with distilled deionized CO_2-free water, and then NaCl (146 mg, 2.50 mmol) was added. This process gave a 2 g/dl solution (25 cm^3) of the terpolymer **6**-M_2-5 in the presence of 0.67 equiv. of NaOH in 0.1 N NaCl. The solution could be diluted with 0.1 N NaCl to obtain various concentration of the polymer in the presence of 0.67 equiv. of NaOH in 0.1 N NaCl. For polymer solutions in salt-free water no NaCl was added.

Likewise, the solutions of 2 g/dl of the terpolymer **6**-M_2-5 in the presence of 0.55, 0.80 and 1.00 equiv. of NaOH were prepared by treating 0.500 g (1.714 mmol) of the polymer as above with (1.714×0.55), (1.714×0.80) and (1.714×1) equivalents of NaOH to obtain the solutions of APE/PSB **7** ($x=0.40$; $z=0.55$; $y=0.05$), APE/PB **7** ($x=0.15$; $z=0.80$; $y=0.05$) and anionic polyelectrolyte (APE) **8**, respectively.

Stock solutions of other terpolymers in the presence of various equivalents of NaOH in 0.1 N NaCl as well as salt-free water were prepared in the similar way.

3. Results and discussion

3.1. Synthesis and solubility of the terpolymers and physical characterization

The monomers **4**(M_1)/**5**(M_2)/SO_2 were cycloterpolymerized using AIBN as the initiator to give the polysulfobetaines (PSB) **6** in excellent yields (Scheme 2). The results of the polymerization, carried out under similar conditions, and the intrinsic viscosities of the resultant polymers in dilute solutions

Table 1
Terpolymerization of the monomers $M_1/M_2/SO_2$

Entry no.	Sample	M_1 (mmol)	M_2(mmol)	Feed[a] M_1:M_2	Polymer[a] **6** M_1:M_2	Yield (%)	Intrinsic viscosity[b] (dl g^{-1})
1[c]	**6**-M_2-0	10.0	0	100:0	100:0	87.8	1.09
2	**6**-M_2-1.5	19.7	0.300	98.5:1.5	98.3:1.7	92.8	1.11
3	**6**-M_2-2.5	19.5	0.500	97.5:2.5	97.7:2.3	88.4	1.05
4	**6**-M_2-3.5	19.3	0.700	96.5:3.5	96.7:3.3	89.8	1.14
5	**6**-M_2-5.0	19.0	1.00	95.0:5.0	95.2:4.8	89.7	1.07
6	**6**-M_2-7.5	18.5	1.50	92.5:7.5	93.0:7.0	89.7	0.974
7	**6**-M_2-10	18.0	2.00	90.0:10.0	ND[d]	85.4	0.652[e]

Polymerization reactions were carried out in DMSO (7.0 g) containing 20 mmol each of (M_1+M_2) and SO_2 in the presence of AIBN (64 mg) at 59 °C for 28 h.

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

[b] Intrinsic viscosity of APE **8** obtained by extrapolation of the linear parts of the viscosity plots usually in the range 0.25–0.031% polymer (PSB **6**) solution in the presence of 1 equiv. of NaOH in 0.1 N NaCl at 30 °C (measured with an Ubbelohde viscometer ($K=0.005718$).

[c] Taken from Ref. [16].

[d] Not determined due to cloudy nature of the solution that gave very broad signals.

[e] Cloudy solution throughout the concentration range.

in the presence of 1 equiv. of NaOH are given in Table 1. The entry 1 in Table 1 describes the copolymer **6**-M_2-0 indicating the absence of the hydrophobic monomer **5** (M_2). The entries 2–5 describe the incorporation of the octadecyl monomer **5** in the mol% range 1.5–10. The terpolymer **6**-M_2-5 (entry 5), for instance, indicates the incorporation of 5 mol% hydrophobic octadecyl monomer **5**.

Internal neutralization of the charges in polybetaines is known to lead the polymer backbone to adapt collapsed coil conformation as a result of intra- and inter-chain interactions [18,19]. When the net charge of an ionic polymer approaches zero, attraction between oppositely charged units leads to a globule-like conformation, and most often to insolubility in pure water. The zwitterionic copolymer **6**-M_2-0 was found to be insoluble in salt-free water or methanol; the critical (minimum) salt (NaCl) concentrations (CSC) required to promote water solubility at 23 °C has been measured to be 1.5 N [16]. The terpolymers **6**-M_2-1.5-10, on the other hand, were found to be neither soluble in salt-free water or in NaCl solution. The excessive amount of NaCl, required to disrupt the zwitterionic interactions in the collapsed chain conformations, makes the system hostile to hydrophobic pendents. The viscosity measurements of the polymers were thus carried out in the presence of 1 equiv. of NaOH which converts the PSBs (**6**) to their corresponding anionic polyelectrolytes (APE) **8**. The anionic polyelectrolytes were found to be soluble in salt-free water as well as in 0.1 N NaCl.

The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M_2-0 as reported [16]. Fig. 1(a) and (b) displays the ^{1}H NMR spectrum of the **8**-M_2-0 and **8**-M_2-2.5. The incorporation of the hydrophobic monomer M_2 was calculated using ^{1}H NMR integration of its signals around δ 0.77 (for methyl protons of the hydrophobic pendents) and 1.15 ppm [for $(CH_2)_{16}$ of octadecyl pendents] and that of M_1 at δ 1.76 ppm (for the middle CH_2, marked 'e', of the pendent). Hydrophobe incorporations were found to match closely with the feed ratio. This is expected since the polymers are obtained at high conversions. The sulfur analyses (Table 2) ascertained the mole ratio of (M_1+M_2) and SO_2 as 1:1.

The apparent molecular weights $\overline{M}_{w,app}$ and the root mean square radius (r_g) of the polymers are given in Table 3. The polymers of higher hydrophobe-contents (e.g., **8**-M_2-7.5, 10) were insoluble in 0.5 N NaCl and as such their molecular

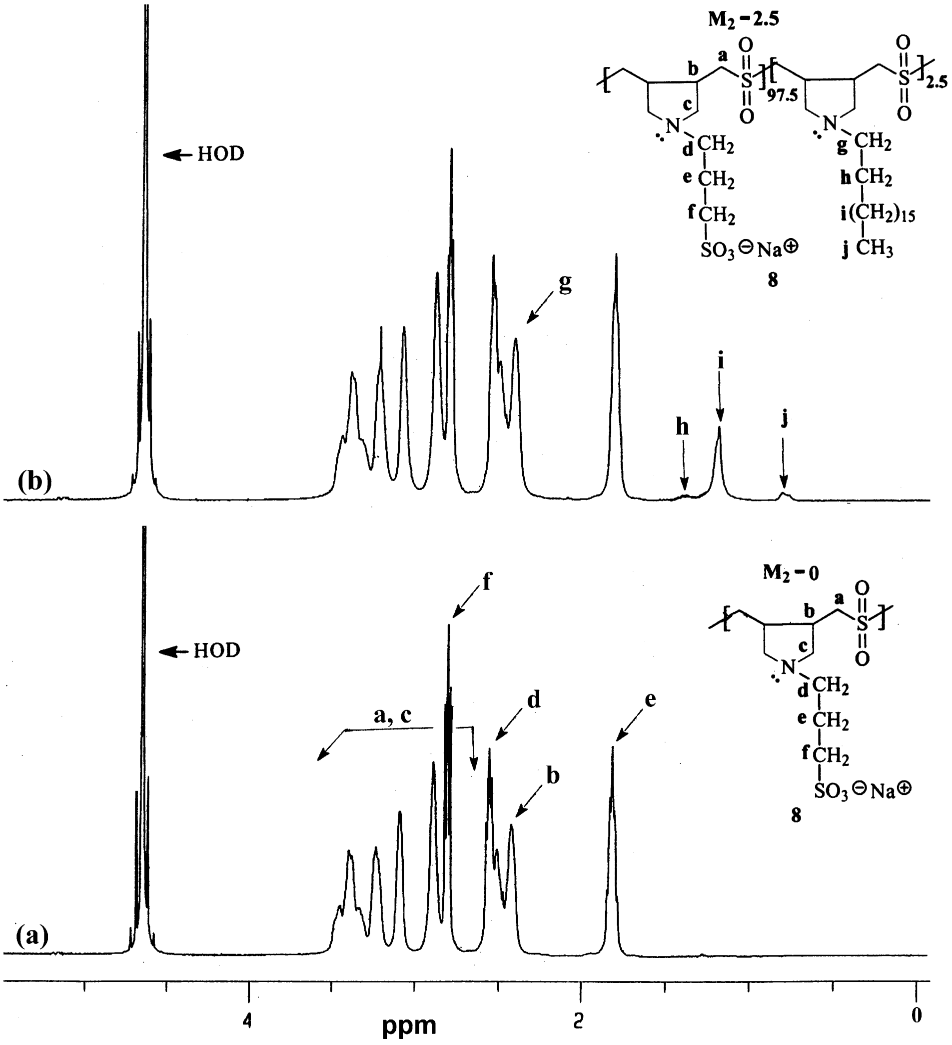


Fig. 1. ^{1}H NMR spectrum of (a) **8**-M_2-0 and (b) **8**-M_2-2.5 in D_2O.

Table 2
Elemental analyses of **6** $(C_9H_{17}NO_5S_2)_x(C_{24}H_{48}ClNO_2S)_{1-x}$

Polymers	Carbon[a]	Hydrogen[a]	Nitrogen[a]	Sulfur[a]
M_2-0	38.5 (38.15)	6.65 (6.05)	4.89 (4.94)	22.1 (22.63)
M_2-1.5	38.2 (38.54)	6.29 (6.12)	4.94 (4.91)	21.8 (22.40)
M_2-2.5	38.5 (38.80)	6.37 (6.17)	4.74 (4.89)	21.9 (22.24)
M_2-3.5	38.7 (39.06)	6.10 (6.21)	4.76 (4.88)	21.7 (22.09)
M_2-5.0	39.0 (39.44)	6.52 (6.29)	4.70 (4.85)	21.5 (21.85)
M_2-7.5	39.8 (40.09)	6.55 (6.40)	4.55 (4.80)	21.0 (21.47)
M_2-10	40.4(40.74)	6.70 (6.52)	4.65 (4.76)	20.7 (21.08)

[a] Found (calculated).

weights were not determined. The co- and ter-polymers, prepared under similar polymerization conditions (initiator and monomer concentrations, reaction conversions, temperature, duration, etc.), are expected to have similar molecular weights. The similarity in the values of the intrinsic viscosities of the polymers (Table 1) seems to suggest that their $\overline{M}_w$should also be similar. The M_w for the polymers varied from 2.81×10^5 to 3.46×10^5 g/mol. The $\overline{M}_{w,app}$ for the polymers containing the hydrophobes were found to be slightly higher than that of the hydrophobe-free sample. The incorporation of the hydrophobes along the backbone seems to result in higher molecular weights. This could be attributed to the partial aggregation of the hydrophobically modified polymers. However, these molecular weights are close enough to allow meaningful assessments of the effects of hydrophobic associations on their solution behaviors (vide infra).

3.2. Viscosity measurements and solution properties

The polymers (**8**-M_2-0-10, i.e., **6**-M_2-0-10 in the presence of 1 equiv. NaOH) are soluble in salt-free water as well as 0.1 N NaCl except that **8**-M_2-10 gave a cloudy solution in 0.1 N NaCl. Viscosity measurements were made by Ubbelohde viscometer. The viscosity plots (not shown) indicated the manifestation of hydrophobic association at a critical association concentration C^*_{HA} of around 1 wt% of all the samples except **8**-M_2-1.5, -2.5 which contained lower proportion of the hydrophobe. Extrapolation of linear part of the viscosity plots in the concentration range 0.250–0.0312 g/dl permitted us to determine the intrinsic viscosities $[\eta]$ as ~1.0 dl/g for all the polymers except **8**-M_2-10 (Table 1). It is worth mentioning that the polymerization conditions are kept similar as rigorously as possible in order to maintain similar degree of polymerization. Increased hydrophobe incorporation leads to increased reduced viscosity in the higher concentration range solutions; however the **8**-M_2-10 has lower viscosity values than that of the other terpolymers and is attributed to its solubility problem. Average number of hydrophobe units per polymer chain is lesser in the case of M_2-1.5, -2.5 and as such a much higher concentration of the polymer will be required for the formation of three-dimensional physical cross-links due to interchain hydrophobic associations. The strong interchain associations form large aggregates (a network structure of polymer chains) as the polymer concentration passes critical association concentration C^*_{HA}; the network structures contribute significantly to the thickening [20–25].

Table 3
Light scattering measurements for the co- and ter-polymers

Entry no.	Sample	$10^{-5}\,\overline{M}_{w,app}$ (g mol^{-1})	R_g[a] (nm)	Solvent
1	**6**-M_2-0	2.81	48.7	1.5 N NaCl
2	**8**-M_2-1.5	3.29	57.1	0.5 N NaCl
3	**8**-M_2-2.5	3.31	53.2	0.5 N NaCl
4	**8**-M_2-3.5	3.46	54.5	0.5 N NaCl

[a] Root mean square radius.

Increased salt concentration (0.5 N NaCl) led to decreased values of intrinsic viscosities $[\eta]$ of around ~0.5 dl/g for the polymers **8**-M_2-2.5, -3.5, -5 as measured at 30 °C using an Ubbelohde viscometer. The sodium ions screen the negative charges on the sulfonates thereby allowing the polymers to adopt compact coil conformations having smaller hydrodynamic volumes. Polymers with higher hydrophobe contents were not soluble in 0.5 N NaCl. The hydrophobic associations began to manifest at a C^*_{HA} of around 1 wt% of the polymers.

Fig. 2 shows the change in intrinsic viscosity in salt-free water, obtained by Fuoss relationship [26], as a function of hydrophobic group content of the polymers APE **8**-M_2-0-10. The decreasing values of intrinsic viscosities with increasing hydrophobe concentration imply that these polymers form mainly intramolecular hydrophobic associations in dilute solutions as a result of random distribution of the hydrophobes [27]. As far as the distribution of the sulfur dioxide is concerned, it does not homopolymerize, rather it forms alternate copolymers with diallyl monomers as described before [5,7,9,11].

Fig. 3 displays the variation of Brookfield viscosity with concentration of **8**-M_2-10 in salt-free water. As evident from the figure the critical association concentration (C^*_{HA}) was found to be around a polymer concentration of 1 g/dl; changing the polymer concentration from 1 to 2 g/dl resulted in an increase in viscosity by a factor of 44 at a shear rate of 0.36 s^{-1}. The associative behavior of the polymers are more pronounced in the lower shear rate range as expected since higher shear rates lead to disruptions of hydrophobic associations. This observation is similar to that frequently observed for

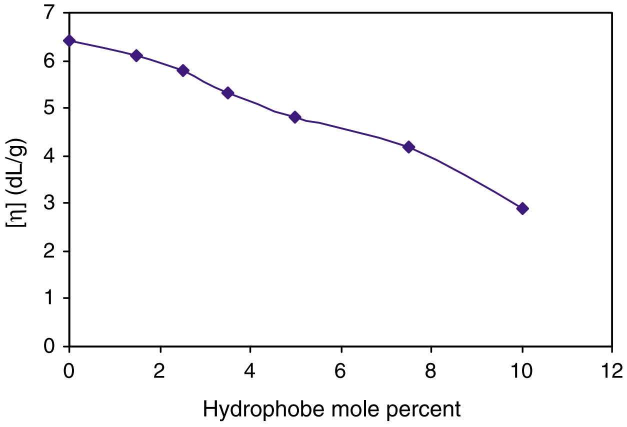


Fig. 2. Effects of hydrophobic group content on the intrinsic viscosity $[\eta]$ of APE **8**-M_2-0-10 in salt-free water at 30 °C with an Ubbelohde viscometer.

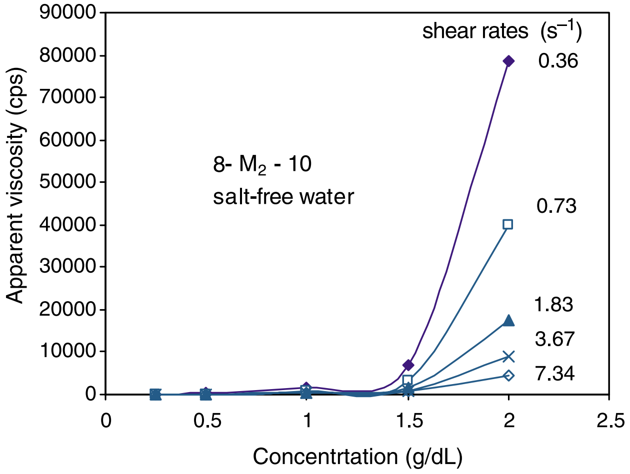


Fig. 3. Variation of viscosity with concentration of APE **8**-M$_2$-10 at various shear rates in salt-free water at 30 °C.

hydrophobically modified associative polymers [20–25]. The strong interchain associations form large aggregates (a network structure of polymer chains) as the polymer concentration passes C*$_{HA}$. The network structures thus contribute significantly to the thickening.

For the purpose of comparison, variation of viscosity with shear rates of **8**-M$_2$-3.5, -5, -7.5 and -10 at a concentration of 2 g/dl in salt-free water is shown in Fig. 4. Increase in hydrophobe contents resulted in increased viscosity as a result of enhanced hydrophobic interactions. The polymers **8**-M$_2$ containing 3.5, 5, 7.5 and 10 mol% hydrophobe have apparent viscosity values of 80, 135, 17 200 and 78 500 cps, respectively, at a shear rate of 0.36 s^{-1}. Polymers with higher hydrophobe-content are known to demonstrate higher degree of intramolecular association [27]. However, the highest viscosity value obtained for **8**-M$_2$-10 demonstrates the predominance of interchain hydrophobic associations even in the presence of 10 mol% hydrophobes. In salt-free water the polymer backbone is extended and the average distance between the randomly distributed hydrophobes may not permit effective internal micellization.

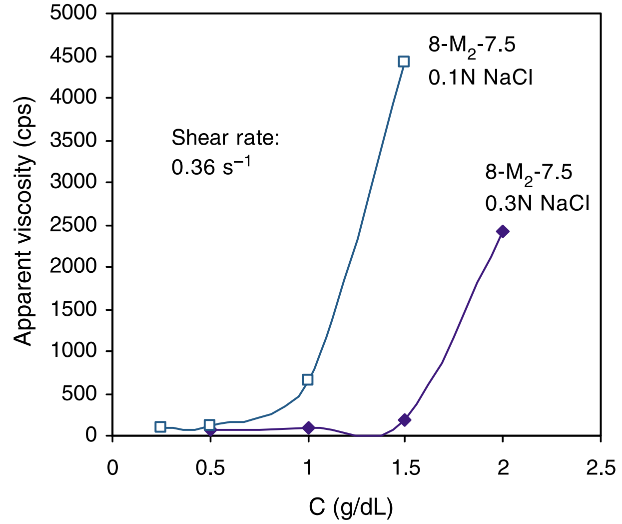


Fig. 5. Variation of viscosity with concentration of APE **8**-M$_2$-7.5 at a shear rate of 0.36 s^{-1} in 0.1 and 0.3 N NaCl at 30 °C.

Figs. 5 and 6 display the variation of viscosity at various concentrations of NaCl. As evident from the Fig. 5 the critical association concentration (C*$_{HA}$) was found to be around a polymer concentration of 1 g/dl. The viscosity values decrease with the increase in salt concentration. The decreased repulsion between the charges in the polymer chains lead to a compaction of the polymer coil, and as a result the viscosity is expected to decrease with increasing concentration of the added NaCl. The presence of NaCl on the other hand makes the aqueous system more hostile to the hydrophobes thus forces them to associate inter- or intra- molecularly. In the case of **8**-M$_2$-7.5, the decrease in viscosity values with increasing concentration of NaCl implies the greater significance of polymer compaction by shielding as well as intramolecular hydrophobic associations in an environment increasingly hostile to the hydrophobes. The **8**-M$_2$-10 gave cloudy solution in 0.1 N NaCl as

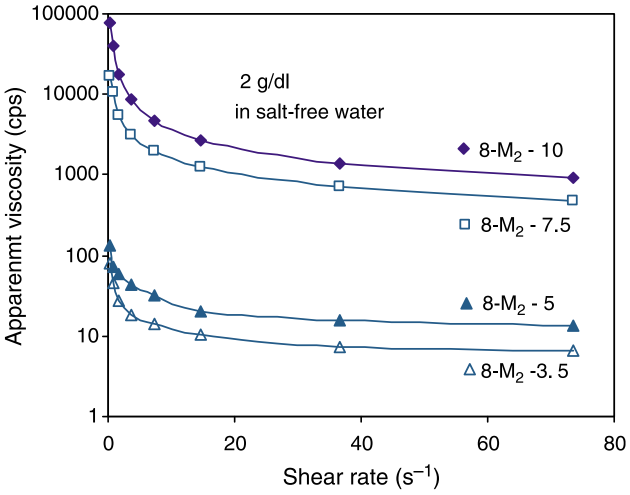


Fig. 4. Variation of viscosity of a 2 g/dl solution of APE **8**-M$_2$-3.5, -5, -7.5, -10 with shear rates in salt-free water at 30 °C.

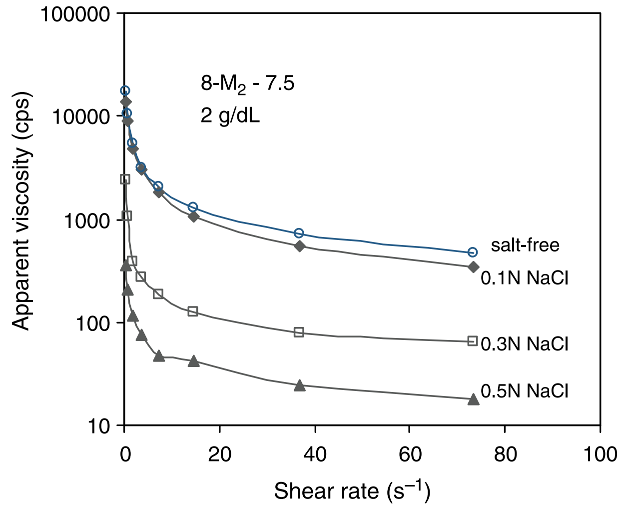


Fig. 6. Variation of viscosity of a 2 g/dl solution of APE **8**-M$_2$-7.5 at various shear rates and NaCl concentration at 30 °C.

a result of 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.

A contrasting salt effect was observed in the case of the polymer **8**-M_2-5. Viscosity dependency of **8**-M_2-5 at a concentration of 2 g/dl at various NaCl concentrations (0–0.5 N) is shown in Fig. 7. The polymer in salt-free water, 0.1, 0.3 and 0.5 N NaCl was found to have apparent viscosity values of 135, 2810, 210 and 80 cps, respectively, at a shear rate of 0.36 s^{-1}. In contrast to **8**-M_2-7.5, the viscosity values thus increase considerably for the polymer **8**-M_2-5 by changing the solvent from salt-free water to 0.1 N NaCl. While the viscosity value decreases in 0.3 N NaCl in compare to the viscosity in 0.1 N NaCl, it still remains higher than that in salt-free water. Viscosity attains its lowest values upon further increasing the NaCl concentration to 0.5 N. The Fig. 7 thus displays the role of added salt (NaCl) in an interesting demonstration of coil compaction as well as hydrophobic association. In the presence of added salt, the increase in viscosity correlates well with the known effects of NaCl on hydrophobic association [28]. The increase in viscosity values with increasing concentration of NaCl implies the greater significance of the interchain hydrophobic associations in an environment increasingly hostile to the hydrophobes than the polymer compaction by shielding the anionic charges on the pendents. At the highest NaCl concentration (0.5 N), further compaction of the polymer coil may encourage intramolecular micellization thereby decreasing the viscosity values.

One of the major objectives of the study is to investigate the effects of zwitterionic and anionic charge densities on the associative properties of the pH-responsive terpolymers synthesized for this work. The presence of protonated nitrogens in the polymer backbone permitted us to vary the ratio of the zwitteionic and anionic charge densities by treating the polymers **6** with appropriate amounts of sodium hydroxide. The treatment of the polymers with 0.55, 0.67, 0.80 and 1 equiv. of NaOH is approximated to generate terpolymers **7** with the ratio of [(zwitterionic (x)+cationic (y)] and anionic (z) charge densities as 45:55, 33:67, 20:80 and ∼0:100, respectively. It is to be mentioned here that polymers containing higher than ∼50 mol% zwitterionic moieties were found to be insoluble in salt-free as well as salt (NaCl)-added water. The viscosity behavior of the **7**-M_2-5 with concentration of the polymers in the presence of various equivalents of NaOH in 0.1 N NaCl at a shear rate of 0.36 s^{-1} is shown in Fig. 8. The viscosity attains its maximum value in the presence of 0.67 equiv. of NaOH, and decreases upon further addition of NaOH. This seems to be the case with various concentrations of the polymer. Internal neutralization of the charges in polyzwitteriones is known to lead the polymer backbone to adapt collapsed coil conformation as a result of intra- and interchain interactions [21,22]. The viscosity values were found to increase with the increase in the APE fraction (z). This is expected since the decrease in the zwitterionic fraction (x) provokes an extension of the polymer backbone as a result of increased repulsion among the charged SO_3^- groups. When the net charge of an ionic polymer approaches zero, attraction between oppositely charged units leads to a globule-like conformation, and most often to insolubility in pure water. While the presence of ionic sites of similar charges (SO_3^- groups in the APE fraction) along the hydrophilic backbone can lead to a better solubility in water and a stronger thickening efficiency due to coil expansion, the increased interchain electrostatic repulsions may not permit the polymer chains to approach close enough to demonstrate hydrophobic associations. At a $(x+y)/z$ ratio of 33:67 the combined effects of the coil expansion and hydrophobic association was found to lead to the maximum viscosity value (Fig. 8). At lower $(x+y)/z$

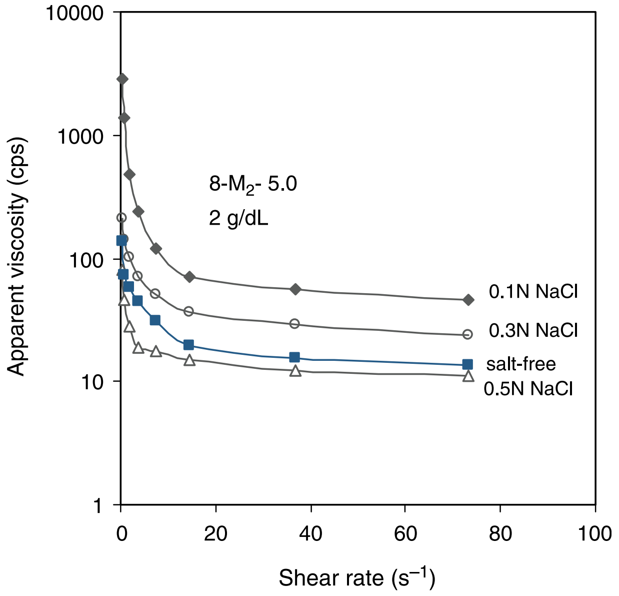


Fig. 7. Variation of viscosity of a 2 g/dl solution of APE **8**-M_2-5 at various shear rates and NaCl concentration at 30 °C.

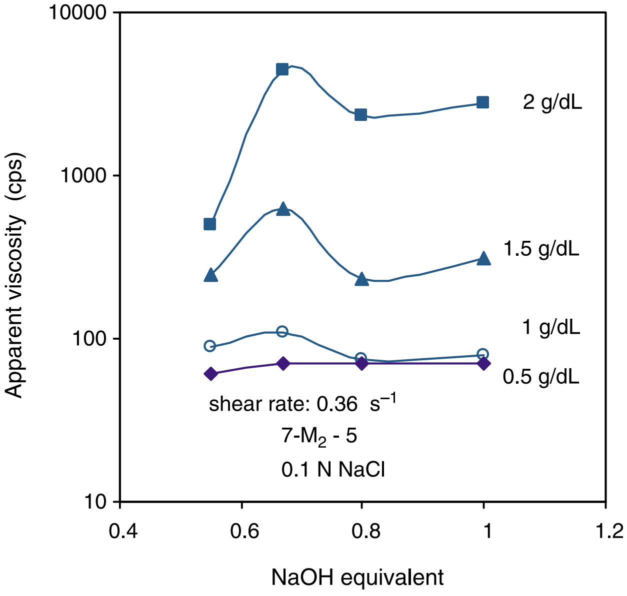


Fig. 8. Variation of viscosity with concentration of APE/PSB **7**-M_2-5 at a shear rate of 0.36 s^{-1} in 0.1 N NaCl in the presence of various equivalents of NaOH at 30 °C.

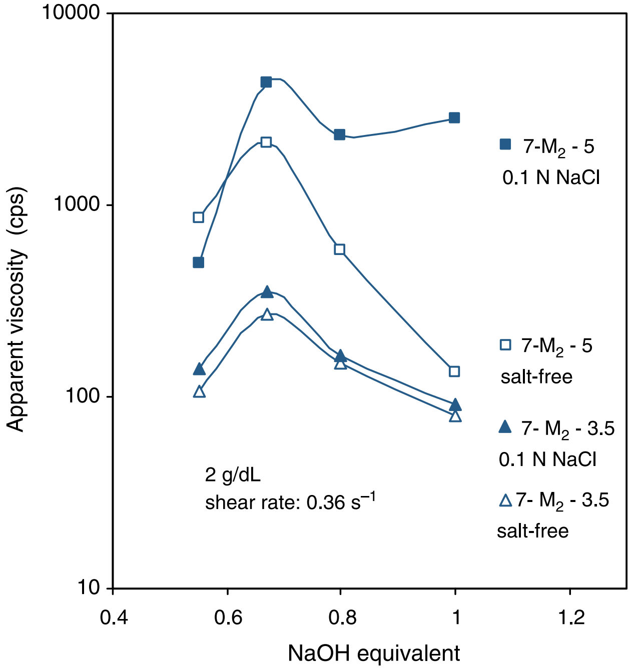


Fig. 9. Variation of viscosity of a 2 g/dl solution of APE/PSB **7**-M_2-5 and -3.5 at a shear rate of 0.36 s^{-1} in salt-free and 0.1 N NaCl in the presence of various equivalents of NaOH at 30 °C.

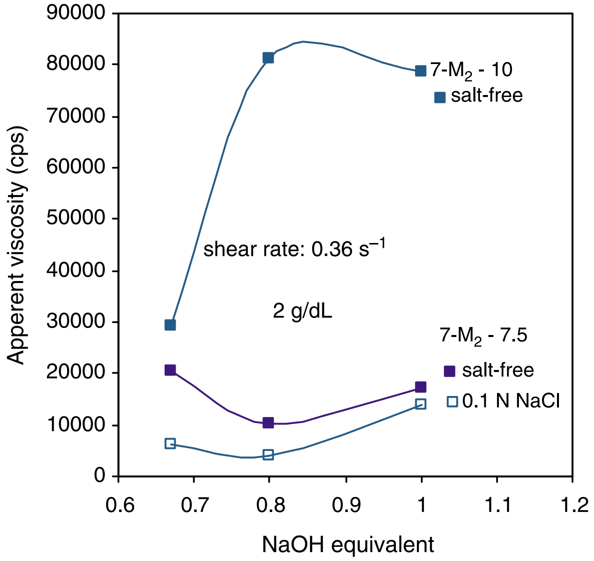


Fig. 10. Variation of viscosity of a 2 g/dl solution of APE/PSB **7**-M_2-10 in a salt-free water and **7**-M_2-7.5 in a salt-free and a 0.1 N NaCl at a shear rate of 0.36 s^{-1} in the presence of various equivalents of NaOH at 30 °C.

ratios, the effect of coil expansion due to a higher APE fraction is more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher $(x+y)/z$ ratio the coil contraction becomes the predominant effect.

Fig. 9 shows the viscosity of a 2 g/dl solution of **7**-M_2-3.5 and -5 in salt-free water as well as in 0.1 N NaCl at a shear rate of 0.36 s^{-1} in the presence of various equivalents of NaOH. It is evident from the Fig. that the viscosity values are greater in 0.1 N NaCl than in salt-free water and also, as in the previous case, the viscosity attains its maximum value in the presence of 0.67 equiv. of NaOH. In the presence of NaCl, the chain contraction in the anionic fraction (z) due to screening of the charges by NaCl is more than compensated by the increased hydrophobic associations as well as chain expansion in the zwitterionc fraction (x).

Fig. 10 shows the viscosity versus equivalents of NaOH at a shear rate of 0.36 s^{-1} for a 2 g/dl solution of **7**-M_2-7.5 and -10 in salt-free water as well as in 0.1 N NaCl. As mentioned earlier the polymer **7**-M_2-10 was found to be insoluble in 0.1 N NaCl. While **7**-M_2-10 generated from **6**-M_2-10 by treating with 0.67 equiv. of NaOH remained somewhat cloudy in salt-free water, the corresponding polymers in the presence of 0.80 and 1 equiv. NaOH gave clear solutions. Increasing the NaOH equivalent to 0.80 increases the viscosity while at 1 equiv. NaOH the viscosity declines. The polymer **7**-M_2-7.5 in salt-free water behaved like the other polymers; it has the maximum viscosity in the presence of 0.67 equiv. of NaOH in salt-free water. However the solubility problem in 0.1 N NaCl did not reflect the similar trend in viscosity behavior; the **7**-M_2-7.5 was found to give cloudy solution in the presence of 0.67 equiv. of NaOH. It has been found that polymer **6** having higher hydrophobe contents required higher equivalents of NaOH for their solubility.

The basicity constants (K) of the copolymer APE 8-M_2-0 has been reported by us [16] as 'apparent' in salt-free water as well as in 0.1 N NaCl; K values were found to decrease progressively with the increase in the degree (α) of protonation of the anionic polyelectrolyte. The log K^0 values (i.e. pH values at $\alpha=0.5$) of 8.51 and 7.54 in salt-free water and 0.1 N NaCl, respectively, indicate the more basic character of the nitrogen in the former medium. The pH values for the terpolymer 8-M_2-3.5 (2 g/dl), treated with 0.55, 0.67, 0.80 and 1 equiv. of NaOH, were found to be 8.6, 9.3, 10.3 and 13.1, respectively in salt-free water; the corresponding values in 0.1 N NaCl were determined to be 8.1, 8.8, 9.9 and 12.9. The pH values for the other terpolymers also revealed the similar trends. The presence of NaCl thus makes the polymer solutions less basic as a result of a change in conformation and hydration of the macromolecular chains [16]; the lower basicity constant tends to shift the equilibrium ($Z^- + H_2O \rightleftharpoons ZH^{\pm} + OH^-$) to the left side. As one proceeds from the fully zwitterionic ($\pm\pm\pm\pm\ldots$) polymer, the anionic moieties ($-$), generated as a result of neutralization with NaOH, would be randomly placed as far apart as possible to minimize electrostatic repulsions. The 'apparent' (i.e., continually changing) nature of the basicity constants may imply the random instead of blocky distribution of the charges; the negative ($-$) charges placed in between the zwitterions ($\pm$) will experience a decreased overall negative charge density in the macromolecule. On the other hand, the 'sharp' (i.e., unchanged) basicity constant values are expected in a blocky distribution of the charges since the negative charge density remains more or less the same in such an environment. The best possible arrangement of the zwitterionic and anionic charges in a 1:1 ratio is expected to be $\pm-\pm-\pm-$.

4. Conclusions

The work involves an interesting class of interconvertible polymers. Since the PSB/APE **7** and APE **8**, are derived from the same PSB **6**, they all have identical degree of polymerization thus allowing a meaningful assessment of their solution properties. The hydrophobe incorporation has considerably enhanced the viscosity values for the polymers presented here. The best pH-range for application purposes was found to be ∼8.1–13. The viscosity of the pH-responsive polymers PSB/APE **7** was found to be the highest for the polymer chain containing zwitterionic and anionic charge densities in a ratio of 33:67, respectively. Interchain bridging (open associations) is thus found to be the most effective with polymer chains having a probable charge distribution of $\pm--\pm--\pm--$, i.e., every zwitterionic unit is followed by two anionic units. The work demonstrated the balance of zwitterionic and anionic charge densities required for the enhancement in the viscosity values of the ionic polymers. The pH-induced change in the conformation of PB/APE **6** can be manipulated in the effective use of this hydrophobically modified polymer in protein separation; similar pH-responsive polycarbobetaines has been found to be useful in protein partitioning in aqueous two-phase polymer systems [29].

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