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Synthesis and solution properties of hydrophobically associating ionic polymers made from diallylammonium salts/sulfur dioxide cyclocopolymerization

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Abstract

Sulfur dioxide, *N*,*N*-diallyl-*N*-carboethoxymethylammonium chloride and the hydrophobic monomers *N*,*N*-diallyl-*N*-dodecylammonium chloride or *N*,*N*-diallyl-*N*-octadecylammonium chloride were cyclocopolymerized in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator to afford water-soluble cationic polyelectrolyte (CPE) having five-membered cyclic structure on the polymeric backbone. The CPE on acidic (HCl) hydrolysis of the pendent ester groups gave the corresponding cationic acid salt (CAS) which was converted to the anionic polyelectrolyte (APE) by treatment with sodium hydroxide. The solution properties of the CPE and APE containing varying amount of the hydrophobic monomers in the range 0–10 mol% were investigated by viscometric techniques. The polymers showed that concentration (C^*_{HA}) of less than 1 wt% was required for the manifestation of hydrophobic association, and displayed significant hydrophobic association in salt (NaCl)-free as well as salt-added solutions.

Keywords: Hydrophobic association; Associating ionic polymers; Diallylammonium monomers

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1. Introduction

In recent years, an increasing number of studies have focused on the hydrophobic association of water-soluble polymers [1,2]. The copolymerization of a water-soluble monomer with a few mol% of a hydrophobic comonomer in a homogeneous solution in mixed solvents gives polymers with random distribution of the hydrophobes as isolated units. Whereas, the miceller systems [2] involving hydrophilic monomer (~3 wt%) in the continuous water phase and hydrophobic monomer inside the micelles ensure a random distribution of the hydrophobes as small blocks in the hydrophilic polymer chains [3–7]. The concentration-dependent intermolecular associations in the microblocky copolymers lead to superior viscosity behavior in comparison to the random copolymers which exhibit largely intramolecular associative behavior [8–11].

Although acrylamide is mostly used as the main water-soluble monomer, the miceller polymerization process has also been used in the synthesis of hydrophobically modified polyelectrolytes and polyampholytes using suitable ionic comonomers [12–18]. Above a certain polymer concentration (called concentration required for hydrophobic associations, C^*_{HA}) in aqueous solution, intermolecular associations of the hydrophobic groups lead to a reversible formation of three-dimensional physical cross-links of polymer chains. The shear thinning feature associated with the reversible nature of these physical cross-links led to their applications in water-borne coatings, paints, cosmetics, and enhanced oil recovery [19–23]. The shear thinning or thixotropy behavior of these polymers makes it possible to avoid the irreversible mechanical degradation, which occurs for high molecular weight polymers when subjected to high shear stresses [24,25].

In contrast to polymers containing neutral hydrophilic acrylamide and neutral hydrophobic derivative of acrylamide, the presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a great variety of behaviors [18]. While the

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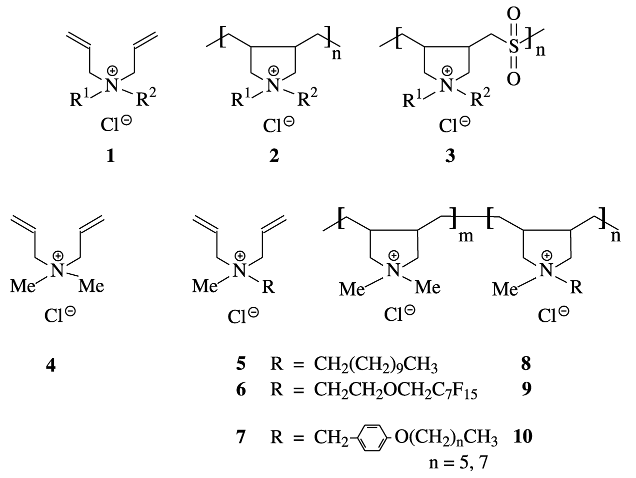
repulsion between the charges within a polymer chain leads to coil expansion in water, the interchain electrostatic repulsions lower the degree of association. In the presence of added salt (e.g. NaCl), the screening of the charges leads to chain contraction but increased hydrophobic intermolecular associations. Ion-containing polyacrylamides usually require a higher hydrophobe content or the presence of added salt in order to manifest increased interchain associations [12,14,26].

The discovery of cyclopolymerization of *N*,*N*-diallyl quaternary ammonium salts **1** to **2** by Butler [27], and subsequently, their copolymerizations with sulfur dioxide to **3** [28–30] led to the synthesis of an array of water-soluble cationic polyelectrolytes [31–35] of tremendous scientific and technological interest (Scheme 1). There are, however, only a few reports [36–38], which describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique. Previous kinetic studies [39] have indicated that monomer concentrations of 50–65 wt% is required to obtain polymers with high conversion and high molecular weight, and low residual double bonds. Cyclopolymerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than microblocky copolymers even though the hydrophobic monomer possesses surfactant properties [36]. The rheological properties of the copolymers **8**, **9** and **10**, derived from cyclopolymerizations of the monomers **(4)**/**(5)**, **(4)**/**(6)** and **(4)**/**(7)**, respectively, have been studied (Scheme 1) [37,38]. At the same concentration, the viscosity of the copolymers **8** and **9** were found to be significantly higher compared to that of the homopolymer of **4**. Above the hydrophobic association concentration (C^*_{HA}) the viscosity increased sharply; C^*_{HA} were found to be in the range 15–17% for the copolymers **8** and **9** with a hydrophobe content of 8.22 mol%. These hydrophobically associating ionic copolymers, thus, have an undesirable fairly high C^*_{HA} compared to the hydrophobically associating non-ionic copolymers of acrylamide (C^*_{HA} less than 1%).

In our continuing study of ionic polymers, we now report the synthesis and solution properties of amphiphilic terpolymers **17** and **18** derived from cyclocopolymerization of the hydrophilic monomer (M_1) **14**/sulfur dioxide/hydrophobic comonomer (M_2) **15** (and **16**) (Scheme 2). The work will indeed provide an opportunity to study the effect of length of the hydrophobic pendents, the charges on the polymer chain (e.g. polymers having the same degree of polymerization but cationic backbone in **18** and anionic in **20**) on the C^*_{HA} as well as the overall viscosity behavior of these new class of associating polymers.



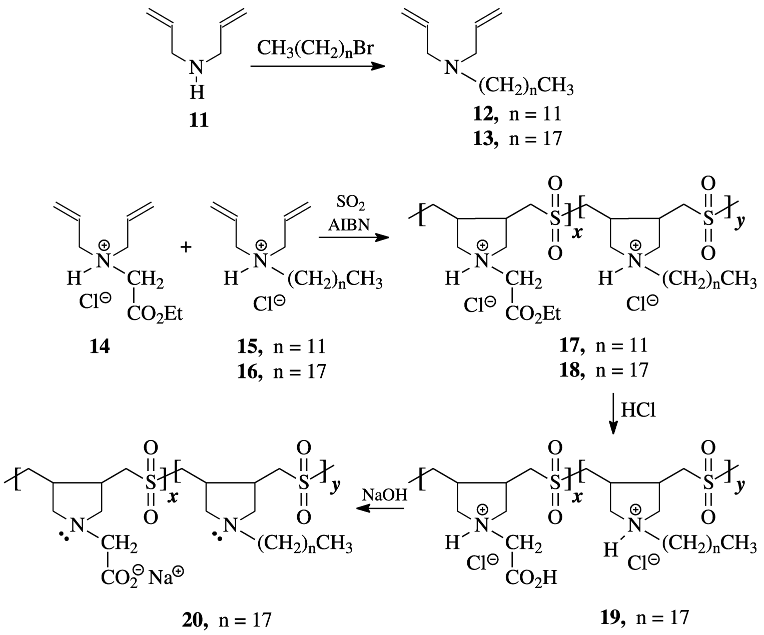
Scheme 1.

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 analyses were carried out in a Carlo-Erba elemental analyzer Model 1102. IR spectra were recorded on a Perkin Elmer 16F PC FTIR spectrometer (Spectral resolution, 4 cm^{-1}; Number of scans, 19). ^1H and ^{13}C NMR spectra of the polymers were measured in D_2O using dioxane as internal standard on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made with an 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 the dissolved gases. 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 weight of the samples was determined by light scattering experiments at 21 °C. Solutions of the cationic polyelectrolytes (CPE) (polymer concentration range: 0.03–0.1 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 not used as a solvent owing to the insolubility of the CPEs in this solvent. Millipore disposable filters of pore size 0.02 (m were used to remove dust particle from the solutions of polyelectrolyte and the solvent (water). 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



Scheme 2.

Refractometer (Bellingham and Stanley, UK) was used to measure the differential refractive indices (d*n*/d*c*) of different polyelectrolyte solutions. Molecular weight determination of the hydrophobiccally modified polymers was complicated owing to hydrophobic associations. As a result we can expect that the light scattering measurements lead to an apparent weight, $\bar{M}_{\mathrm{w,app}}$ rather than true molecular weight. Measurement of hydrodynamic radius (R_{h}) for CPE-C_{12}-7, CPE-C_{18}-3.5, CPE-C_{18}-5 was conducted using Wyatt DLS correlator at 21 °C. The DLS detector was placed at an angle of 90° to the excitation beam.

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 mmHg). All glassware were cleaned using deionized water. *N*,*N*-diallyl-*N*-carboethoxymethylammonium chloride **(14)** was prepared as described in a previous report [40].

2.3. *N,N-Diallyl-N-octadecylamine* ***(13)***

A solution of 1-bromooctadecane (18.4 g, 55.0 mmol) and diallylamine **11** (8.28 g, 85 mmol) in toluene (6 cm^3) was refluxed under N_2 for 24 h (bath temp: 130 °C). At the end, the reaction mixture was cooled and stirred with a solution of NaOH (2.65 g, 66 mmol) in water (100 cm^3) and extracted with ether (75 cm^3). The organic layer was dried (Na_2SO_4), concentrated and distilled to obtain the diallyl derivative **13** (15.3 g, 79.4%) as a colorless liquid, $\mathrm{bp}_{0.05\ \mathrm{mbarHg}}$:170–175 °C. (Found: C, 82.17%; H, 13.41%; N, 3.88%. $C_{24}H_{47}N$ requires C, 82.44%; H, 13.55%; N, 4.01%); $\nu_{\max}$ (neat) 3076, 2924, 2852, 1642, 1464, 1361, 1267, 1080, 994, 916, and 720 cm^{-1}. δ_{H} ($CDCl_3$) 0.88 (3 H, t, $J = 7.1$ Hz), 1.26 (30 H, m), 1.44 (2 H, m), 2.40 (2 H, apparent t, $J = 7.7$ Hz), 3.08 (4 H, d, $J = 6.8$), 5.13 (4 H, m), 5.85 (2 H, m); δ_{C} ($CDCl_3$) 14.13, 22.71, 26.94, 27.53, 29.39, 29.65 (3 C), 29.71 (8 C), 31.95, 53.43, 56.88 (2 C), 117.20 (2 C), and 135.92 (2 C); ($CDCl_3$, 77.02, middle carbon).

2.4. *N,N-Diallyl-N-dodecylammonium chloride* ***(15)***

Dry HCl gas was bubbled through a solution of *N*,*N*-diallyl-*N*-dodecylamine **12** [41] (10.0 g, 37.7 mmol) in ether (75 cm^3). The solution became milky; the ammonium salt settled down on the bottom of the flask and the supernatant liquid became colorless. After removal of the ether by a gentle stream of N_2, the syrupy liquid of amine salt **15** was washed with hexane to remove any unprotonated amine. The colorless salt **15** was dried under vacuum to a constant weight (11.1 g, 97.5%). (Found: C, 71.3%; H, 12.25%; N, 4.5%. $C_{18}H_{36}ClN$ requires C, 71.60%; H, 12.02%; N, 4.64%). $\nu_{\max}$. (neat) 3396, 3084, 2926, 2854, 2529 (broad), 1644, 1460, 1057, 999, 941, and 722 cm^{-1}; δ_{H} (D_2O) 0.74 (3 H, t, $J = 6.8$ Hz), 1.17 (18 H, m), 1.62 (2 H, m), 2.95 (2 H, apparent t, $J = 6.8$ Hz), 3.69 (4 H, m), 5.49 (4 H, m), 5.86 (2 H, m), (HOD: 4.65 ppm); δ_{C} (D_2O) 14.66, 23.43, 24.08, 27.28, 29.82, 30.26, 30.35, 30.50, 30.58, 30.64, 32.77, 52.13, 55.88 (2 C), 126.84 (2 C), and 127.04 (2 C) (dioxane, 67.4 ppm).

Table 1
Terpolymerization of the monomers **14**/**15**/SO_2 and **14**/**16**/SO_2

Entry no	Sample	**14** (M_1) (mmol)	**15** C_{12} (M_2) (mmol)	**16** C_{18} (M_2) (mmol)	Feed[a] M_1:M_2	Polymer[a] M_1:M_2	Yield (%)	Intrinsic viscosity[b] (dl g^{-1})	
								17/**18** CPE	**20** APE
1	M_2-0	30	–	–	100:0	100:0	85.6	0.600	0.967
2	C_{12}-1	29.7	0.3	–	99:1	98.7:1.3	88.8	0.634	-
3	C_{12}-3	29.1	0.9	–	97:3	96.5:3.5	87.0	0.568	-
4	C_{12}-7	27.9	2.1	–	93:7	92:8	84.6	0.186	-
5	C_{12}-10	27.0	3.0	–	90:10	89:11	81.5	0.130[c]	-
6	C_{18}-1.5	29.55	–	0.45	98.5:1.5	98.5:1.5	93.2	0.514	1.09
7	C_{18}-2.5	29.25	–	0.75	97.5:2.5	97.3:2.7	87.2	0.501	1.03
8	C_{18}-3.5	28.95	–	1.05	96.5:3.5	96:4	86.8	0.581	0.963
9	C_{18}-5	28.5	–	1.5	95:5	94.8:5.2	90.1	0.446[c]	0.800

Polymerization reactions were carried out in DMSO (7.85 g) containing 30 mmol of SO_2 in the presence of AIBN (145 mg) at 58 °C for 20 h.

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

[b] Obtained by extrapolation of the linear parts of the curves in Figs. 2–4 usually in the range 0.5–0.0625% polymer solution in 0.1 N NaCl at 30 °C (measured with an Ubbelohde viscometer ($K = 0.005718$).

[c] Cloudy solution throughout the concentration range.

2.5. *N,N-Diallyl-N-octadecylammonium chloride* (***16***)

Dry HCl gas was bubbled through a solution of *N,N*-diallyl-*N*-octadecylamine **13** (10.0 g, 28.6 mmol) in ether (75 cm^3). The salt **16** precipitates out as a white powder. The salt was filtered and recrystallized from ether (0 °C) and was dried under vacuum to a constant weight (9.53 g, 86.3%); m.p. 69–70 °C; (Found: C, 74.4%; H, 12.6%; N, 3.5%. $C_{24}H_{48}ClN$ requires C, 74.66%; H, 12.53%; N, 3.63%); ν_{max} (KBr) 3425, 3080, 2920, 2849, 2613, 2436 (broad), 1464, 1364, 996, 935, and 725 cm^{-1}; δ_H ($CDCl_3$) 0.88 (3 H, t, $J = 6.8$ Hz), 1.30 (30 H, m), 1.84 (2 H, m), 2.93 (2 H, m), 3.62 (4 H, m), 5.53 (4 H, m), 6.17 (2 H, m); δ_C ($CDCl_3$): 14.13, 22.70, 23.31, 26.85, 29.00, 29.38 (2 C), 29.48, 29.58, 29.68 (3 C), 29.71 (4 C), 31.95, 51.79, 54.67 (2 C), 125.49 (2 C), and 126.48 (2 C); ($CDCl_3$, 77.04 ppm, middle carbon).

2.6. *General procedure for the terpolymerization of* ***14/15/SO₂*** *and* ***14/16/SO₂***

All the polymerizations were carried out using conditions as described in Table 1. In a typical experiment, SO_2 was absorbed in a solution of the monomers **14**/**15** (i.e. M_1/M_2) or **14**/**16** in DMSO in a 50 cm^3 round-bottom flask. The required amount of the initiator (AIBN) (as listed in Table 1) was then added under N_2 and the closed flask was magnetically stirred at 58 °C for 20 h. Magnetic stir bar stopped moving after 3 h. The reaction flask was briefly opened after 10 h under N_2 to release the N_2 formed during decomposition of AIBN. The reaction mixture, which remained transparent throughout the polymerization process, was soaked in methanol (50 cm^3) for 3 h at 20 °C and 20 min at 60 °C. After decanting the methanol, the polymer was washed with methanol (2 × 20 cm^3). The polymer was dried under vacuum at 55 °C for 4 h, then crushed to powder and again soaked in acetone (50 cm^3) for 3 h [washing was continued until the ^1H NMR spectrum revealed the absence of the unreacted monomer]. Acetone was decanted, and the resulting white polymer was dried under vacuum at 50 °C to a constant weight. The hygroscopic white terpolymers, cationic polyelectrolytes, CPE **17** and **18**, were stored in a desiccator. The elemental analyses (Table 2) ascertained the mole ratio of ($M_1 + M_2$):M_3(SO_2) as 1:1 as reported [40] for the copolymer M_2-0. The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M_2-0 as reported [40]. The ^1H NMR spectra for M_2-0 and CPE-C_{18}-2.5 are shown in Fig. 1.

Table 2
Elemental analyses of CPE **17**·$1H_2O$ $(C_{10}H_{20}ClNO_5S)_x(C_{19}H_{40}ClNO_3S)_{1-x}$, CPE **18**·$1H_2O$ $(C_{10}H_{20}ClNO_5S)_x(C_{25}H_{52}ClNO_3S)_{1-x}$, and CAS **19**·$1H_2O$ $(C_8H_{16}ClNO_5S)_x(C_{25}H_{52}ClNO_3S)_{1-x}$

Polymers	Carbon[a]	Hydrogen[a]	Nitrogen[a]	Sulfur[a]
CPE-M_2-0	39.5 (39.80)	6.7 (6.68)	4.5 (4.64)	10.4 (10.62)
CPE-C_{12}-1	39.7 (39.98)	6.8 (6.71)	4.4 (4.63)	10.7 (10.59)
CPE-C_{12}-3	40.4 (40.33)	6.7 (6.78)	4.7 (4.61)	10.3 (10.54)
CPE-C_{12}-7	40.8 (41.03)	7.0 (6.92)	4.5 (4.56)	10.3 (10.44)
CPE-C_{12}-10	41.8 (41.55)	6.9 (7.03)	4.4 (4.53)	10.1 (10.36)
CPE-C_{18}-1.5	39.9 (40.14)	6.9 (6.74)	4.5 (4.61)	10.2 (10.56)
CPE-C_{18}-2.5	40.1 (40.36)	6.8 (6.78)	4.4 (4.60)	10.3 (10.52)
CPE-C_{18}-3.5	40.7 (40.59)	6.7 (6.83)	4.7 (4.58)	10.2 (10.48)
CPE-C_{18}-5	41.3 (40.92)	6.7 (6.89)	4.7 (4.55)	10.5 (10.42)
CAS-M_2-0	34.9 (35.10)	6.1 (5.89)	4.8 (5.12)	11.5 (11.71)
CAS-C_{18}-1.5	35.1 (35.51)	6.2 (5.96)	4.8 (5.09)	11.3 (11.63)
CAS-C_{18}-2.5	35.6 (35.78)	6.1 (6.01)	4.9 (5.06)	11.2 (11.58)
CAS-C_{18}-3.5	36.4 (36.05)	5.9 (6.06)	5.2 (5.04)	11.5 (11.53)
CAS-C_{18}-5	36.9 (36.46)	6.0 (6.14)	5.2 (5.01)	11.3 (11.46)

[a] Found (calculated).

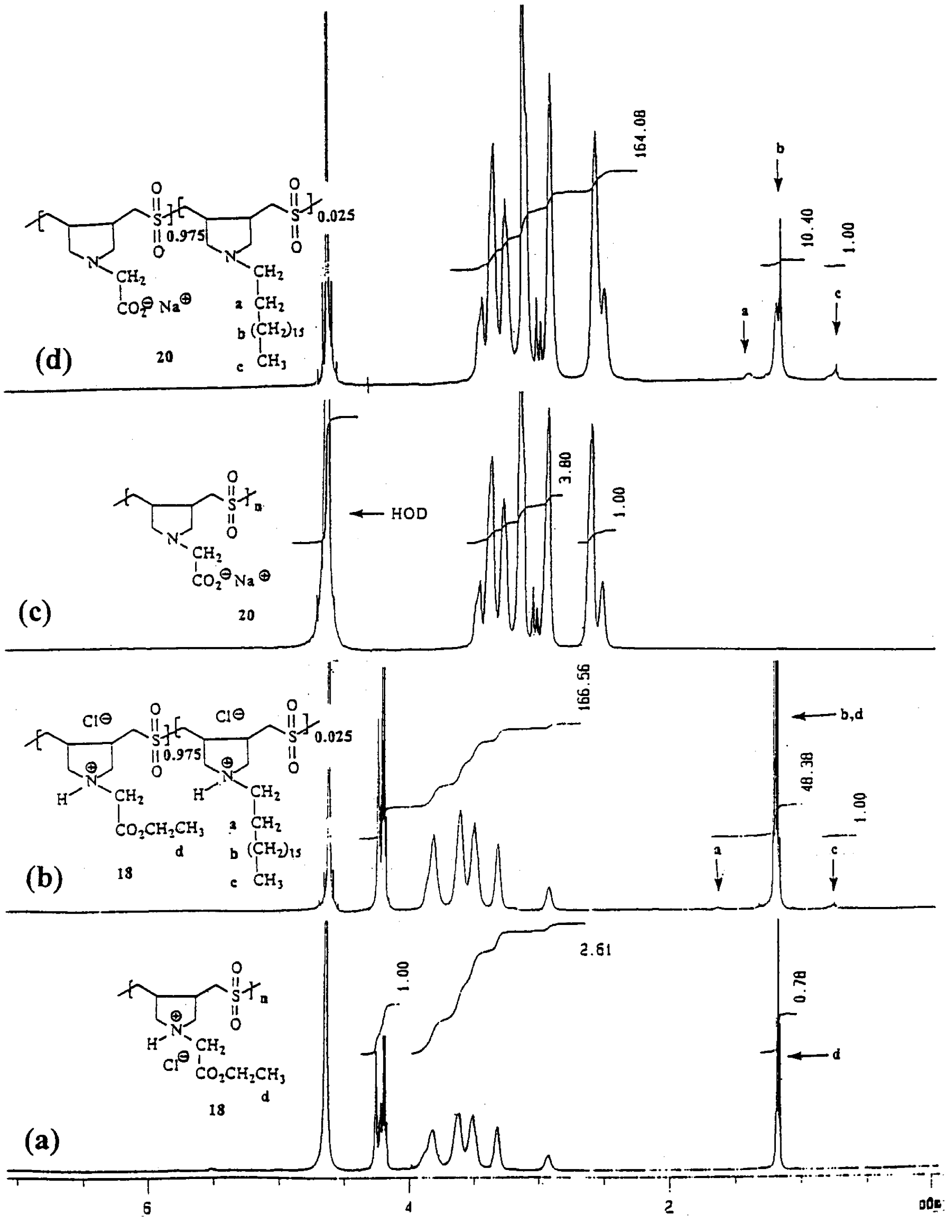


Fig. 1. ^{1}H NMR spectrum of the (a) CPE **18** ($C_{12/18}$-0), (b) CPE **18** (C_{18}-2.5), (c) APE **20** ($C_{12/18}$-0), (d) APE 20 (C_{18}-2.5) in D_2O.

*2.7. General procedure for the acidic hydrolysis of the CPE **18***

A solution of the CPE C_{18}-0 (entry 1, Table 1) (5.0 g, 16.5 mmol) in 6 M HCl (45 cm^3) was stirred in a closed flask at 50 °C for 48 h (or until the hydrolysis of the ester group was complete as indicated by the absence of the ethoxy proton signals in the ^{1}H NMR spectrum). During hydrolysis, the product gradually precipitated in the reaction mixture. The insoluble polymer was separated washed with distilled water (20 cm^3). After that, it was dried under vacuum at 50 °C for 6 h. The polymer, cationic acid salt (CAS) **19** was then crushed into powder and redried under vacuum to a constant weight (4.2 g, 93%) at 50 °C. Similarly, all the terpolymers **18** containing C_{18} hydrophobe were hydrolyzed in well over 90% isolated yields. The elemental analyses (Table 2) supported, as before [40], the presence of 1 mole of water per mole of the repeating units. The onset of thermal decomposition (closed capillary) was found to be 235–245 °C (decomposed, turned brown, charred at 290 °C). The IR spectra and elemental analyses (Table 2) of the terpolymers (CAS) **19** closely resembled those of the copolymer M_2-0 as reported [40]. Since CAS **19** polymers are insoluble in water, the ^{1}H NMR spectra were measured in D_2O after its conversion to APE **20** by basification as reported [40]. The ^{1}H NMR spectra for M_2-0 and APE-C_{18}-2.5 are shown in Fig. 1.

2.8. *Conversion of CAS to APE by basification and its use in viscosity measurements*

All the CAS terpolymers **19** containing C_{18} hydrophobe including the CAS derived from entry 1 were converted to the corresponding APE **20** by adding 2.1 equiv. of aqueous NaOH, and the resultant solutions were used for viscosity measurement. For instance, a stock solution of APE was prepared by dissolving 0.600 g (2.20 mmol) of CAS **19** M_2-0 in 22.0 cm^3 of 0.210 N NaOH (4.62 mmol). The release of 2.20 mmol of NaCl thus made the system 0.1 N NaCl. The solution was then diluted with 0.1 N NaCl to make the concentration of CAS **19** as 2 g/dl in 0.1 N NaCl or approximately 2 g/dl of the APE **20**. [CAS (**19**·$1H_2O$) and APE (**20**·$2H_2O$) have very similar molar masses of 273.73 and 277.27, for the repeating units, respectively].

3. Results and discussion

3.1. *Synthesis of the terpolymers and physical characterization*

The hydrophilic monomer **14** (M_1) was prepared as described before [40]. Hydrophobic monomers (M_2) **15** and **16** were prepared in excellent yields from the corresponding amines **12** and **13**, respectively. The monomers **14**/**15**/SO_2 and **14**/**16**/SO_2 were cyclocopolymerized using AIBN as the initiator to give the cationic polyelectrolytes (CPE) **17** and **18** in excellent yields (Scheme 2). The results of the cyclocopolymerization, carried out under similar conditions, and the intrinsic viscosities of the resultant polymers in dilute solutions are given in Table 1. The entry 1 in Table 1 describes the copolymer M_2-0 indicating the absence of the hydrophobic monomers **15** or **16** (M_2). The entries 2–5 describe the incorporation of the dodecyl monomer **15** in mol% range 1–10, whereas the entries 6–9 describes the incorporation of the octadecyl monomer **16** in mol% range 1.5–5. The CPE terpolymer C_{12}-10 (entry 5), for instance, indicates the incorporation of 10 mol% hydrophobic dodecyl monomer **15**, whereas C_{18}-5 stands for 5 mol% hydrophobic octadecyl monomer **18**. The CPEs **18** (entries: 6–9, Table 1) and the M_2-0 (entry 1) were hydrolyzed in 6 M HCl to produce the water-insoluble cationic acid salts (CAS) **19** which, on treatment with 2.1 equiv. of NaOH, afforded the anionic polyelectrolytes (APE) **20** and APE-M_2-0 ($y = 0$).

Table 3
Light scattering measurements for cationic polyelectrolytes (CPE) in 0.5 N NaCl

CPE	$10^{-5}\bar{M}_{w,app}$	R_g (nm)
M_2-0	1.95	45
C_{12}-1	2.14	49
C_{12}-3	2.1	47
C_{18}-1.5	2.14	49
C_{18}-2.5	2.5	53

The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M_2-0 as reported [40]. Fig. 1a–d displays the ^1H NMR spectrum of the CPE **18** (M_2-0), CPE **18**-C_{18}-2.5, APE **20** (M_2-0), APE **20**-C_{18}-2.5 in D_2O, respectively. It is evident, after comparing the proton spectra of the polymers that the CH_3-CH_2OC and the CH_3CH_2-OC protons, which appeared at δ 1.18 ppm (t) and 4.21 ppm, respectively, for the CPE **18**, are absent in the spectrum of the APE **20**, thus indicating the complete removal of the ester groups by hydrolysis. The incorporation of the hydrophobic monomers was calculated using ^1H NMR integration of the signals around δ 0.75 (for methyl protons of the hydrophobic pendents) and 1.10–1.27 ppm [for methyl protons of the ester groups, $(CH_2)_9$ of dodecyl pendents, or $(CH_2)_{15}$ for 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 $(M_1 + M_2)$:SO_2 as 1:1.

The $\bar{M}_{w,app}$ and the radius of gyration (R_g) of some of the polymers are given in Table 3. The polymers of higher hydrophobe-contents (e.g. CPE-C_{18}-3.5, CPE-C_{18}-5, etc.) were insoluble in 0.5 N NaCl, and as such their molecular weights were not determined. However, the copolymers, prepared under similar copolymerization conditions (initiator and monomer concentrations, reaction conversions, temperature, duration, etc.), are expected to have similar molecular weights. The $\bar{M}_{w,app}$ for the CPEs vary from 1.95×10^5 to 2.5×10^5 g/mol; these similar molecular weights allow meaningful assessments of the effects of hydrophobic association on the solution behavior. It should be noted, however, that the $\bar{M}_{w,app}$ of the polymers containing hydrophobe is high compared to hydrophobe-free sample. This could be attributed to the partial aggregation of the hydrophobocally modified polymers. Measurement of hydrodynamic radius (R_h) for CPE-C_{12}-7, CPE-C_{18}-3.5, CPE-C_{18}-5 was conducted using Wyatt DLS correlator. The results, given in Fig. 2, reveals a sharp increase of hydrodynamic radius, thus indicating the onset of hydrophobic associations especially for the CPE-C_{18}-5 polymer solutions at C^*_{HA} of less than 1 g/dl.

3.2. *Viscosity measurements*

The CPE terpolymers C_{12}-10 and C_{18}-5 were found to give slightly cloudy solution in 0.1 N NaCl throughout the concentration ranges of viscosity measurements. Viscosity data for CPE **17** and **18** prepared under identical conditions are presented in Figs. 3 and 4, respectively. Fig. 3 indicates some hydrophobic association for the sample C_{12}-7. However, we were gratified with the results presented in Fig. 4. The 2 wt% solution of the CPE C_{18}-3.5 has a reduced viscosity value of 109 dl/g (not shown in the Figure), and the hydrophobic association began to manifest at around

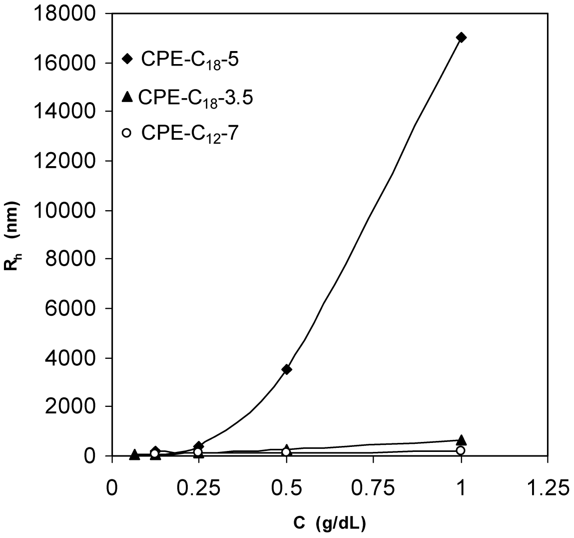


Fig. 2. Variation of hydrodynamic radius (R_h) of CPE-C_{18}-3.5, -5 and CPE-C_{12}-7 at various concentrations at 21 °C in salt-free water.

C^*_{HA} value of less than 1 wt% of the polymers. The CPE C_{18}-5 has lower viscosity values than that of the other terpolymers and is attributed to its solubility problem. Fig. 5 displays the viscosity data for the APE **20** and its corresponding M_2-0 in 0.1 N NaCl. It is to be noted that while the anionic polymers have higher viscosity values than the corresponding CPEs in the dilute range (Fig. 4), the associative behavior of the CPEs are more pronounced in the semi-dilute range. It is interesting to observe that while the CPE C_{18}-5 **(18)** was partially soluble in water, the corresponding APE C_{18}-5 **(19)** was readily soluble, and we cannot even measure the viscosity value of its 2 wt% solution with the Ubbelohde viscometer; the solution looked like a gel.

Extrapolation of linear part of the viscosity plots (Figs. 3–5) in the concentration range 0.5–0.0625 g/dl permitted us to determine the intrinsic viscosities [η] values as ~0.55 and ~1.0 dl/g for the CPEs and their corresponding APEs, respectively (Table 1). However, as the incorporation of the hydrophobe increases, as in the polymers CPE C_{12}-7 and C_{12}-10, 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. It is worth mentioning that the polymerization conditions are kept similar as rigorously as possible in order to maintain similar degree of polymerization. Even though the CPEs **(18)** have smaller distances between the neighboring positive charges, the widely separated but highly exposed anionic pendents in APEs **(20)** seem to be more effective in expanding the polymer chains owing to increased repulsion between the charges. This is due to the fact that, in the presence of NaCl, the chloride ions are more effective in screening the positive

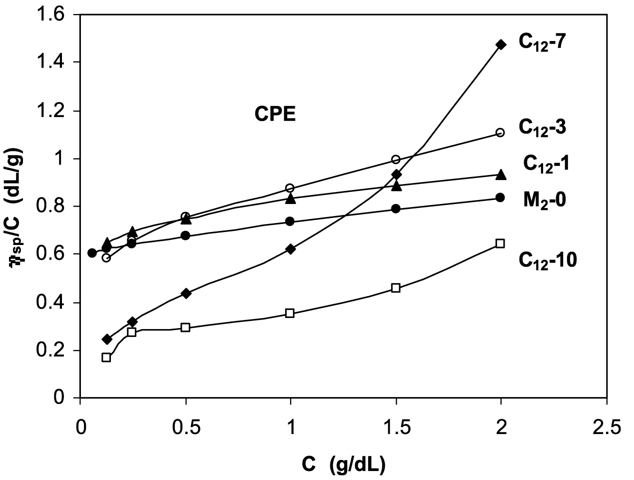


Fig. 3. The viscosity behavior of the CPE **17** 0.1 N NaCl at 30 °C with an Ubbelohde viscometer.

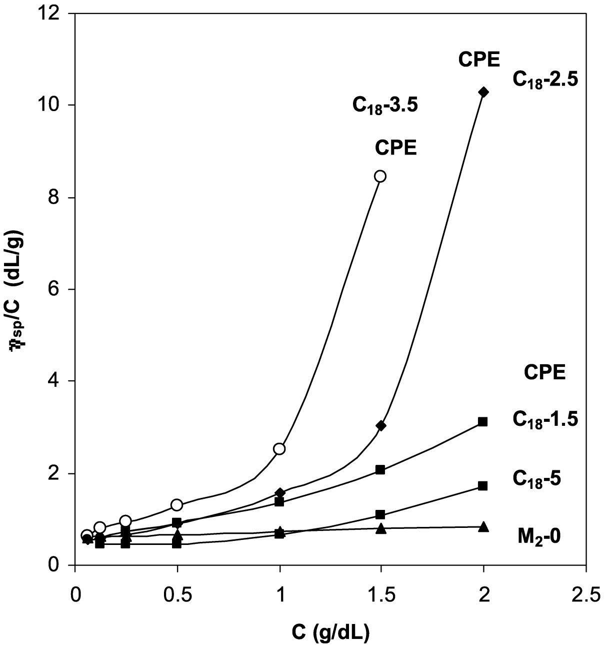


Fig. 4. The viscosity behavior of the CPE **18** 0.1 N NaCl at 30 °C with an Ubbelohde viscometer.

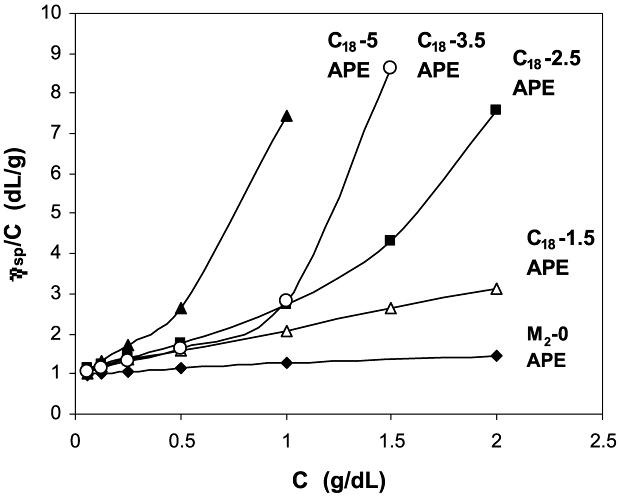


Fig. 5. The viscosity behavior of the APE **20** 0.1 N NaCl at 30 °C with an Ubbelohde viscometer.

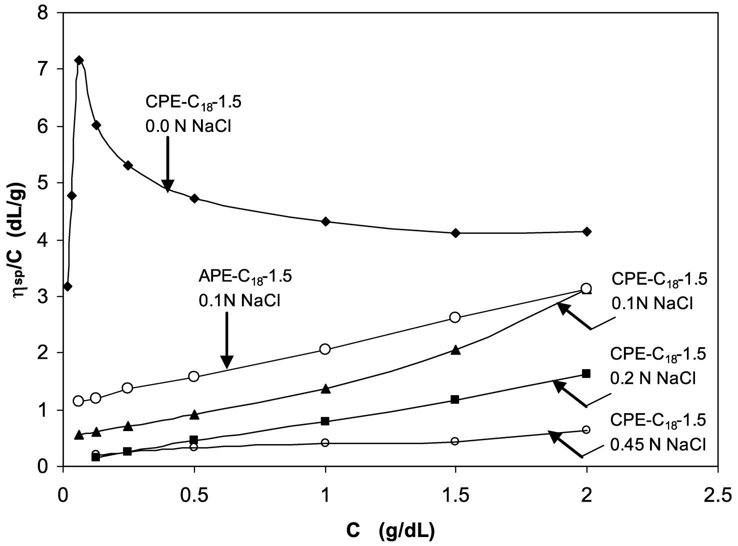


Fig. 6. The viscosity behavior of the CPE **18** C_{18}-1.5 and APE **20** C_{18}-1.5 in the presence and absence of NaCl at 30 °C with an Ubbelohde viscometer.

nitrogens in the CPEs, while the sodium ions having larger hydration shells are unable to approach the $-CO_2-$ close enough to effectively shield the negative charges in the APE. The viscosity plot for the CPE C_{12}-7 (Fig. 3) demonstrates contrasting associative behavior of the polymer. At lower polymer concentrations, hydrophobic chains have little chance of interacting intermolecularly with each other; intrachain associations are dominant compared to interchain associations and as such, internal micellaization reduces the hydrodynamic radius of the polymer coil. At higher polymer concentrations, interchain associations lead to higher viscosity values for the CPE C_{12}-7.

In the absence of added salt, the viscosity plots for polyelectrolytes are expected to be concave upwards as shown in Fig. 6 for the CPE C_{18}-1.5. However, at higher dilution in salt-free water, the reduced viscosities, after reaching a maximum, tend to fall off; the existence of the maximum in the reduced viscosity is a normal behavior of salt-free polyelectrolyte solutions [42]. Upon addition of the strong electrolyte (NaCl), the viscosity behavior of CPE becomes normal and the reduced viscosities decrease with increasing concentrations of added salt. Solution of CPE C_{18}-1.5 remains clear in 0.45 N NaCl but becomes cloudy in 0.5 N NaCl. The same figure displays the higher viscosity values for the APE C_{18}-1.5 than its corresponding cationic counterpart CPE C_{18}-1.5 in 0.1 N NaCl—the former was derived from the latter and thus they both are expected to have similar degree of polymerization. The viscosity values for the C_{18}-1.5 polymer having low mol% hydrophobe increased linearly with concentration but failed to demonstrate any associative property.

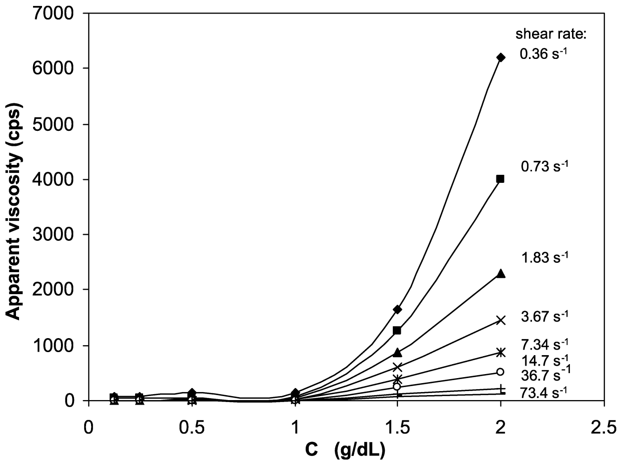


Fig. 7. Variation of viscosity with concentration of APE **20** C_{18}-5 at various shear rates in 0.1 N NaCl at 30 °C.

Fig. 7 depicts the dependency of solution viscosity of the APE C_{18}-5 at 30 °C in 0.1 N NaCl on the polymer concentration and shear rate. The viscosity is sharply decreased at higher shear rates—a typical shear thinning behavior. However, at the low shear rates, the hydophobically associating polymers exhibited a sharp increase in viscosity with increasing polymer concentration. This observation is similar to that frequently observed for hydrophobically modified associative polymers. The association concentration C^*_{HA} was found to be around 1 g/dl. The strong interchain associations form large aggregates (a network structure of polymer chains) as the polymer concentration passes C^*_{HA}. The network structures contribute significantly to the thickening [4,8,12,43–45].

Figs. 8 and 9 display the dependency of solution viscosity of the CPE C_{18} in salt-free water. Hydrophobic associations, as indicated by non-linear increase in the viscosity values, occur below 1% polymer concentration for the polymers having grater than 1.5 mol% hydrophobes. For a 2% polymer concentration and shear rate of 1.83 s^{-1}, CPE C_{18}-5 was found to have an apparent viscosity value which is 460 times greater than that of the zero hydrophobe polymer (CPE M_2-0).

The dependency of solution viscosity on the polymer

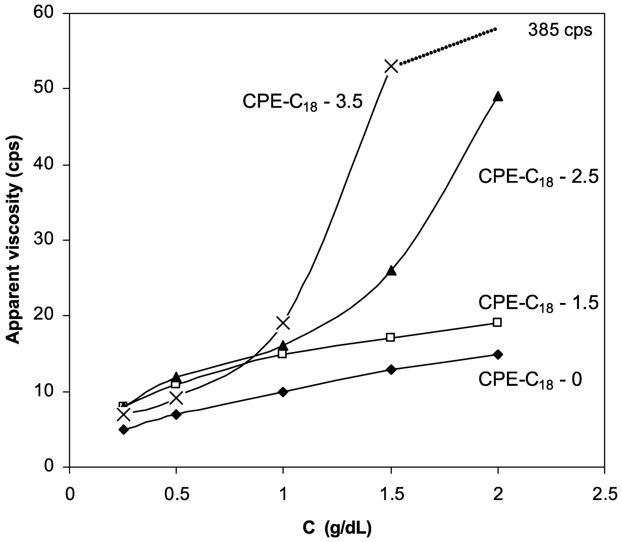


Fig. 8. Variation of viscosity with concentrations of CPE **18** C_{18}-0, 1.5, 2.5, 3.5 at a shear rate of 1.83 s^{-1} in salt-free water at 30 °C.

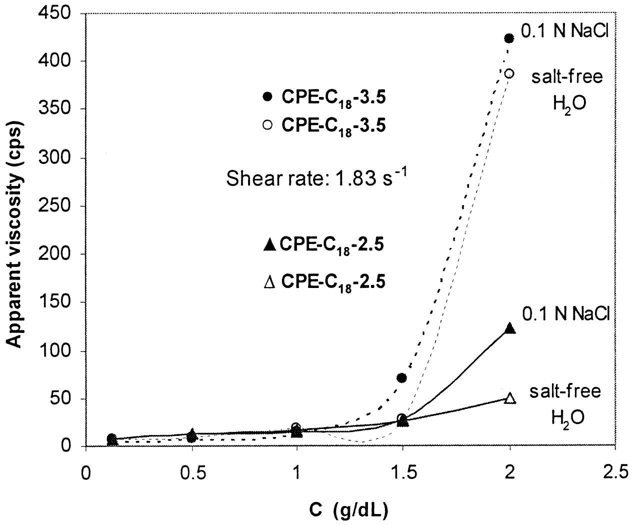


Fig. 10. Variation of viscosity with concentrations of CPE-C_{18}-2.5 and -3.5 at a shear rate of 1.83 s^{-1} in salt-free water and 0.1 N NaCl at 30 °C.

concentration for the CPE C_{18} containing variable mol% of the hydrophobe in the presence and absence of added salt are depicted in Fig. 10. In the presence of added salt, the increase in viscosity correlates well with the known effects of NaCl on hydrophobic association [46]. The CPE C_{18}-1.5 (not shown in Fig. 10), however, has higher values of viscosity in salt-free water than in 0.1 NaCl in the entire range of shear rates and concentrations. Interchain associations are not an important factor in the CPE C_{18}-1.5 since its hydrophobe content is low; the repulsion between the non-screened positive charges in the polymer chain leads to coil expansion hence higher viscosity in salt-free water. The situation is different in the case of CPE C_{18}-2.5 and -3.5; the polymers at concentrations higher than C^*_{HA} are more viscous in 0.1 N NaCl than in salt-free water due to enhanced hydrophobic associations. At higher hydrophobe contents, especially at 5 mol%, the addition of salt makes the aqueous environment so hostile for the hydrophobic pendents that they tend to precipitate as seen in the case of CPE C_{18}-5 in 0.1 N NaCl (Fig. 4).

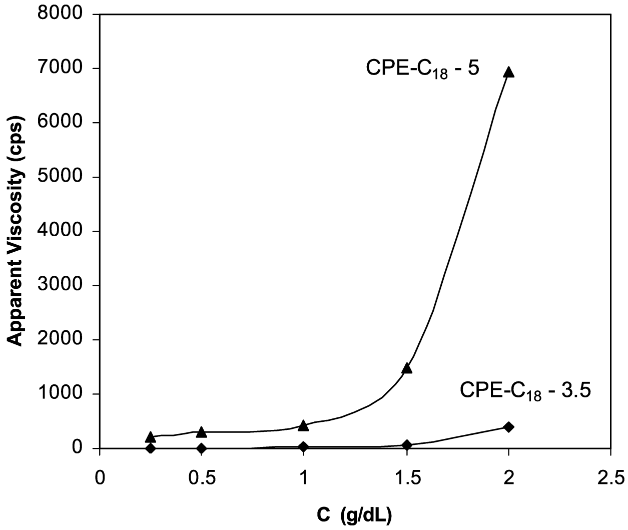


Fig. 9. Variation of viscosity with concentrations of CPE **18** C_{18}-3.5 and -5.0 at a shear rate of 1.83 s^{-1} in salt-free water at 30 °C.

Figs. 11 and 12 display the effect of temperature on the solution viscosity of 2 g/dl solution of CPE C_{18}-5 in salt-free water and APE C_{18}-5 in 0.1 N NaCl. A monotonous decrease in viscosity is observed with increasing temperature for the CPE C_{18}-5. The lowering of solution viscosity with increasing temperature has been reported for hydrophobically associating water-soluble polymers [8,45,47,48]. This effect could be attributed to the weakening of the hydrophobic effect at elevated temperatures due to the increased mobility of the polymer chains, which gives rise to loss of interchain liaisons and/or an increase in polymer solubility as the temperature increases. For the APE, atypical viscosity behavior was observed. As evident from Fig. 12, the viscosity increases as the temperature increases,

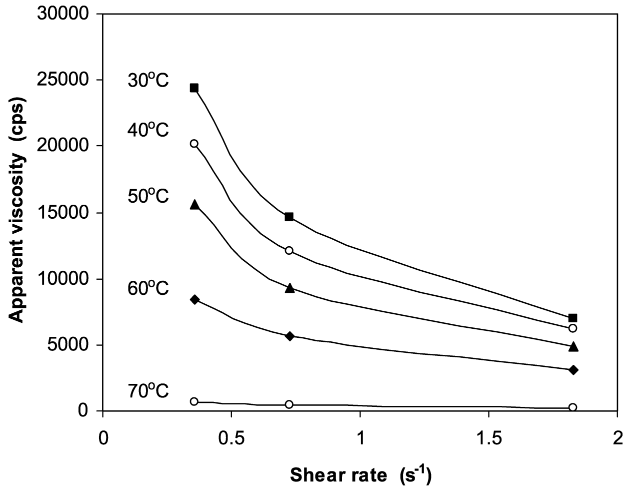


Fig. 11. Variation of viscosity of a 2% solution of CPE-C_{18}-5 at various shear rates and temperature in salt-free water.

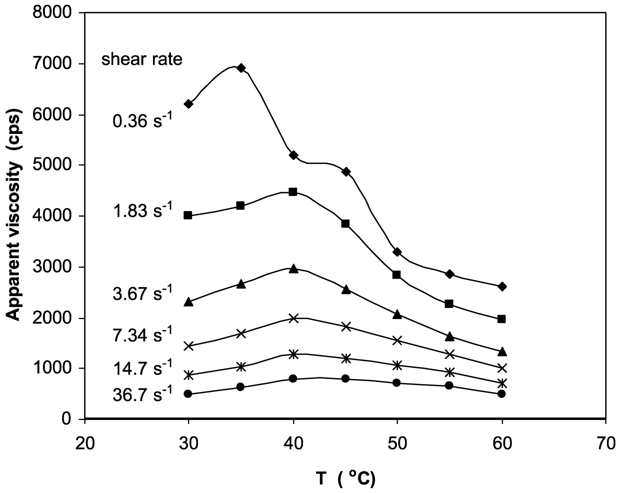


Fig. 12. Variation of viscosity of a 2% solution of APE-C_{18}-5 at various shear rates and temperature in 0.1 N NaCl.

and reaches a maximum at 35 °C at the lowest shear rate ($0.36\ s^{-1}$) employed. At all other shear rates ($0.73-14.68\ s^{-1}$) the viscosity reaches the maximum at 40 °C and then decreases as the temperature was further increased. The viscosity changes with temperature are much more complex. The viscosity increases observed upon heating are consistent with an entropy driven increase in hydrophobic bonding [49,50]. Above 40 °C the viscosity decreases with temperature presumably as a result of changes in the hydration spheres of the hydrophobic groups or in the structure of water itself. The viscosity values at other polymer concentrations (1.5 or 1.0 g/dl), however, did not show any maximum in the temperature range 30–60 °C.

4. Conclusions

The anionic polyelectrolytes (APE) **20** are found to be more water soluble and salt tolerant than their CPE counterparts **18** having similar degree of polymerizations. The solubility characteristics are mainly controlled by the ‘skin’ of the polymers exposed to the solvent. Obviously the APEs have more ionic skins than the CPEs since the former has anionic pendents away from the polymer backbone while the latter has the positive charges embedded in the chains. The hydrophobe incorporation has considerably enhanced the viscosity values in the C_{18} polymer series, whereas the presence of even large amount of hydrophobe in the C_{12} series failed to achieve interchain associations in the studied concentration range (0.0625–2 g/dl). A typical polyelectrolyte is an extended chain with the ionic atmosphere projecting out radially [12]. The electrostatic repulsive forces between the chains do not permit them to move to a safe distance required for the dodecyl pendents ($C_{12}H_{25}$) to manifest interchain associations. This may be the reason for the lower degree of association and very high C^*_{HA} values of 15–17 g/dl for the cyclopolymers **8** and **9** having $\sim C_{11}$ pendents [37]. The octadecyl pendents ($C_{18}H_{37}$), on the other hand, can associate intermolecularly because the extended length of the pendents allows them to mingle with each other without exposing the chains to experience the adverse effect of electrostatic repulsions. To our knowledge, sulfur dioxide is used for the first time to synthesize associating ionic polymers using Butler's cyclocopolymerization process. The low C^*_{HA} ($\sim$1 g/dl) observed for the C_{18} polymer series is indeed a notable improvement over the C^*_{HA} values for the reported associating cyclopolymers [37].

Acknowledgements

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References

[1] Glass JE. In: Glass JE, editor. Polymers in aqueous media: performance through association, advances in chemistry 223. Washington, DC: American Chemical Society; 1989.
[2] Candau F, Selb J. Adv Colloid Interface Sci 1999;79:149. and references cited therein.
[3] Hill A, Candau F, Selb J. Macromolecules 1993;26:4521–32.
[4] Volpert E, Selb J, Candau F. Macromolecules 1996;29:1452–63.
[5] Ezzell SA, McCormicK CL. Macromolecules 1992;25:1881–6.
[6] Candau F, Bigg S, Hill A, Selb J. Prog Org Coat 1994;24:11–19.
[7] Regalado EJ, Selb J, Candau F. Macromolecules 1999;32:8580–8.
[8] Shaikh S, Ali SA, Hamad EZ, Abu-Sharkh BF. J Polym Engng Sci 1999;39:1962–8.
[9] Yahaya GO, Ahdab AA, Ali SA, Hamad EZ, Abu-Sharkh BF. Polymer 2001;42:3363–72.
[10] Dowling KC, Thomas JK. Macromolecules 1990;23:1059–64.
[11] Biggs S, Hill A, Selb J, Candau F. J Phys Chem 1992;96:1505–11.
[12] McCormick CL, Middleton JC, Cummins DF. Macromolecules 1992; 25:1201–6.
[13] McCormick CL, Middleton JC, Grady CE. Polymer 1992;33: 4184–90.
[14] Branham KD, Snowden HS, McCormick CL. Macromolecules 1996; 29:254.
[15] Lacik I, Selb J, Candau F. Polymer 1995;36:3197–211.
[16] Candau F, Joanny JF. In: Salamone JC, editor. Polymeric materials Encyclopedia, vol. 7. Boca Raton, FL: CRC Press; 1996. p. 5476.
[17] Kujawa P, Rosiak JM, Selb J, Candau F. Mol Cryst Liq Cryst 2000; 354:401–7.
[18] Kujawa P, Rosiak JM, Selb J, Candau F. Macromol Chem Phys 2001; 202:1384–97. and references cited therein.
[19] Winnik MA, Yekta A. Curr Opin Colloid Interface Sci 1997;2: 424–36.
[20] Glass JE, editor. Hydrophilic polymers: performance with environmental acceptability, Adv Chem Ser 248. Washington, DC: American Chemical Society; 1996.
[21] Glass JE, editor. Associating polymers in aqueous solution, ACS Symposium Series 765. Washington DC: American Chemical Society; 2000.
[22] Hester RD, Squire DRJ. J Coat Technol 1997;69:109–14.
[23] Taylor KC, Nasr-El-Din HA. J Pet Sci Engng 1998;19:265–80.

[24] Nasr-El-Din HA, Hawkins BF, Green KA. SPE 21028. Society of Petroleum Engineers Inc; 1991. p. 293–306.

[25] Sorbie KS. Polymer-improved oil recovery. Boca Raton, FL: CRC Press; 1991.

[26] Yang Y, Schulz D, Steiner A. Langmuir 1999;15:4335–43.

[27] Butler GB, Ingley FL. J Am Chem Soc 1951;73:895–6.

[28] Harada S, Katayama M. Makromol Chem 1966;90:177–86.

[29] Harada S, Arai K. Makromol Chem 1967;107:64–7.

[30] Ali SA, Ahmed SZ, Wazeer MIM, Hamad EZ. Polymer 1997;38: 3385–93.

[31] Butler GB. J Polym Sci 1996;34:913–23.

[32] Butler GB. Cyclopolymerization and cyclocopolymerization. New York: Marcel Dekker; 1992.

[33] McCormick CL. J Polym Sci 1996;34:911–2.

[34] Ottenbrite RM, Ryan Jr WS. Ind Engng Chem Prod Res Dev 1980;19: 528–32.

[35] Chemical Economics Handbook. Menlo Park (CA): Stanford Research Institute; 1983. p. 581–10111, 581–5022L, 581–1012D.

[36] Butler GB, Do CH. In: Shalaby W, McCormick CL, Butler GB, editors. Water-soluble polymers, ACS Symposium Series 467. Washington, DC: ACS; 1991. p. 151.

[37] Gopalkrishnan FS, Butler GB, Hogen-Esch TE, Zhang NZ. In: Shalaby W, McCormick CL, Butler GB, editors. Water-soluble polymers, ACS Symposium Series 467. Washington, DC: ACS; 1991. p. 175.

[38] Chang Y, McCormick CL. Polymer 1994;35:3503–12.

[39] Boothe JE, Flock HG, Hoover MF. J Macromol Sci Chem 1970;4: 1419–30.

[40] Al-Muallem HA, Wazeer MIM, Ali SA. Polymer 2002;43:1041–50.

[41] Richardson MF, McCormick CL. Polym Prepr 1998;39:312–3.

[42] Eisenberg H, Pouyet J. J Polym Sci 1954;13:85–91.

[43] Zhang YX, Da AH, Butler GB, Hogen-esch TE. J Polym Sci, Polym Chem Ed 1992;30:1383–91.

[44] Kathman EE, McCormick CL. J Polym Sci, Polym Chem Ed 1997;35: 243–53.

[45] Kopperud HM, Hansen FK, Nystrom B. Macrmol Chem Phys 1998; 199:2385–94.

[46] Saito S. J Polym Sci, Polym Chem Ed 1969;7:1789–801.

[47] Yahaya GO, Ali SA, Al-Naffa MA, Hamad EZ. J Appl Polym Sci 1995;57:343–52.

[48] McCormick CL, Nonaka T, Johnson CB. Polymer 1988;29:731–9.

[49] Tanford C. The hydrophobic effect. New York: Wiley; 1980.

[50] Ben-Naim A. Hydrophobic interactions. New York: Plenum; 1980.