Rheological behavior of associating ionic polymers based on diallylammonium salts containing single-, twin-, and triple-tailed hydrophobes

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ARTICLE INFO

ABSTRACT

The cycloterpolymerizations of N,N-diallyl-(4-octyloxy)benzyl-, N,N-diallyl-(3,5-dioctyloxy) benzyl-, and N,N-diallyl-(3,4,5-trioctyloxy)benzyl-ammonium chloride (0–8 mol%) with hydrophilic monomer N,N-diallyl-N-carboethoxymethylammonium chloride and sulfur dioxide afforded a series of cationic polyelectrolytes (CPE). The CPEs were treated with HCl and NaOH to produce the corresponding pH-responsive cationic acid salts (CAS) and polybetaines (PB), anionic polyelectrolytes (APE) as well as polymers PB/APE containing various proportions of zwitterionic (PB) and anionic fractions (APE) in the polymer chain. Likewise, the cycloterpolymerizations of these single-, twin-, and triple-tailed hydrophobes (0–12 mol%) with hydrophilic monomer diallyldimethylammonium chloride and sulfur dioxide afforded a series of CPE in excellent yields. The polymers were characterized by different techniques including NMR and IR. The solution properties of the series of CPE were investigated by rheological techniques. The studied water soluble polymers showed different rheological behavior depending on their structure (hydrophobe type and content) as well as salinity and pH. The high shear thinning and the formation of networks at low shear would likely promote the use of such polymers in enhanced oil recovery applications.

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1. Introduction

Associating water soluble polymers have gained prominence during the past decades because of their interesting rheological behavior in aqueous solutions [1,2]. These are amphiphilic polymers containing a small proportion of hydrophobic groups incorporated in hydrophilic polymer chains. While regular polymers build viscosity through a combination of concentration and molecular weight, associating polymers depend on the formation of physical network via intermolecular association of the hydrophobic groups leading to reversible formation of three dimensional physical cross-links of polymer chains. The most salient features of such network are their significant enhancement of viscosity and elastic behavior compared to that of polymers without associating groups. The physical links in the networks may be disrupted when the strain rate is high and sustained, but reform when the imposed stress drops. The primary advantage of associative polymers is that they contribute less elasticity than regular linear high molecular weight polymers, which is desirable in some coating processes [3]. The shear thinning feature associated with the reversible nature of these physical cross links led to their applications as rheology modifiers (particularly thickening agents) especially in aqueous based formulations within numerous industrial domains such as water-borne coatings, paints, cosmetics and enhanced oil recovery [4–6].

The presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a great variety of interesting behaviours [7]. The balance

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of hydrophobic interaction and electrostatic repulsion in hydrophobically associating ionic polymers determines whether the polymer will undergo hydrophobic self association. Primarily, this balance is a function of the number of charges and hydrophobes in the polymer as well as the size of the hydrophobe [8].

In addition to forming highly viscous solution, aqueous system containing hydrophobically modified water soluble polymers may organize into viscoelastic hydrogels. The hallmark of viscoelastic material is the presence of a rubbery plateau in its dynamic rheological spectra. This means that under oscillatory applied shear, there exits some range of applied frequency, ω (s^{-1}), over which the material behaves more like an elastic solid than a viscous liquid, and its response is independent of applied frequency. Thus the storage (or "elastic") modulus, G', exceeds the loss modulus G'', and G' is independent of ω. In contrast, in polymer solutions, G'' is greater than G' over the entire frequency range since the polymer solution is more viscous than elastic. Thus the physical distinction between a hydrogel and a polymer solution is that the intermolecular linkage points in a gelled network are mechanically stable over some range of applied shear stress, while those in a solution are not [9].

Since the discovery that free radical polymerization of diallyl quaternary ammonium salt yields water soluble cyclopolymers instead of cross-linked polymers [10], homo and co-cyclopolymers of scientific and technological interest have been synthesized from various diallyamine compounds [11–14]. There are some reports, which describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique [15–18].

Recently, our research group reported [19,20] the synthesis and solution properties of a series cycloterpolymers of sulfur dioxide, N,N-diallyl-N-carboethoxymethylammonium chloride **1** with varying amount of hydrophobic monomers N,N-diallyl-N-benzylammonium choloride **2** containing single-(**a**), twin-(**b**), and triple-tailed (**c**) hydrophobes [18]. Incorporation of small amounts of the hydrophobic comonomer has dramatically enhanced the viscosity values. The low critical association concentration C^*_{HA} (<0.5 g/dL) observed for the twin and triple-tailed polymer series is indeed a notable improvement over the C^*_{HA} of 15–17 g/dL for similar cyclopolymers [20].

Our present study, reports the synthesis, solution properties and viscoelastic behavior of a series of new cycloterpolymers of sulfur dioxide, diallyldimethylammonium chloride **8** with varying amount of hydrophobic monomers 2(a–**c**) (Scheme 1). The study also examines the viscoelastic behavior of hydrophobically modified polyelectrolytes cationic acid salt (CAS) **4**, obtained from hydrolysis of cationic polyelectrolyte (CPE) **3** as a function of zwitterions (x) and anions (z) fraction. CAS **4** samples are completely converted to corresponding anionic polyelectrolyte (APE) **7** in the presence of 2.0 equivalent of NaOH, while neutralization with 1.0 equiv. of NaOH leads to polybetaine (PB) **5**. Treatments of CAS **4c** (M_2-2.67) (containing 2.67 mol% incorporated hydrophobe **2c**) with NaOH in the range of 1–2 equivalents resulted in corresponding polybetaine (PB)/APE **6** having different fractions of zwitterions (x) and anions (z) (scheme 1). The rheological behavior of

these pH-responsive polymers and APE **7** as a function of hydrophobe content was examined.

2. Experimental

2.1. Physical methods

Melting points were 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 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- and ^{13}C-NMR spectra of the polymers were measured in D$_2$O using dioxane as internal standard on a JEOL LA 500 MHz spectrometer (see Fig. 1). Viscosity measurements were made with an Ubbelohde viscometer (having Viscometer Constant of 0.005718 cSt/s at all temperatures). Digital Brookfield rotational viscometer with UL adaptor accessories or SC4–18 spindle accessories was used to measure apparent viscosities at various shear rates and temperatures. Molecular weights of the samples were determined by light scattering experiments at 21 °C. Solutions of the cationic polyelectrolyte (CPE) **9** containing no hydrophobe (y = 0) (polymer concentration range: 0.03 to 0.1 g/dL) were prepared in 0.5 M NaCl solution; the presence of salt allows the screening of the positive 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 used as a solvent for the hydrophobically modified polymers. Millipore disposable filters of pore sizes 0.2 μm and 0.02 μm were used to remove dust particle from the polymer solutions and pure solvent, respectively. 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 (dn/dc) of different polyelectrolyte 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 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 glass ware were cleaned using deionized water. Diallyldimethylammonium chloride **(8)**
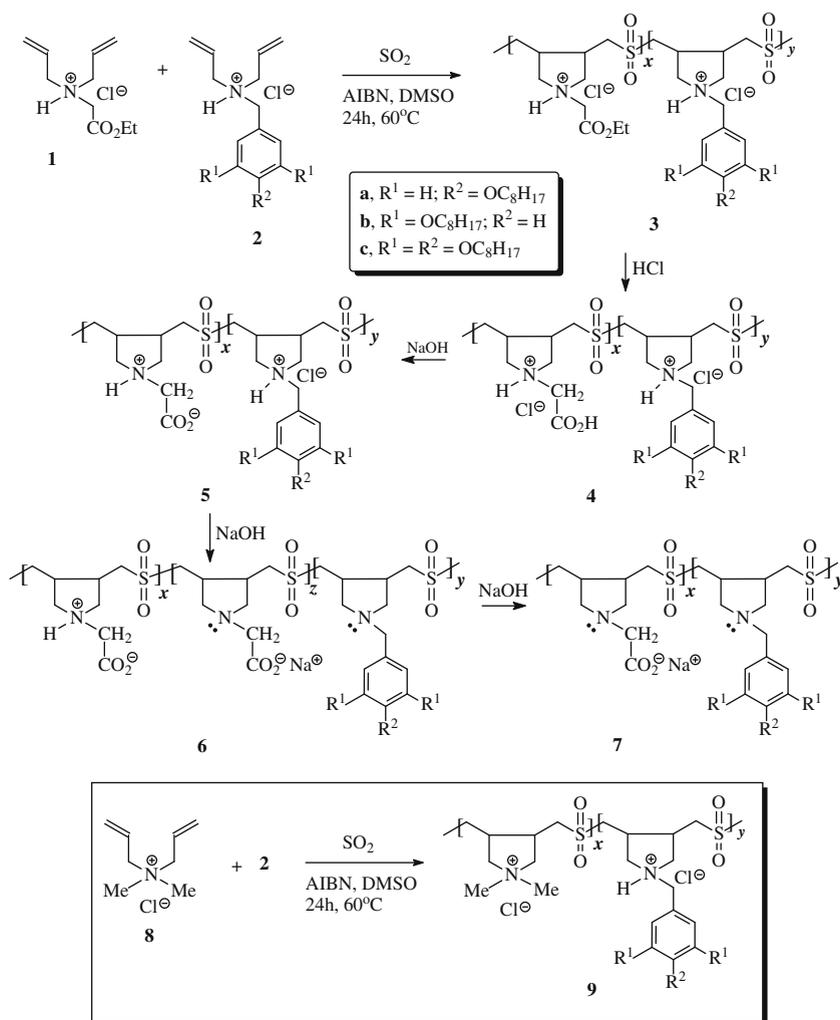
Scheme 1.

2.3. Apparent molecular weight of the CPEs 3

Terpolymer **3b**-M₂-8 (entry 3, Table 1), for instance, indicates the incorporation of 8.0 mol% of the twin-tailed hydrophobe (M₂) **2b**; whereas the CPEs **3c** describes the incorporation of the triple-tailed **2c**. Apparent molecular weight ($\overline{M}_{w,app}$) of the cationic polyelectrolytes **3** (using polymer concentration range: 0.03 to 0.1 g/dL prepared in a 1:1 (v/v) ethanol/0.1 N NaCl mixture) were determined to be in the range $(1.7–2.1) \times 10^5$ g/mol.

2.4. Conversion of CAS 4 to PB/APE 6 and APE 7 by basification and its use in rheology measurements

Details of conversion of CPE **3** to CAS **4** and PB/APE **6** and APE **7** by basification are reported elsewhere [18]. The treatment of CAS **4** with NaOH in the range 1–2 N equivalent resulted in the formation of PB/APE **6** contain-

ing varying proportion of the zwitterionic and anionic fractions. To ensure complete dissolution, the solutions were left at room temperature for 24 h and stirred using magnetic stir bar for 1 h to obtain a homogeneous solution.

2.5. General procedure for the synthesis of CPEs 9 via terpolymerization of 2/8/SO₂

All the polymerizations were carried out using conditions as described in the Table 2. In a typical experiment, SO₂ was absorbed in a solution of the monomers **8/2** (i.e., M₁/M₂) in DMSO in a 25 cm³ round-bottom flask. The required amount of the initiator (AIBN) (as listed in Table 2) was then added under N₂ and the closed flask was stirred using a magnetic stir bar at 60 °C for 24 h. The stir bar stopped moving after 2–3 h. The reaction flask was briefly opened after 10 h to release the N₂ formed during decomposition of AIBN. The reaction mixture was then slurried in methanol and precipitated from acetone. The process was repeated and the resultant polymer was dried under vacuum at 50 °C to a constant weight. The polymers
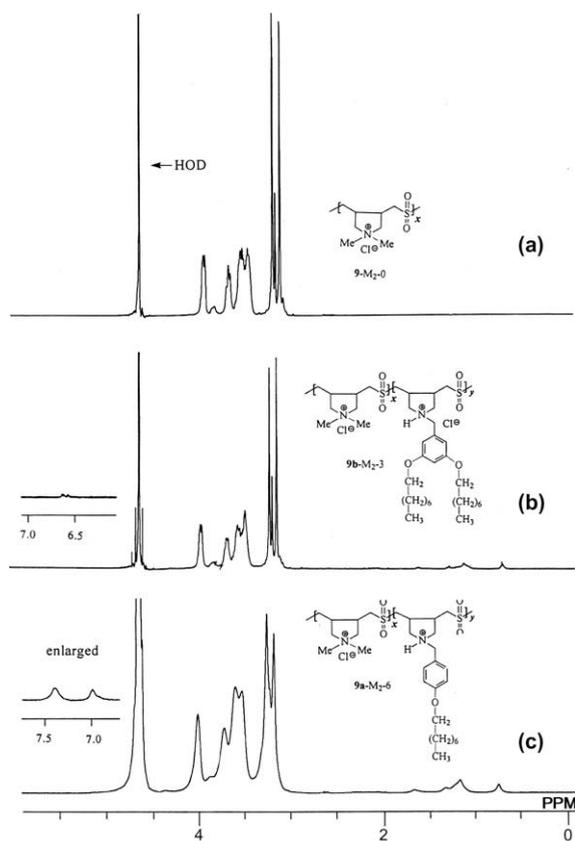
Fig. 1. ^{1}H NMR spectrum of (a) **9**-M$_2$-0, (b) **9b**-M$_2$-3 and (b) **9a**-M$_2$-6 in D$_2$O.

containing higher hydrophobe content were found to be soluble in methanol. The hygroscopic white terpolymers CPE **9** were stored in a desiccator. The elemental analysis ascertained the mole ratio of (M$_1$ + M$_2$):M$_3$(SO$_2$) as 1:1. The onset of thermal decomposition of the polymers (closed capillary) was found to be in the range 235–250 °C (decomposed, turned brown, charred at 280 °C).

Apparent molecular weight ($\overline{M}_{w,app}$) of the cationic polyelectrolytes **9**-M$_2$-0 (in 0.5 M NaCl), **9a**-M$_2$-6, **9b**-M$_2$-6 and **9c**-M$_2$-3 (in methanol) – associating polymers usually do not give true molecular weights – were determined to be 1.23 × 10^5, 1.36 × 10^5, 1.38 × 10^5, 1.43 × 10^5 g/mol, respectively.

2.6. Rheological measurements

Dynamic shear measurements of the polymer solutions over a wide range of frequencies were conducted using a constant strain Advanced Rheometric Expansion System (ARES) fitted with a stainless steel cone and plate sample cell operating in dynamic mode. The radius of the plate is 50 mm, cone angle is 0.1 rad and the gap between the cone and plate was set to 0.048 mm. A shear strain amplitude (γ_o) of 10% was used, after a strain sweep test on selected samples showed that this γ_o was sufficiently small to produce rheological properties in the linear viscoelastic range. Reproducibility of frequency sweep measurements is shown in Fig. 2 for **9b**-M$_2$-3 sample. The displayed results represent two independent measurements on fresh loadings of the same sample. Excellent agreement of both dynamic viscosity and storage modulus shows the degree of reproducibility of these measurements. All experiment were conducted at 25 ± 1 °C and performed in a descending −ω order from 10^2 to 10^{-2} rad/s.

3. Results and discussion

3.1. Synthesis and physical characterization of the terpolymers

The cationic polyelectrolyte CPE **3** was synthesized via cycloterpolymerization of sulfur dioxide, N,N-diallyl-N-carboethoxymethylammonium chloride **1** and the hydrophobic monomer **2** following the procedure earlier reported [19]. The CPE **3** were hydrolyzed in 6 N HCl to produce the water-insoluble cationic acid salts CAS **4** (M$_2$-4) which, on treatment with 1.67, 1.85, and 2.0 equivalents of NaOH, resulted in a solution of PB/APE **6** and APE

Table 1
Terpolymerization[a] of the monomers **1**(M$_1$)/**2**(M$_2$)/ SO$_2$.

Entry No.	Sample	M$_1$ (mmol)	M$_2$[b] (mmol)	Feed[c] M$_1$:M$_2$	Polymer[c] M$_1$:M$_2$	Yield%	Intrinsic viscosity (dL/g)	
							Salt-free[d]	0.10 N[e]
1	**3**-M$_2$-0	15.0	0	100:0	100:0	95.3	0.991	0.559
2	**3b**-M$_2$-4	14.4	0.60	96:4	95.9:4.1	89	0.522	0.293
3	**3b**-M$_2$-6	14.1	0.90	94:6	94.6:5.6	91	0.653	ND[g]
4	**3b**-M$_2$-8	13.8	1.20	92:8	92.4:7.6	85	0.685[f]	ND[g]
5	**3c**-M$_2$-2.67	14.6	0.40	97.3:2.67	97.1:2.9	90	0.680	ND[g]
6	**3c**-M$_2$-4	14.4	0.60	96:4	96.0:4.0	80	0.795[f]	ND[g]

[a] Polymerization reactions of **2** and **1** to give **3** were carried out in DMSO (5.0 g) containing 15.0 mmol of SO$_2$ in the presence of AIBN (75.0 mg) at 60 °C for 24 h (Ref. [18]).
[b] M$_2$ in entries 1, (2–4) and (5,6) are **2a**, **2b**, and **2c**, respectively.
[c] Mol% in the feed and polymer (as determined by ^{1}H NMR).
[d] Obtained by Fuoss relationship [20] (measured with an Ubbelohde viscometer (K = 0.005718).
[e] Obtained by extrapolation of the linear parts of the curves usually in the range 0.25–0.03125 g/dL polymer solution in 0.1 N NaCl at 30 °C measured with an Ubbelohde viscometer (K = 0.005718).
[f] The polymer gave slight cloudy solutions.
[g] Not determined – insoluble.

Table 2
Terpolymerization[a] of the monomers **8**(M$_1$)/**2**(M$_2$)/ SO$_2$.

Entry No	Sample	M$_1$ (mmol)	M$_2$[b] (mmol)	Feed[c] M$_1$:M$_2$	Polymer[c] M$_1$:M$_2$	Yield%	Intrinsic viscosity[d] (dL/g)
1	**9**-M$_2$-0	25.0	0	100:0	100:0	87	0.683
2	**9a**-M$_2$-4	24.0	1.00	96:4	96:4	91	0.404
3	**9a**-M$_2$-6	23.5	1.50	94:6	94.1:5.9	88	0.319
4	**9a**-M$_2$-12	22.0	3.00	88:12	87.8:12.2	74	0.175
5	**9b**-M$_2$-3	24.25	0.75	97:3	97.2:2.8	92	0.630
6	**9b**-M$_2$-6	23.5	1.50	94:6	94:6	92	ND[e]
7	**9b**-M$_2$-9	22.75	2.25	91:9	89.8:10.2	89	ND[e]
8	**9c**-M$_2$-1.2	24.5	0.50	98:2	98.8:1.2	84	0.620
9	**9c**-M$_2$-2.2	24.0	1.00	96:4	97.8:2.2	88	ND[e]
10	**9c**-M$_2$-3.0	23.5	1.50	94:6	97.4:3.0	65	ND[e]

[a] Polymerization reactions of **2** and **8** to give **9** were carried out in DMSO (6.5 g) containing 25 mmol each of (M$_1$ + M$_2$) and SO$_2$ in the presence of AIBN (125 mg) at 60 °C for 24 h.
[b] M$_2$ in entries (2–4), (5–7) and (8–10) are **2a**, **2b**, and **2c**, respectively.
[c] Mol% in the feed and polymer (as determined by ^{1}H NMR).
[d] Obtained by Fuoss relationship [20] (measured with an Ubbelohde viscometer (K = 0.005718).
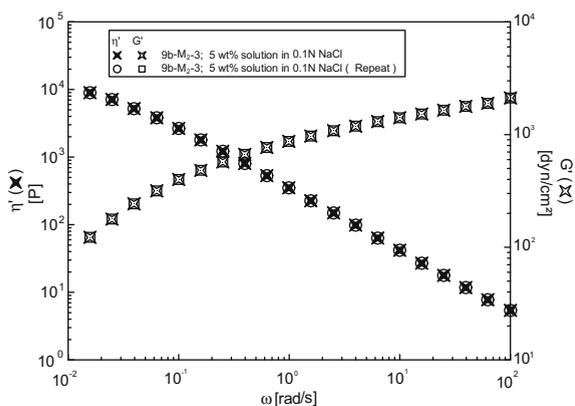[e] Not determined – insoluble.

Fig. 2. Reproducibility of data : variation of dynamic viscosity and storage modulus with frequency for a 5 wt.% solution of **9b**-M$_2$-3 polymer in 0.1 N NaCl.

7 in an approximate PB/APE ratios of 33:67, 15:85, and ~0:100, respectively. Prior to the addition of alkali, CAS **4** polymer contains insoluble carboxylic acid groups in the form of latex particles. The addition of NaOH solution neutralizes the acid group (–COOH) on the polymer chain, and as a result the carboxylic acid groups are converted to the ionized carboxylate form which has better solubility. CAS **4** terpolymer as well as its corresponding PB **5** (obtained by treating CAS **4** with **1** equivalent of NaOH) was found to be insoluble in salt-free or salt-added solution. Critical NaOH equivalent required for the solubility of CAS **4** (M$_2$-4) was around 1.40; this amount of NaOH would result in the formation of PB/APE **6** with x:z ratio of approximately 60:40 (Scheme 1).

The cationic polyelectrolyte CPE **9** was synthesized via cycloterpolymerization of sulfur dioxide, diallyldimethylammonium chloride **8** and the hydrophobic monomer **2** in excellent yields (Scheme 1) (Table 2). All the synthesized polymers were found to be soluble in salt-free water. While the hydrophobe-free copolymer M$_2$-0 was insoluble in methanol, the terpolymers with higher hydrophobe con-

tents dissolved readily in methanol. Some of these polymers containing higher proportions of hydrophobes were found to be insoluble in 0.1 N NaCl.

Viscosity of the solutions having polymer concentration greater than C^*_{HA} increased exponentially instead of linearly, while below C^*_{HA}, η_{red} increased in a linear fashion. Reduced viscosity as a function of concentration was plotted according to Huggins equation, and extrapolation of the linear part of the viscosity plots (η_{sp}/C versus C) in the concentration range 0.25–0.031 g/dL in 0.1 N NaCl permitted us to determine the intrinsic viscosity [η] values of the polymers (Table 2). However, as the incorporation of the hydrophobe increases, as in the polymers **9a**, the [η] values tend to decrease and this could be attributed to intramolecular associations of the hydrophobes leading to a decrease in the hydrodynamic volumes of the polymer chains [17].

To allow meaningful assessment of the associative behaviors of the synthesized polymers, the polymerization conditions were kept similar as rigorously as possible in order to obtain polymers having similar degree of polymerizations. The resultant copolymer **9**-M$_2$-0 (0.5 M NaCl) and the terpolymers – single-tailed **9a,** twin-tailed **9b** and triple-tailed **9c**- have very similar apparent molecular weights $\overline{M}_{w,app}$ (see Section 2.3) as reflected in similar values of [η] (see Table 2). The results of the polymerization, carried out under similar conditions, and the intrinsic viscosities of the resultant polymers in dilute solutions are given in Table 2. The entry 1 in Table 2 describes the copolymer M$_2$-0 indicating the absence of the hydrophobic monomer **2** (M$_2$). The terpolymer **9a**-M$_2$-6 (entry 3), and **9b**-M$_2$-6 (entry 6) for instance, indicates the incorporation of 6 mol% hydrophobic monomer **2a** and **2b,** respectively. However, in the cases of the hydrophobe **2c**, the incorporation of the hydrophobe was found to be less than the amount present in the feed; for instance, **9c**-M$_2$-3 (entry 10) indicates 3 mol% of the hydrophobe while the feed contained 6 mol%.

The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M$_2$-0 as reported elsewhere [21,22]. Fig. 1a–c display the

^{1}H NMR spectrum of the **9**-M$_2$-0 and **9b**-M$_2$-3 and **9a**-M$_2$-6, respectively. The incorporation of the hydrophobic monomers was calculated using ^{1}H NMR integration of the signals around $\delta 0.72$ (for methyl protons of the hydrophobic pendents) and 1.08–1.20 ppm [for $(CH_2)_{15}$ of octadecyl pendents]. 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.

3.2. Copolymer composition

The copolymers **9** were synthesized by varying the feed ratios of **8/2**. The ^{1}H NMR spectra may be used for the estimation of copolymer composition by the following method of calculation:

For polymers having hydrophobes of a single tailed (**9a**), twin tailed (**9b**) and triple tailed (**9c**) octyloxy groups, the integrated area (M) in the range $\delta 0.5$–1.75 ppm belongs to 15H, 30H and 45H marked f′ and G′, respectively (Scheme 2). As such the area of a single H belonging to the hydrophobe should equate to M/15 or M/30 or M/45 for **9a**, **9b** and **9c**, respectively. The rest of the aliphatic protons, i.e. a total of 16 protons (marked **a–d**) for the hydrophilic monomer unit and 14, 16 and 18 protons (marked **a′–e′**) for the hydrophobic unit in **9a**, **9b** and **9c**, respectively, appeared in the range $\delta 3.0$–4.5 ppm. If one subtract the area (of the protons belonging to the hydrophobes in the range $\delta 3.0$–4.5 ppm), which is 14 M/15, 16 M/30 and 18 M/45 for **9a**, **9b** and **9c**, from the total area (T) under $\delta 3.0$–4.5 ppm, then one gets the area for a single H belonging to the hydrophilic unit as (T-14 M/15)/16, (T-16 M/30)/16, and (T-18 M/45)/16 for the copolymer **9a**, **9b** and **9c**, respectively. Mol% of the hydrophobe in **9a**, **9b** and **9c** should then equate to 100(M/15)/[(M/15) + (T-14M/15)/16], 100(M/30)/[(M/30) + (T-16M/30)/16], 100(M/45)/[((M/45) + (T-18 M/45)/16], respectively.

3.3. Viscosity measurements

Fig. 3 displays the variation of viscosity with concentration of **9b**-M$_2$-6 at various shear rates in salt-free water at 30 °C. The hydrophobic associations began to manifest at around C^*_{HA} of 0.5 g/dL of the polymers; at 2 g/dL the polymer solution looked like a gel. 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.
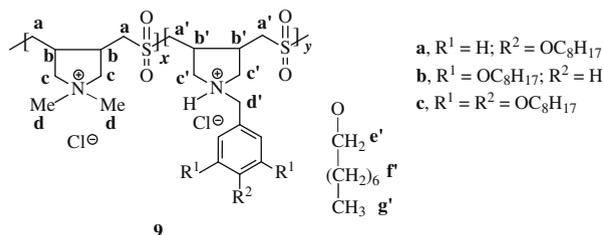
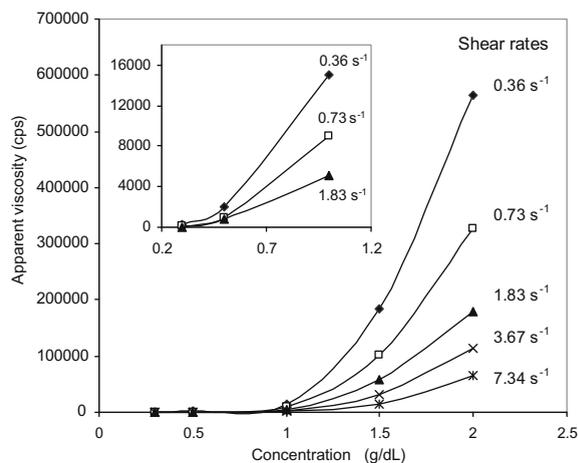**Fig. 3.** Variation of viscosity with concentration of **9b**-M$_2$-6 at various shear rates in salt-free water at 30 °C (Inset showing the variation in the lower concentration range).

Fig. 4 displays the variation of viscosity of a 2 g/dL solution of the polyelectrolytes **9** at various shear rates in salt-free water at 30 °C. The plots reveal the increase in viscosity values with the increase in the amount of hydrophobe incorporated in the polymers except in the case of polymers having very high hydrophobe content. The data in Fig. 4 reveal the ratio of viscosity of **9**-M$_2$-0, **9b**-M$_2$-3, **9b**-M$_2$-6, **9b**-M$_2$-9, at a shear rate of 0.36 s^{-1} as 1:26:8660:680, respectively. The **9b**-M$_2$-6 polymer is thus found to have higher viscosity than its **9**-M$_2$-0 counterpart by a factor of 8660; the tremendous increase in the viscosity value must be attributed to the intermolecular hydrophobic associations between the polymer chains. Further increase in hydrophobe concentration to 9 mol% in **9b**-M$_2$-9 resulted in a decrease in viscosity. This is consistent with studies which indicated that random copolymers with higher proportion of hydrophobes form mainly intramolecular hydrophobic associations [17]. Both **9b**-M$_2$-6 and **9b**-M$_2$-9 are expected to form intramolecular as well as intermolecular hydrophobic associations; however, the contribution of each type of associations depends on the concentration of the polymer in solution and the
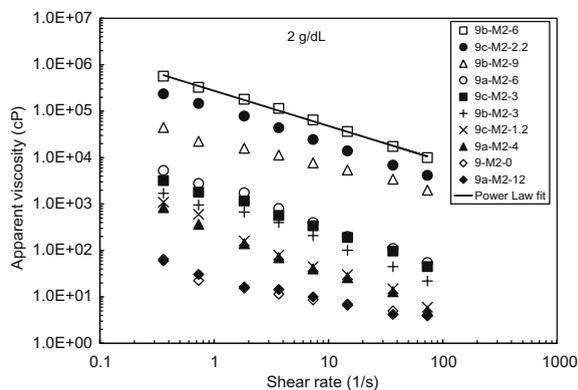

Scheme 2.

Fig. 4. Variation of viscosity of a 2% solution of polymers **9** at various shear rates in salt-free water at 30 °C.

amount of the hydrophobes. While intramolecular associations are preferred in dilute solutions in which internal micellisations lead to decreased hydrodynamic volume and viscosity, the intermolecular associations are manifested in solutions having polymer concentration greater than C^*_{HA}. The Figure also revealed that polymers **9a**-M$_2$-6 (single-tailed) and **9b**-M$_2$-3 (twin-tailed), both having 6 mol% octyloxy tails per polymer chain, were found to have apparent viscosity values of 5280, and 1700 cP, respectively, at a shear rate of 0.36 s^{-1}, while the corresponding values for the **9a**-M$_2$-12 (single-tailed) and **9b**-M$_2$-6 (twin-tailed), both having 12 mol% octyloxy tails per polymer chain, were 60 and 564,000 cP. The tremendous increase in viscosity values for **9b**-M$_2$-6 (twin-tailed) must then be attributed to the superior intermolecular associations between the twin-tailed hydrophobes, while overwhelming dominance of intramolecular associations in **9a**-M$_2$-12 (single-tailed).

3.4. Dynamic shear measurements

The results of the rheological measurements for the investigated polymers are shown in Figs. 5–12. The loss modulus, G'', represents the viscous component, while the storage modulus, G', reflects the elastic part of the polymer. All the measurements were performed in the frequency, ω, range 100–0.1 rad/s. It should be noted that all reported rheological data in this paper are above the torque limits of the ARES rheometer.

Fig. 5 shows G' and G'', dependency on ω for **3b**-M$_2$-4, **3b**-M$_2$-8 and **3c**-M$_2$-2.67 in salt-free water. The objective of this Figure is to show the effect of the number of tails on G' and G''. Polymers **3b**-M$_2$-4 (twin-tailed), **3b**-M$_2$-8 (twin-tailed), and **3c**-M$_2$-2.67 (triple-tailed), have 4×2, 8×2 and 2.67×3 mol% octyloxy tails, respectively. G'' values generally increase and then decrease with the increase in ω a typical Maxwellian viscoelastic fluid with no plateau modulus. On the other hand, G' usually increases with ω and a plateau modulus, G_e observed at low ω. The magnitude of G_e is proportional to the intensity of entanglements

or cross-links. As the ω increases, the intermolecular hydrophobic associations are disrupted and this results in a decrease in viscosity. This indicates that the network links are very sensitive to shear and disrupt under the slightest shear which might be caused by the high electrostatic repulsion, the highly swollen nature of the network and the slight hydrophobic overlap resulting from the strong repulsion. Due to the impact of polymer concentration, values of G'' for the **3c**-M$_2$-2.67 are consistently lower than that of **3b**-M$_2$-4 over the entire frequency range studied even though the two polymers have the same number of octyloxy tails per polymer chain (8 mol% tails). Similar observations were obtained for **9b**-M$_2$-3 (twin-tailed) and **9c**-M$_2$-2 (triple-tailed), with similar number of tails (i.e. 6 mol%) (results are not shown here). Nevertheless, a comparison of G'' of the 4 wt.% solution of twin-tailed **3b**-M$_2$-4 (8 mol% tails) and the 2 wt.% solution of twin-tailed **3b**-M$_2$-8 (16 mol% tails) reveals the following: at low-ω, the 4 wt.% solution with 8 tails has similar values of G'' as the 2 wt.% solution with 16 tails; at high ω, the decrease of G'' with increasing ω (shear thinning) for the 4 wt.% solution with 8 tails is faster. This suggests that the impact of doubling the polymer concentration of the 2 wt.% solution or doubling the number of tails is similar at low ω since both the concentration and the tails lead to similar increase in chain size. This explanation is supported by the previous intrinsic viscosity data (see Table 1, entries 2 and 4). However, at high frequencies the decrease in G'' of the 4 wt.% solution of **3b**-M$_2$-4 (8 mol% tails) is higher than that of the 2 wt.% of **3b**-M$_2$-8 (16 mol% tails) due to the high disruption of the intermolecular hydrophobic associations in the 4 wt.% solution.

On the other hand, G' values for the 4 wt.% (**3b**-M$_2$-4; 8 mol% tails) and 2 wt.% (**3b**-M$_2$-8; 16 mol% tails) show increase in G' with ω dependence at low frequency. The increase in the polymer concentration from 2 wt.% to 4 wt.% while reducing the number of tails by the same factor lead to major increase in the elasticity over the whole frequency range. Unlike the previous G'' data, the impact on G' is obvious which is likely due to increase in the number of entanglements caused by doubling the number of polymer chains rather than doubling the number of tails in the same chains. However, for the **3c**-M$_2$-2.67, G' is almost independent of ω and a plateau modulus is reached denoting the formation of a network. Therefore, triple-tailed polymers can be used to obtain networks at lower concentrations.

The **3c**-M$_2$-2.67 were hydrolyzed in 6 N HCl to produce the water-insoluble cationic acid salt CAS **4c** which, on treatment with 1.67 equiv. of NaOH, afforded the solution of PB/APE **6c** in an approximate PB/APE ratio of 33:67. While the presence of ionic sites of similar charges (CO$_2^-$ 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, intermolecular electrostatic repulsions lead to a lowering of the degree of hydrophobic association. Synergistic effect may be observed where the electrostatic repulsions can result in chain expansion and the hydrophobic groups may also maintain interpolymer association. It has been reported that at approximate PB/APE of 33:67, combined effect of
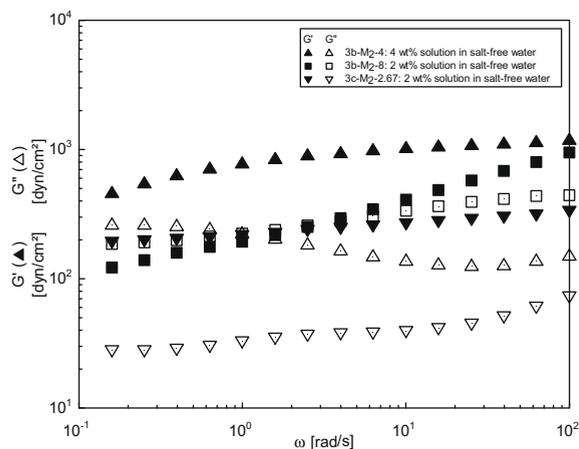

Fig. 5. Variation of storage and loss modulus with frequency of a 2 wt.%, 4 wt.% solution of **3b**-M$_2$-4, **3b**-M$_2$-8 and **3c**-M$_2$-2.67 polymer in salt-free water.

coil expansion and hydrophobic association was found to lead to maximum viscosity values [23].

Fig. 6 shows the effect of concentration on dynamic viscosity and storage modulus of tripled tailed PB/APE **6c**-M$_2$-2.67. Both solutions exhibit shear thinning behavior but the dynamic viscosity values of the 3 wt.% samples are consistently higher than that of 2 wt.% over the entire range studied. However, the increase in the polymer concentration from 2 to 3 wt.% resulted in an increase in the shear thinning as indicated by the values of the power-law index (n) that are shown on the high shear viscosity data. These values of n are comparable with reported power-law index for aqueous solutions [24]. It should be noted that a simple molecular theory leads to a power-law expression for high shear rates, with $n = 1/3$. On the other hand, the storage modulus increases with the increase in polymer concentration, which is expected (Fig. 6).

Fig. 7a reveals the effect of hydrophobic content and polymer concentration on the dynamic viscosity values of PA/APE **6b** and **6c** at different frequencies. The viscosity values of the polymer with high hydrophobic content (6 mol% twin-tailed PA/APE **6b**-M$_2$-6) are much higher than that of the low hydrophobic content (4 mol% twin-tailed PA/APE **6b**-M$_2$-4) at the same polymer concentration. Even though PA/APE **6c**-M$_2$-2.67 (2.67 mol% triple-tailed) and PA/APE **6b**-M$_2$-4 (4 mol% twin-tailed) each has 8 mol% octyloxy tails per polymer chain, the viscosity values of the tripled tailed are consistently lower than that of the twin tailed polymer at all frequencies (Fig. 7a). The viscosities of the 2 wt.% solution of **6b**-M$_2$-6 (6 mol% twin-tailed) in 0.1 N NaCl and 3 wt.% solution of **6b**-M$_2$-4 (4 mol% twin-tailed) were similar over the whole frequency range. The twin tailed systems showed similar dynamic viscosity behavior with a strong shear thinning.

On the other hand, results of G' for the same previous samples are shown in Fig. 7b. G' increases with ω while the storage modulus of the 3 wt.% of **6b**-M$_2$-4 showed a weak dependency on frequency over the entire range and approached a plateau modulus. The storage modulus of
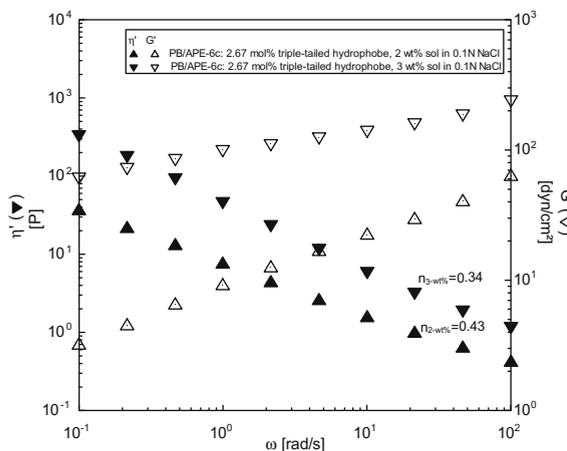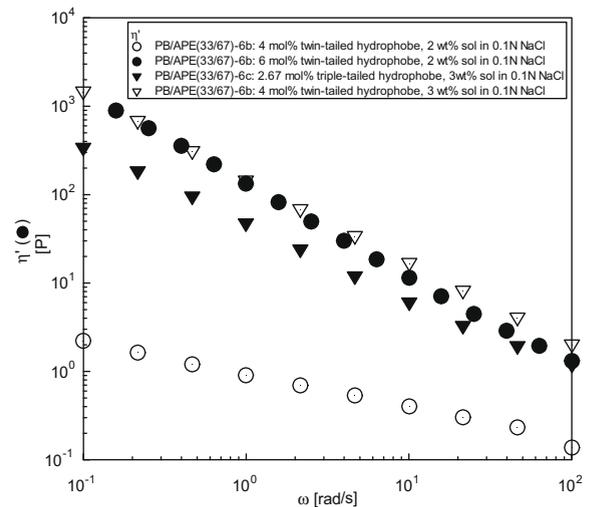

Fig. 7a. Variation of dynamic shear viscosity with frequency of a 2 wt.%, 3 wt.% solution of **6b** and **6c** polymer in 0.1 N NaCl.
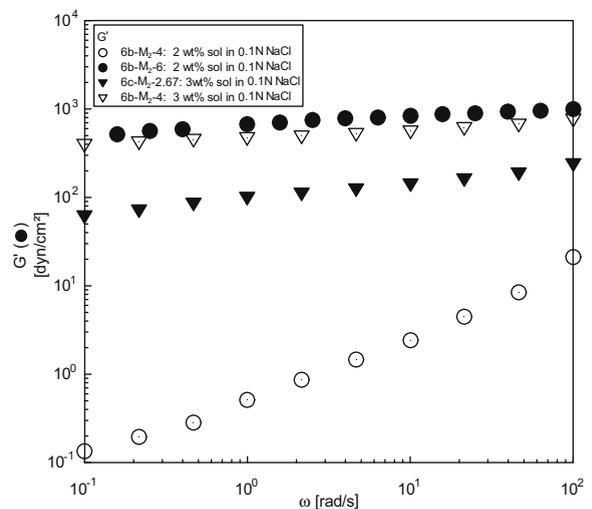

Fig. 7b. Variation of G' with frequency of a 2 wt.%, 3 wt.% solution of **6b** and **6c** polymer in 0.1 N NaCl.

PB/APEs **6b**-M$_2$-6 and **6c**-M$_2$-2.67 which contain 6 mol% twin-tailed and 2.67 mol% tripled-tailed hydrophobes, respectively, also showed weak dependency on frequency and reaches a plateau. This solid-like behavior of high hydrophobe polymer is likely due to the presence of strong intermolecular hydrophobic associating networks, which increases the number of active junctions [25]. So, increasing the concentration of the **6b**-M$_2$-4 (twin-tailed) from 2% to 3% resulted in the formation of networks in the presence of 0.1 N NaCl.

Also, increasing the hydrophobe content from 4 in **6b**-M$_2$-4 to 6 mol% in **6b**-M$_2$-6 at 2 wt.% concentration resulted in a major increase in elasticity and the behavior changed from a typical liquid behavior to a solid-like

Fig. 6. Variation of dynamic shear viscosity and storage modulus with frequency of polymer in 0.1 N NaCl.

behavior with network structures. Results of G' suggest the dominance of network behavior over the whole frequency range as shown in Fig. 7b. The observed shear thinning suggests that the large domains are broken into smaller domains due to shear. Breakdown of structures and domains with increased shear rate is usually associated with a decrease in viscosity; however, the results of G' are not typical and here we would like to provide a tentative explanation. Usually G' increases with increased frequency in typical non-interacting domains. However, the results of G' suggest that the charge interactions between the smaller domains are still strong keeping G' almost constant.

The cationic acid salt CAS **4** samples are completely converted to corresponding anionic polyelectrolyte APE **7** in the presence of 2.0 equiv. of NaOH. The effect of anionic charge density on the rheological properties of the polymer solutions was studied and the results of G' and G'' of the 2 wt.% polymer solutions of APE **7** containing twin- and tripled-tailed hydrophobes are presented in Fig. 8. The increase in hydrophobe content of the anionic triple-tailed polyelectrolyte APE **7c** from 2.67 mol% in **7c**-M$_2$-2.67 to 4 mol% in **7c**-M$_2$-4 resulted in significant increase in G''. Similar effect is observed for the 2 wt.% solution of **7c**-M$_2$-4 in 0.1 N NaCl where the viscosity of the triple-tailed polymer (at $\omega = 0.1$ rad/s) is ~77 times that of the twin-tailed **7b**-M$_2$-4. For G' data, the similar shear thinning behavior observed for both the **7b**-M$_2$-4 (4 mol% twin-tailed) and the **7c**-M$_2$-2.67 (2.67 mol% triple-tailed) is supported by a typical increase in G' with ω. This suggests that these systems form non-interacting domains due to neutralization effect that results from the addition of NaOH.

In Fig. 9, G' and G'' are shown for the 8 wt.% solution of **9a**-M$_2$-6 (6 × 1 = 6 tails) and the 5 wt.% solution of **9b**-M$_2$-3 (3 × 2 = 6 tails) in 0.1 N NaCl. The viscosity data for the twin-tailed **9b**-M$_2$-3 is showing shear thinning over the whole frequency range keeping G'' almost constant at $2 \ast 10^2$ dyne/cm^2 ($G'' = \eta' \ast \omega$). However, the single-tailed **9a**-M$_2$-6 showed a typical Maxwellian behavior with $G'' > G'$ at low ω and $G' > G''$ at high ω. It is clear that changing the hydrophobe from single- to twin-tailed enhances the shear thinning of the polymer and the shear thinning can take place at lower polymer concentrations (<5 wt.%). In addition, the 5 wt.% solution of twin-tailed **9b**-M$_2$-3 showed higher elasticity than the 8 wt.% solution of single-tailed **9a**-M$_2$-6 having the same number of tails (6 tails) per polymer chain. Here, the change from single-tailed to twin-tailed resulted in major enhancement in elasticity and enhanced the shear thinning.

In Fig. 10, the dynamic viscosity and storage modulus for **9b**-M$_2$-9 in salt-free water is displayed at different concentrations. The viscosity data for the twin-tailed hydrophobic polymer is showing shear thinning over the whole frequency range. However, at dilute concentration (2 wt.%), the dynamic viscosity curve showed a change of slope at $\omega = 10$ rad/s. The value of the power-law index (0.29) at high shear rate for the 3 wt.% solution is close to

Fig. 9. Variation of storage and loss modulus with frequency of a 5 wt.%, 8 wt.% solution of **9a**-M$_2$-6 and **9b**-M$_2$-3 polymer in 0.1 N NaCl.
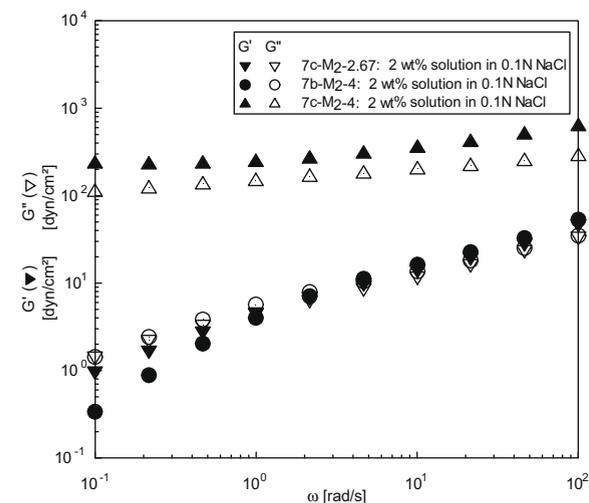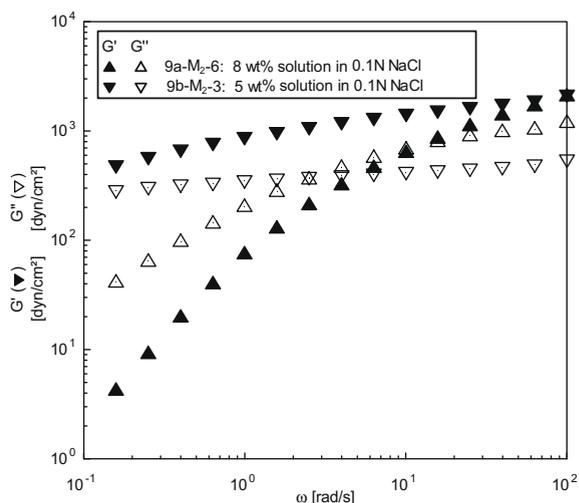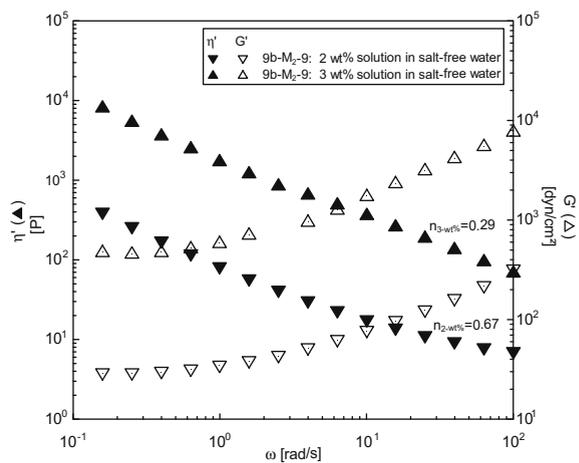

Fig. 8. Variation of storage modulus and loss with frequency of a 2 wt.% solution of **7b**-M$_2$-4, **7c**-M$_2$-2.67 and **7c**-M$_2$-4 polymer in 0.1 N NaCl.

Fig. 10. Variation of dynamic shear viscosity and storage modulus with frequency of a 2 wt.%, 3 wt.% solution of **9b**-M$_2$-9 polymer in salt-free water.
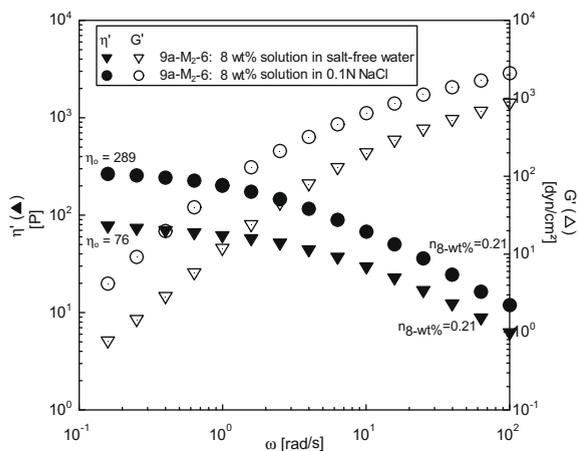
Fig. 11. Variation of dynamic shear viscosity and storage modulus with frequency of 8 wt.% solution of **9a**-M$_2$-6 polymer in salt-free water and 0.1 N NaCl.

values predicted by a simple molecular theory as discussed earlier. However, the n value for the 2 wt.% solution is on the high side and G′ showed a change in slope in the same vicinity. This suggests that for the 2 wt.% solution the high shear rate regime is yet to be reached. This suggestion is in agreement with our previous observations in Fig. 6 where the 3 wt.% solution thins faster than the 2 wt.% solution. A tentative explanation for the break in the viscosity curve of the 2 wt.% solution is the disengagement of one hydrophobic block from a cross-link which does not permit the relaxation of the entire chain since the chain is still "anchored" by many other stickers [26].

On the other hand, Fig. 11 shows $\eta'(\omega)$ and $G'(\omega)$ for the **9a**-M$_2$-6 in salt-free water and in 0.1 N NaCl solution. The two solutions are used at the same concentration (8 wt.%); however, the main purpose of this test is to study the effect of salt. The single-tailed hydrophobe solution showed enhanced viscosity and elasticity as a result of the presence
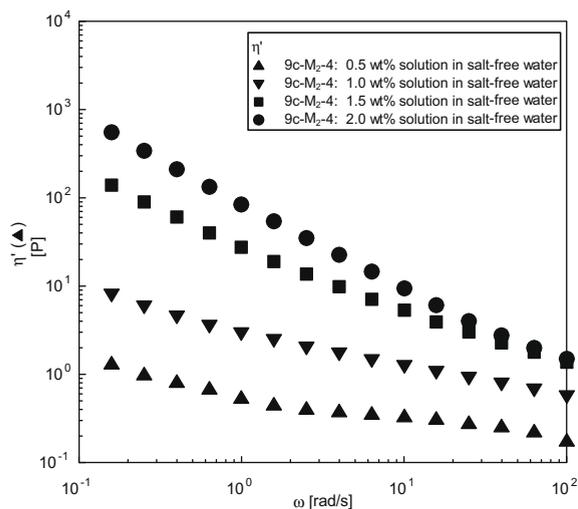

Fig. 12a. Variation of dynamic shear viscosity with frequency of a 0.5 wt.%, 1 wt.%, 1.5 wt.% and 2 wt.% solution of **9c**-M$_2$-4 polymer in salt-free water.
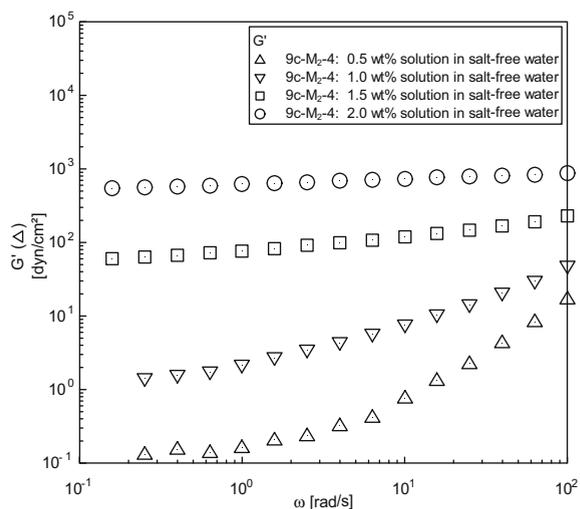

Fig. 12b. Variation of storage modulus with frequency of a 0.5 wt.%, 1 wt.%, 1.5 wt.% and 2 wt.% solution of **9c**-M$_2$-4 polymer in salt-free water.

of NaCl. It is clear that NaCl interactions with the cationic polyelectrolyte lead to increased coil size. The values of zero-shear viscosities can give indirect measure of this coil expansion due to the presence of the salt. The addition of 0.1 N NaCl solution increased the viscosity of the salt-free solution by a factor of 4. In the presence of chloride ions, the relative significance of the opposing effects of polymer compaction by shielding and increased hydrophobic associations on the viscosity determines the viscosity values [27]. Also, major enhancement of elasticity is observed over the whole frequency range. At high shear rates, the values of the power-law index for the two solutions are comparable with reported n values for aqueous solutions and can be predicted by simple molecular theory [24]. Although the shear thinning of the two solutions is similar; however, the salt persists to keep both η' and G' higher than the salt-free solution over the whole frequency range.

In Figs. 12a and 12b, the effect of polymer concentration is studied by using **9c**-M$_2$-4 in salt-free environment. The concentration is varied from 0.5–2 wt.%. The η' data shown in Fig. 12a shows shear thinning over the whole frequency range and a change in the slope of the viscosity curve is observed. At low ω, the increase in polymer concentration from 0.5 to 2 wt.% lead to increase in both η' and G' by a factor of $\sim$ 500 and 5000, respectively. The change in slope is observed in both η' and G' curves and at polymer concentrations of 1.5 and 2 wt.% a network is formed as suggested by G' data shown in Fig. 12b. The suggested explanations for the change in slope are similar to those discussed earlier in Fig. 8. Similar observations are drawn from the data on **9b**-M$_2$-6 (results not shown here).

4. Conclusions

In conclusion, the increase in viscosity of cationic polyelectrolytes (CPE) was observed with the increase in the amount of hydrophobe incorporated in the polymers except in the case of polymers having very high hydrophobe content. Further increase in hydrophobe concentration to

9 mol% resulted in a decrease in viscosity. This is consistent with studies which indicated that random copolymers with higher proportion of hydrophobes form mainly intramolecular hydrophobic associations.

The tremendous increase in viscosity values for the twin-tailed **9b**-M_2-6 is suggested to be attributed to the superior intermolecular associations between the twin-tailed hydrophobes, while overwhelming dominance of intramolecular associations in the single-tailed **9a**-M_2-12. For CPE-**9c** and **9b**, the impact of doubling the polymer concentration of the 2 wt.% solution or doubling the number of tails is similar at low shear rates since both the concentration and the tails lead to similar increase in chain size. This explanation is supported by the intrinsic viscosity data. However, at high frequencies the shear thinning of the 4 wt.% solution (8 tails) is higher than that of the 2 wt.% (16 tails) due to the high disruption of the intermolecular hydrophobic associations in the 4 wt.% solution. For tripled-tailed PB/APE-**6c,** the solutions exhibit shear thinning behavior. However, the increase in the polymer concentration resulted in an increase in the shear thinning as indicated by the values of the power-law index (n). These values of n are comparable with reported power-law index for aqueous solutions. The storage modulus of PB/APE-**6b** and PB/APE-**6c** which contain 6 mol% twin-tailed hydrophobe and 2.67 mol% tripled-tailed hydrophobe, respectively, showed weak dependency on frequency and reaches a plateau. This solid-like behavior of high hydrophobe polymer is due to the presence of strong intermolecular hydrophobic associating networks, which increases the number of active junctions.

Also, increasing the hydrophobe content from 4 to 6 mol% in twin-tailed hydrophobe at 2% concentration resulted in a major increase in elasticity and the behavior changed from a typical liquid behavior to a solid-like behavior with network structures. Neutralization of CAS by the addition of NaOH resulted in the formation of non-interacting domains. It is clear that the increase in the number of hydrophobes per chain from single to twin enhances the shear thinning of the polymer and the shear thinning can take place at lower polymer concentrations (<5 wt). In addition, the 5 wt.% twin-tailed hydrophobe showed higher elasticity than the 8 wt.% solution single-tailed having the same number of tails (6 tails). The change from single-tailed to twin-tailed resulted in major enhancement in elasticity and enhanced the shear thinning. For the **3c**-M_2-2.67, G' is almost independent of ω and a plateau modulus is reached denoting the formation of a network. Therefore, triple-tailed polymers can be used to obtain networks at lower concentrations. For **9a**-M_2-6 in salt-free water and in 0.1 N NaCl solution the shear thinning of the two solutions is similar; however, the salt persists to keep both η' and G' higher than the salt-free solution over the whole frequency range.

Finally, the studied water soluble polymers showed different rheological behavior depending on their structure (hydrophobe type and content) as well as salinity and pH. The high shear thinning and the formation of networks at low shear would likely promote the use of such polymers in enhanced oil recovery applications.

Acknowledgements

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