Synthesis and Viscosity of Hydrophobically Modified Polymers Containing Dendritic Segments

Shaikh A. Ali,[1] Yunusa Umar,[1] Hasan A. Al-Muallem,[1] Basel F. Abu-Sharkh[2]

[1]Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[2]Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

ABSTRACT: The cycloterpolymerizations of a newly synthesized dendritic quadruple-tailed hydrophobic diallylammonium chloride with the hydrophilic monomer N,N-diallyl-N-carboethoxymethylammonium chloride and sulfur dioxide afforded a series of water-soluble cationic polyelectrolytes (CPEs) containing various proportions (0–1 mol %) of the hydrophobe. At a shear rate of 0.36 s^{-1} at 30°C, salt-free water solutions of the CPEs (4 g/dL) containing 0, 0.35, 0.53, 0.65, and 0.93 mol % of the hydrophobe had apparent viscosity values of 140, 1200, 180,000, 308,000, and 858,000 cps, respectively. The study clearly demonstrated an increase in the viscosity values with increasing incorporation of the hydrophobes. The CPEs on acidic hydrolysis of the pendant ester groups gave corresponding pH-responsive cationic acid salts, which upon treatment with NaOH, were converted to the polybetaines (PBs), anionic polyelectrolytes (APEs), and PB/APEs containing various proportions of PB and APE fractions in the polymer chain. The effects of charge type and charge density on the polymer chain were investigated. Polymer surfactant interactions were investigated with the cationic surfactant cetyltrimethylammonium bromide; a considerable increase in the viscosity values of the CPE was observed in the presence of the surfactant. The superior viscosity behavior for the polymers containing the quadruple-tailed hydrophobe was attributed to the blocky nature of the comonomer. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1781–1792, 2008

Key words: cyclopolymerization; dendrimers; hydrophilic polymers; solution properties; surfactants

INTRODUCTION

In the recent past, there has been increasing interest in the synthesis and properties of hydrophobically modified water-soluble polymers.[1,2] The copolymerization of a water-soluble monomer with a few molar percentage of a hydrophobic comonomer in a homogeneous solution affords amphiphilic polymers with a random distribution of the hydrophobes as isolated units. However, micellar copolymerization systems[2] involving a hydrophilic monomer ($\sim$ 3 wt %) in a continuous water phase and a hydrophobic monomer inside the micelles favor a random distribution of the hydrophobes as small blocks in the hydrophilic polymer chains because of the local concentration of the hydrophobes inside the micelles.[3–7] Above a hydrophobic association concentration (C_{HA}*), these polymers form reversible three-dimensional physical crosslinks of polymer chains, which are responsible for the increased solution viscosity. The concentration-dependent intermolecular associations in the microblock copolymers lead to superior viscosity behavior in comparison to random copolymers, which exhibit largely intramolecular associative behavior.[8–11]

The discovery of the cyclopolymerization of N,N-diallyl quaternary ammonium salts by Butler and Ingley[12,13] and, subsequently, their copolymerization with sulfur dioxide[14] led to the synthesis of an array of water-soluble cationic polyelectrolytes (CPEs)[15] of tremendous scientific and technological interest. The resulting polymer architecture, having cyclic units embedded in the backbone, has been recognized as the eighth major structural type of synthetic polymers.[16] There are, however, only a few reports[17–23] that describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique. Previous kinetic studies[24] have indicated that monomer concentrations of 50–65 wt % are required to obtain polymers with high conversions, high molecular weights, and low residual double bonds. The cyclopolymerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than microblock copolymers, even though the hydrophobic monomer possesses surfactant properties.[18]

In a series of copolymers (**1**; Scheme 1) with hydrophobic contents of 3–30 mol %, it was found
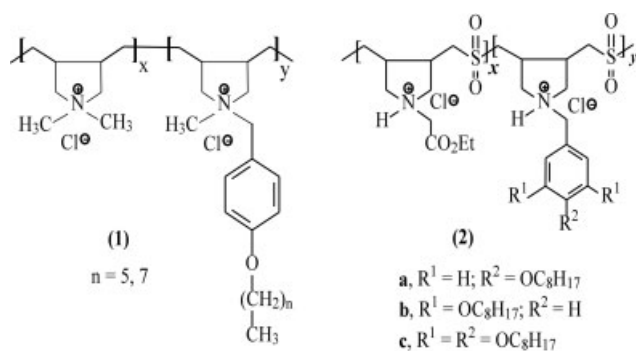
Scheme 1.

that the intrinsic viscosities ($[\eta]$'s) continuously decreased with increasing hydrophobic content, which indicated that the copolymers formed mainly intramolecular hydrophobic associations.[17] We recently reported[25] the comparative solution properties of associating CPEs (**2**) having single-, twin- and triple-tailed hydrophobes (Scheme 1). For the terpolymers **2a–2c,** having an identical number of octyloxy pendants (8 mol %), it has been shown that the microblocky nature of the triple-tailed hydrophobe in **2c** led to a dramatic enhancement of viscosity at concentrations above its C_{HA}^* value of 0.3 wt %. The presence of 8 mol % octyloxy pendants in the single-tailed hydrophobe in **2a,** however, failed to achieve interchain associations in the studied concentration range (0.25–2.0 g/dL). The superior viscosity behavior of the polymers containing the triple-tailed

hydrophobe was attributed to the blocky nature of the comonomer. In the absence of a micellar polymerization process, the work has, thus, paved the way to the synthesis of ionic associating polymers having superior viscosity behaviors by the utilization of blocky hydrophobic monomers.

The encouraging results obtained with the triple-tailed hydrophobe prompted us to synthesize a novel dendritic quadruple-tailed hydrophobic monomer (**9**) from readily available starting materials, as shown in Scheme 2. In our continuing studies of associating ionic polymers, we report herein the synthesis and solution properties of CPEs (**11**) and their corresponding pH-responsive anionic polyelectrolytes (APEs; **14**) by the cyclopolymerization of hydrophilic monomer **10** (M_1) with SO_2 in the presence of various amounts of hydrophobic monomer **9** (M_2; Scheme 3). To the best of our knowledge, the introduction of hydrophobe **9** would represent the bulkiest hydrophobe used so far in Butler's cyclopolymerization reactions.
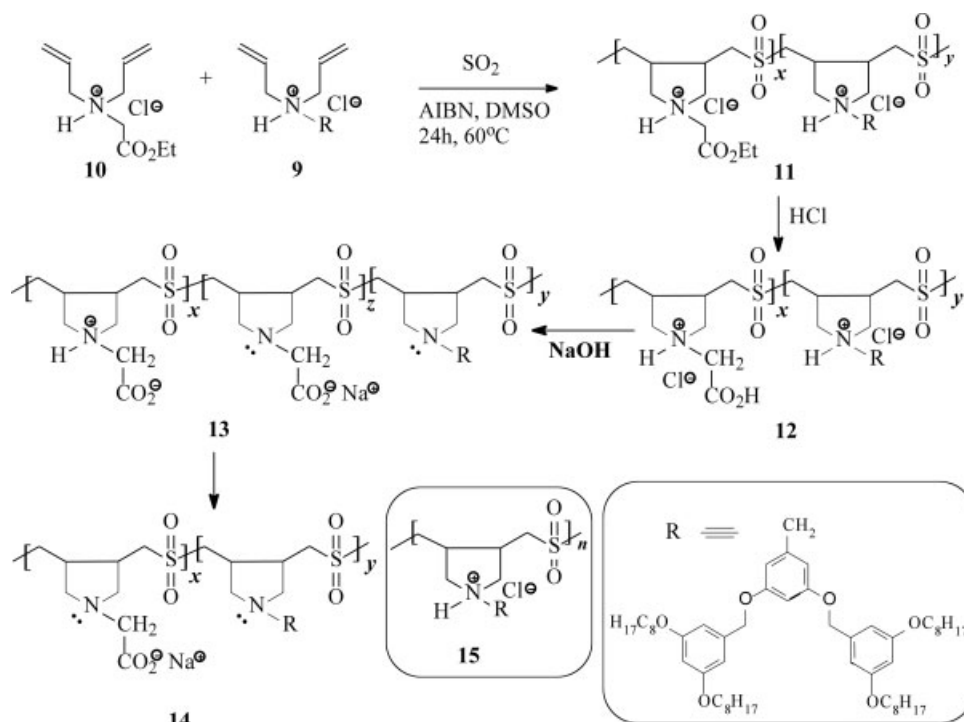
EXPERIMENTAL

Physical methods

Elemental analysis was carried out on a EuroVector elemental analyzer model EA3000. IR spectra were recorded on a PerkinElmer 16F PC Fourier transform infrared spectrometer (Boston, MA). ^{1}H-NMR spectra of the polymers were measured in $CDCl_3$ or D_2O

^{a}(**8**) is the conjugate amine of **9**
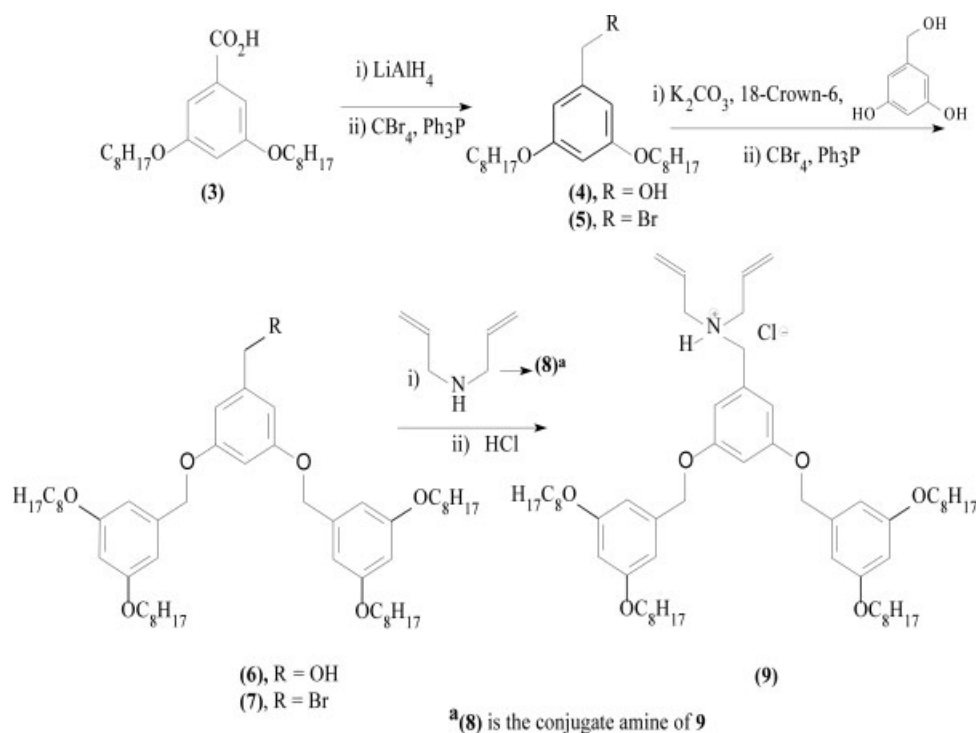
Scheme 2.

Scheme 3.

on a Jeol LA 500-MHz spectrometer (Tokyo, Japan). Viscosity measurements were made with an Ubbelohde viscometer (with a viscometer constant of 0.005718 cSt/s at all temperatures) with CO_2-free water under N_2 to avoid CO_2 absorption, which may have affected the viscosity data. A gentle stream of N_2 was passed through distilled deionized water at 90°C for 15 min to remove the dissolved gases. A Brookfield digital rotational viscometer with a ultra low (UL) adaptor or SC4-18 spindle accessories was used to measure the apparent viscosities at various shear rates and temperatures. The polymer solutions were continuously purged with N_2 to avoid CO_2 absorption, which may have affected the viscosity data.

The molecular weights of the polymer samples were determined by light-scattering experiments at 21°C. Solutions of CPE **11** (polymer concentration range = 0.03–0.1 g/dL) were prepared in a 1 : 1 (v/v) methanol/0.1N NaCl mixture; the presence of salt allowed the screening of the charges to minimize ionic interactions and allow the polymer chains to form random coils. Methanol helped to disrupt hydrophobic associations so we did not obtain exaggerated values of apparent molecular weights ($M_{w,app}$'s). Millipore disposable filters (Billerica, MA) (pore size = 0.02 μm) were used to remove dust particles from the solutions of the polymers. The measurements were performed on each solution immediately after filtration. Static light-scattering experiments were performed with a Dawn Eos light-scattering instrument (Wyatt Technology Corp.,

Santa Barbara, CA). The system light source was a linearly polarized gallium arsenide laser. The laser was positioned so that the incident beam was vertically polarized. A RFM-340 refractometer (Bellingham & Stanley, Kent, UK) was used to measure the differential refractive indices of the different polymer solutions.

Materials

2,2'-Azobisisobutyronitrile (AIBN) from Fluka Chemie AG (Buchs, Switzerland) was purified by crystallization from a chloroform–ethanol mixture. Dimethyl sulfoxide (DMSO) was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg). All other chemicals were purchased from Aldrich (St. Louis, MO) and were used as received. All glassware were cleaned with deionized water. N,N-diallyl-N-carboethoxymethylammonium chloride (**10**) was prepared as described in a previous article.[26]

3,5-Dioctyloxybenzyl alcohol (4)

LiAlH$_4$ (35 mmol) was added in three portions over 10 min to a stirred solution of 3,5-dioctyloxybenzoic acid (**3**;[25] 30.0 mmol) in ether (200 cm^3) at 20°C. After it was stirred for 2 h, the reaction mixture was quenched by the dropwise addition of water (5 cm^3). The white granular salts were washed with ether. The ether solution was dried (Na$_2$SO$_4$) and concentrated. The crude reaction product was purified by

flash chromatography over silica with hexane/ether as the eluent to give **4** as a colorless liquid.

Yield: 95.0%. ANAL. Calcd for $C_{23}H_{40}O_3$: C, 75.78%; H, 11.06%. Found: C, 75.6%; H, 10.9%. ν_{max} (neat, cm^{-1}): 3046 (br); 2924, 2855, 1598, 1455, 1384, 1345, 1294, 1165, 1057, 832. δ_H (CDCl$_3$): 0.88 (6 H, t, J = 7.0 Hz), 1.15–1.55 (20 H, m), 1.76 (4 H, q, J = 6.8 Hz), 1.91 (1 H, br), 3.92 (4 H, t, J = 6.7 Hz), 4.58 (2 H, d, J = 5.5 Hz), 6.37 (1H, s), 6.49 (2 H, s). δ_C (CDCl$_3$): 14.11 (2 C), 22.67 (2 C), 26.06 (2 C), 29.27 (2 C), 29.37 (2 C), 30.12 (2 C), 31.84 (2 C), 65.40 (1 C), 68.06 (2 C), 100.51 (1 C), 105.03 (2 C), 143.22 (1 C), 160.50 (2 C; CDCl$_3$ 77.04 ppm middle C).

3,5-Dioctyloxybenzyl bromide (5)

To a mixture of alcohol **4** (9.93 g, 27.2 mmol) and carbon tetrabromide (11.3 g, 34 mmol) in anhydrous tetrahydrofuran (18 cm^3) was added triphenylphosphine (8.9 g, 34 mmol) at °C, and the reaction mixture was stirred under N$_2$ for 40 min. The reaction mixture was poured into water (50 cm^3) and extracted with CH$_2$Cl$_2$ (2 × 50 cm^3). The organic layer was dried (Na$_2$SO$_4$) and concentrated, and the residual crude product was purified by flash chromatography over silica with hexane as the eluent to give bromide **5** (10.7 g, 92%) as a colorless liquid.

ANAL. Calcd for $C_{23}H_{39}BrO_2$: C, 64.63%; H, 9.20%. Found: C, 64.5%; H, 9.1%. ν_{max} (neat, cm^{-1}): 2925, 2854, 1597, 1460, 1384, 1349, 1324, 1295, 1260, 1213, 1168, 1057, 949, 834, 723, 692. δ_H (CDCl$_3$): 0.88 (6 H, t, J = 7.0 Hz), 1.15–1.55 (20 H, m), 1.76 (4 H, q, J = 6.8 Hz), 3.92 (4 H, t, J = 6.7 Hz), 4.40 (2 H, s), 6.38 (1H, s), 6.51 (2 H, s). δ_C (CDCl$_3$): 14.11 (2 C), 22.68 (2 C), 26.05 (2 C), 29.25 (2 C), 29.36 (4 C), 31.83 (2 C), 33.82 (1 C), 68.11 (2 C), 100.41 (1 C), 107.38 (2 C), 139.52 (1 C), 160.42 (2 C; CDCl$_3$ 77.04 ppm middle C).

3,5-Bis(3,5-dioctyloxybenzyloxy)benzyl alcohol (6)

A mixture of bromide **5** (6.18 g, 14.4 mmol), 3,5-dihydroxybenzyl alcohol (1.00 g, 7.13 mmol), anhydrous potassium carbonate (3.0 g, 21.7 mmol), and 18-crown-6 ether (265 mg, 1.38 mmol) in dry acetone (200 cm^3) was stirred with a magnetic stirring bar at 70°C in a closed vessel for 48 h. The reaction mixture was concentrated, taken up in ether (100 cm^3), and washed with water. The organic layer was dried (Na$_2$SO$_4$) and concentrated, and the residual liquid was purified by chromatography with hexane/ether as the eluent to give alcohol **6** as a colorless liquid (5.3 g, 89.2%).

ANAL. Calcd for $C_{53}H_{84}O_7$: C, 76.40%; H, 10.16%. Found: C, 76.2%; H, 10.2%. ν_{max} (neat, cm^{-1}): 3405, 2925, 2856, 1736, 1598, 1454, 1378, 1296, 1164, 1055, 833, 722. δ_H (CDCl$_3$): 0.88 (12 H, t, J = 7.0 Hz), 1.15–1.35 (40 H, m), 1.76 (8 H, q, J = 7.0 Hz), 3.93 (8 H, t,

J = 6.4 Hz), 4.62 (2 H, d, J = 5.5 Hz), 4.95 (4 H, s), 6.39 (2 H, s), 6.53 (1 H, s), 6.55 (4 H, s), 6.60 (2 H, s). δ_C (CDCl$_3$): 14.11 (4 C), 22.66 (4 C), 26.06 (4 C), 29.25 (4 C), 29.36 (8 C), 31.83 (4 C), 65.36 (1 C), 68.08 (4 C), 70.11 (2 C), 100.80 (2 C), 101.34 (2 C), 105.70 (6 C), 138.97 (1 C), 134.36 (1 C), 160.17 (2 C), 160.52 (4 C; CDCl$_3$ 77.04 ppm middle C).

3,5-Bis(3,5-dioctyloxybenzyloxy)benzyl bromide (7)

Alcohol **6** (4.87 g, 5.84 mmol) in tetrahydrofuran (18 cm^3) was converted to bromide **7** with the procedure described previously for the preparation of **5** (*vide supra*). However, a large excess of CBr$_4$ (4.86 g, 14.6 mmol) and PPh$_3$ (3.82 g, 14.6 mmol) were required to force the reaction to completion. The crude product was purified by chromatography with hexane/ether as the eluent to give bromide **7** as a colorless liquid in 95.9% yield.

ANAL. Calcd for $C_{53}H_{83}BrO_6$: C, 71.04%; H, 9.34%. Found: C, 70.7%; H, 9.2%. ν_{max} (neat, cm^{-1}): 2926, 2862, 1600, 1455, 1375, 1333, 1162, 1056, 955, 836, 687. δ_H (CDCl$_3$): 0.89 (12 H, t, J = 7.0 Hz), 1.15–1.35 (40 H, m), 1.76 (8 H, q, J = 7.0 Hz), 3.93 (8 H, t, J = 6.4 Hz), 4.41 (2 H, s), 4.92 (4 H, s), 6.40 (2 H, s), 6.53 (1 H, s), 6.54 (4 H, s), 6.23 (2 H, s). δ_C (CDCl$_3$): 14.10 (4 C), 26.06 (4 C), 29.25 (4 C), 29.36 (12 C), 31.81 (4 C), 31.61 (1 C), 68.09 (4 C), 70.21 (2 C), 100.89 (2 C), 102.23 (2 C), 105.74 (4 C), 108.14 (2 C), 138.74 (1 C), 139.70 (1 C), 160.04 (2 C), 160.53 (4 C; CDCl$_3$ 77.04 ppm middle C).

N,N-Diallyl-N-[3,5-bis(3,5-dioctyloxybenzyloxy)]benzylamine (8)

A solution of dendritic benzyl bromide **7** (5.02 g, 5.6 mmol) and diallylamine (5.4 g, 56 mmol) in ether (60 cm^3) was stirred at 20°C under N$_2$ for 24 h. At the end, the reaction mixture was washed with a 5% K$_2$CO$_3$ solution (30 cm^3) and water (3 × 20 cm^3). The organic layer was dried (Na$_2$SO$_4$), concentrated, and purified by chromatography with a hexane/ether mixture as the eluent to give diallylamine derivative **8** (4.85 g, 95%) as a colorless liquid.

ANAL. Calcd for $C_{59}H_{93}NO_6$: C, 77.67%; H, 10.27%; N, 1.54%. Found: C, 77.4%; H, 10.2%; N, 1.4%. ν_{max} (neat, cm^{-1}): 3075, 2926, 2860, 1600, 1455, 1373, 1161, 1056, 997, 920, 834, 720, 684. δ_H (CDCl$_3$): 0.89 (12 H, t, J = 7.0 Hz), 1.15–1.35 (40 H, m), 1.76 (8 H, q, J = 7.0 Hz), 3.06 (4 H, d, J = 6.4 Hz), 3.50 (2 H, s), 3.93 (8 H, t, J = 6.8 Hz), 4.94 (4 H, s), 5.11–5.20 (4 H, m), 5.85 (2 H, m), 6.39 (2 H, t, J = 2.5 Hz), 6.49 (1 H, t, J = 2.5 Hz), 6.55 (4 H, d, J = 2.4 Hz), 6.60 (2 H, d, J = 2.4 Hz). δ_C (CDCl$_3$): 14.10 (4 C), 26.66 (4 C), 29.07 (4 C), 29.25 (4 C), 29.36 (8 C), 31.83 (4 C), 56.43 (2 C), 57.66 (1 C), 68.06 (4 C), 70.09 (2 C), 100.63 (1 C), 100.81 (2 C), 105.76 (4 C), 107.75 (2 C), 117.34 (2 C),

TABLE I
Terpolymerization of Monomers 10 (M$_1$) and 9 (M$_2$) and SO$_2$[a]

Entry	Sample 11[b]	M$_1$ (mmol)	M$_2$ (mmol)	Feed M$_1$: M$_2$	DMSO (g)	Yield (%)	$[\eta]$[c] (dL/g) 11-CPE	14-APE[d]
1	M$_2$-(0)	35.0	0.00	100 : 0	11	85.1	0.615	1.05
2	M$_2$-(0.25)	34.90	0.0105	99.7 : 0.30	11	89.9	0.598	1.03
3	M$_2$-(0.35)	34.83	0.175	99.5 : 0.50	11	85.7	0.610	0.996
4	M$_2$-(0.53)	34.74	0.263	99.25 : 0.75	11	86.2	0.574	0.974
5	M$_2$-(0.93)	34.48	0.525	98.5 : 1.5	11	85.5	0.583	0.987
6[e]	M$_2$-(0.77)	34.48	0.525	98.5 : 1.5	11	87.0	0.547	0.847
7[e]	M$_2$-(0.29)	34.48	0.525	98.5 : 1.5	7	84.0	0.552	0.867
8[e]	M$_2$-(0.65)	34.48	0.525	98.5 : 1.5	17	58.2	0.383	0.603

[a] The polymerization reactions were carried out in DMSO containing 35.0 mmol of SO$_2$ in the presence of AIBN (175 mg) at 60°C for 24 h.

[b] The molar percentage of the hydrophobic monomer M$_2$ (as determined by ^{1}H-NMR) is in parentheses. For example, M$_2$-(0.25) describes 0.3 mol % in the feed and 0.25 mol % incorporated in the polymer.

[c] Obtained by extrapolation of the linear parts of the curves, usually in the range 0.25–0.0625 g/dL of polymer solution in 0.1N NaCl at 30°C (as measured with an Ubbelohde viscometer; viscometer constant (K) = 0.005718).

[d] Prepared by the treatment of CAS 12 with 2 equiv of NaOH in 0.1N NaCl.

[e] The polymerization reactions were carried out in DMSO containing 35.0 mmol of SO$_2$ in the presence of AIBN (175 mg) at 65°C for 24 h.

135.87 (2 C), 139.16 (2 C), 142.07 (1 C), 159.84 (2 C), 160.49 (4 C; CDCl$_3$ 77.04 ppm middle C).

N,N-Diallyl-N-{3,5-bis[3,5-di(octyloxy)benzyloxy]}benzylammonium chloride (9)

Dry HCl gas was bubbled through a solution of amine 8 (4.5 g) in ether (50 cm^3). Evaporation of the ether afforded hydrochloride salt 9 as a waxy semisolid (in almost quantitative yield), which was dried *in vacuo* until a constant weight was reached.

ANAL. Calcd for C$_{59}$H$_{94}$ClNO$_6$: C, 74.68%; H, 9.99%; N, 1.48%. Found: C, 75.0%; H, 10.1%; N, 1.6%. $\nu_{max.}$ (neat, cm^{-1}): 3420, 2925, 1608, 1456, 1384, 1159, 1052, 946, 836, 720, 683. δ_H (CDCl$_3$): 0.90 (12 H, t, J = 7.0 Hz), 1.15–1.35 (40 H, m), 1.76 (8 H, q, J = 7.0 Hz), 3.50–3.61 (4 H, m), 3.94 (8 H, t, J = 6.8 Hz), 4.03 (2 H, s), 5.02 (4 H, s), 5.40–5.56 (4 H, m), 6.19 (2 H, m), 6.39 (2 H, s), 6.56 (4 H, d, J = 2.4 Hz), 6.64 (1 H, s), 6.94 (2 H, s). δ_C (CDCl$_3$): 13.98 (4 C), 22.54 (4 C), 25.95 (4 C), 29.12 (4 C), 29.16 (4 C), 29.24 (4 C), 31.70 (4 C), 54.16 (2 C), 56.16 (1 C), 67.99 (4 C), 70.31 (2 C), 100.81 (2 C), 103.80 (1 C), 105.80 (4 C), 109.61 (2 C), 125.60 (2 C), 126.41 (2 C), 130.44 (1 C), 138.53 (2 C), 160.30 (2 C), 160.39 (4 C; CDCl$_3$ 77.04 ppm middle C).

General procedure for the terpolymerization of 9, 10, and SO$_2$

All of the polymerizations were carried out under the conditions described in Table I. In a typical experiment, SO$_2$ was absorbed in a solution of monomers 9 and 10 (i.e., M$_2$ and M$_1$) in DMSO in a 25-cm^3 round-bottom flask. The required amount of the initiator was then added under nitrogen, and the reaction mixture in the closed flask was vigorously stirred with a magnetic stirring bar at 60°C for 24 h.

The reaction mixture, which remained transparent throughout the polymerization process, was soaked in acetone, crushed to a powder in a pestle, filtered, and washed with acetone followed by a 9:1 (v/v) acetone/methanol mixture. The resulting white polymer was dried *in vacuo* at 55°C until a constant weight was reached (yield > 80%).

The polymers obtained under entries 2 and 3 in Table I gave clear solutions and were, thus, expected to be almost free of polydendrimers 15. However, polymers from entries 4–8 gave a cloudy mixture in salt-free water, which indicated the presence of a mixture of polymers 11 and 15. The polymers 11 were separated from 15 by the following procedure. A polymer solution ($\sim$ 2.5 wt %) in water was centrifuged to separate the insoluble dendritic polymer 15 from CPE 11. The clear supernatant polymer solution was then freeze-dried to obtain the CPE 11 free of dendritic polymer 15. The water-insoluble polymer 15 was dried *in vacuo* at 55°C until a constant weight was reached. The white polymer was found to be soluble in chloroform but insoluble in methanol. The onset of thermal decomposition (closed capillary) was as follows: 15: 225–230°C (liquefied, turned brown).

ν_{max} (KBr, cm^{-1}): 3423, 2926, 2856, 1744 (w), 1600, 1458, 1380, 1303, 1164, 1057, 837 and 678.

The polymerization reaction under entry 7 in Table I [M$_2$-(0.29)] afforded the maximum amount of the dendritic polymer 15, which constituted about 4 wt % of the initial polymer mixture of 11 and 15.

Thermal decomposition, elemental analyses, and $M_{w,app}$ of CPE 11

The onset of thermal decomposition (closed capillary) was as follows: 11–M$_2$-(0): 232–250°C (decom-

posed, turned brown); **11**–M$_2$-(0.53): 215–225°C (decomposed, turned blackish); **11**–M$_2$-(0.93): 210–220°C (decomposed, turned blackish).

The elemental analyses for CPEs **11** [(M$_1$·SO$_2$·1H$_2$O)$_x$ and (M$_2$·SO$_2$·1H$_2$O)$_{1-x}$] were as follows (the numbers in parentheses represent calculated values where $x \leq 1$): **11**–M$_2$-(0): C, 39.6% (39.80%); H, 6.8% (6.68%); N, 4.5% (4.64%); S, 10.3% (10.62%). **11**–M$_2$-(0.25): C, 39.7% (39.87%); H, 6.8% (6.69%); N, 4.5% (4.63%); S, 10.4% (10.60%). **11**–M$_2$-(0.35): C, 39.6% (39.90%); H, 6.6% (6.69%); N, 4.4% (4.63%); S, 10.3% (10.59%). **11**–M$_2$-(0.53): C, 39.8% (39.95%); H, 6.8% (6.69%); N, 4.4% (4.62%); S, 10.2% (10.58%). **11**–M$_2$-(0.65): C, 40.2% (39.97%); H, 6.9% (6.70%); N, 4.5% (4.62%); S, 10.3% (10.57%). **11**–M$_2$-(0.93): C, 40.0% (40.07%); H, 6.8% (6.71%); N, 4.5% (4.61%); S, 10.3% (10.55%).

The $M_{w,app}$ values of CPE **11**–M$_2$-(0), **11**–M$_2$-(0.25), **11**–M$_2$-(0.35), **11**–M$_2$-(0.53), and **11**–M$_2$-(0.93) (associating polymers usually do not give true molecular weights) were determined to be 1.90×10^5, 2.15×10^5, 2.20×10^5, 2.23×10^5, and 2.29×10^5, respectively.

General procedure for the acidic hydrolysis of CPE 11

All CPEs **11** (Table I) were hydrolyzed to their corresponding cationic acid salts (CASs) **12** in $2N$ HCl at 50°C for 48 h at well over 90% isolated yields with a previously described procedure.[26] CAS **12** also gave satisfactory elemental analyses. The elemental analyses supported the presence of 1 mol of water/mol of repeating units for **11** and **12**.

Conversion of CAS 12 to polybetaine (PB)/APE 13 and APE 14 by basification and its use in viscosity measurements

CAS terpolymer **12**–M$_2$-(0.93) was converted to the corresponding PB/APE **13**–M$_2$-(0.93) ($x = z = 0.495$; $y = 0.0093$) by the addition of 1.5 equiv of aqueous NaOH, and the resultant solution was used for viscosity measurement in $0.142N$ NaCl. The CAS samples contained 2 equiv of acidic protons (NH$^+$ and CO$_2$H) per each unit except that the hydrophobic units carried a single proton (NH$^+$). Thus, a stock solution for PB/APE **13**–M$_2$-(0.93) was prepared by the dissolution of 1.200 g (4.274 mmol) of CAS **12**–M$_2$-(0.93) (it contained 0.93 mol % hydrophobe derived from CPE **11**–M$_2$-(0.93), entry 5, Table I; the molecular mass of the polymer containing 1 mol of H$_2$O per unit was calculated to be 280.77) in a NaOH solution containing 6.391 (i.e., $4.274 + 4.274 \times 0.9907 \times 0.5$) mmol of NaOH (21.21 cm^3 of $0.3013N$ NaOH was used for the purpose). The solution was then diluted to 30 cm^3 with deionized and

distilled water. The release of 4.274 mmol of NaCl, thus, made the system $0.142N$ NaCl. The concentration of CAS **12**–M$_2$-(0.93) in the presence of 1.5 equiv of NaOH was determined to be 4 g/dL in $0.142N$ NaCl. This stock solution, after it was used for the viscosity measurements, was converted to a solution in the presence of 1.64 equiv of NaOH. Thus, to the previous stock solution (27 cm^3) of the polymer (4 g/dL) containing 1.5 equiv of NaOH was added 0.534 mmol [i.e., $(27/30)4.274 \times 0.9907(1.64-1.50)$] of NaOH (1.77 cm^3 of $0.3013N$ NaOH was used for the purpose). To keep the polymer concentration unchanged at 4 g/dL, water (1.77 g) was removed by a gentle stream of N$_2$ at 25°C. Likewise, solutions in the presence of 1.73, 1.82, 1.9, and 2 equiv of NaOH were prepared from the solutions containing 1.64, 1.73, 1.82, and 1.9 equiv of NaOH, respectively. During the viscosity measurements, the solution area exposed to air was continuously purged with N$_2$ to avoid CO$_2$ absorption that may have affected the viscosity data. The data in parentheses indicates the species distributions of PB/APE **13** in solution containing 1.64 equiv of NaOH ($x = 0.356$; $z = 0.634$; $y = 0.0093$), 1.90 equiv of NaOH ($x = 0.099$; $z = 0.892$; $y = 0.0093$), and 2 equiv of NaOH: ($x = 0$; $z = 0.991$; $y = 0.0093$).

RESULTS AND DISCUSSION

Synthesis and physical characterization of the hydrophobic monomer and terpolymers

The dendritic hydrophobic monomer **9** was prepared in excellent yield from readily available starting materials, as outlined in Scheme 2. The alkoxy group could be altered as desired with appropriate alkyl halides; this study thus paved the way to a generalized synthesis of dendritic diallyl quaternary salts. The use of **9** as a comonomer represents, to the best of our knowledge, the first example of a dendritic monomer in the synthesis of associating polymers with Butler's cyclopolymerization technique. It was a quadruple-tailed monomer containing four octyloxy pendants. The hydrophilic monomer **10** (M$_1$), hydrophobic comonomer **9** (M$_2$), and SO$_2$ underwent cyclopolymerization in the solvent DMSO with AIBN as the initiator to give the terpolymer CPE **11** in excellent yields (Scheme 3, Table I). Terpolymer **11**–M$_2$-(0.25) (entry 2, Table I), for instance, describes the polymer obtained from a feed containing 0.3 mol % hydrophobe **9** (M$_2$); the number 0.25 in the parenthesis indicates the molar percentage of hydrophobe incorporated in the polymer as determined by ^{1}H-NMR spectroscopic analysis (*vide infra*). The polymerization conditions were kept similar as rigorously as possible to obtain polymers with similar degrees of polymerization; a similar polymer chain
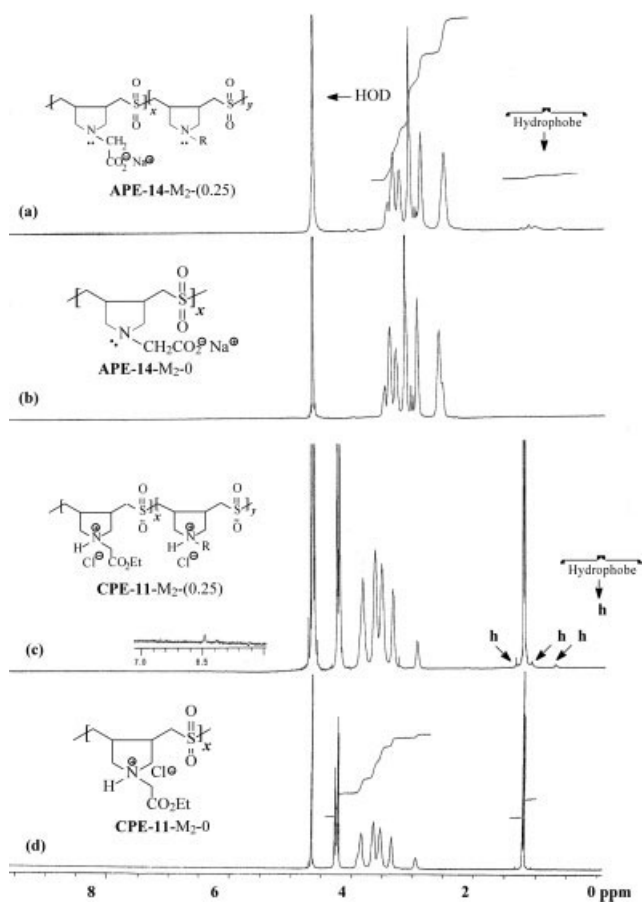
Figure 1 ^{1}H-NMR spectra of (a) APE **14**–M$_2$-(0.25), (b) APE **14**–M$_2$-(0), (c) CPE **11**–M$_2$-(0.25), and (d) CPE **14**–M$_2$-(0) in D$_2$O. HoD represents the residual H in the D$_2$O solvent.

length would allow a comparative assessment of the associative behaviors of the synthesized polymers. The hydrophobic monomer **9** was insoluble in DMSO; under stirring, it remained as dispersed particles in the continuous phase of DMSO. However, the hydrophobe was found to be soluble in the polymerization medium (i.e., DMSO/SO$_2$) in the lower concentration range, whereas at concentrations > 0.5 mol %, complete dissolution of the hydrophobe could not be achieved.

CPEs **11** were hydrolyzed in 2N HCl to produce the corresponding water-insoluble CASs **12,** which on treatment with 1 and 2 equiv of NaOH, afforded water-insoluble PB **13** ($z = 0$) and water-soluble APE **14**. CAS **12** was a pH-responsive polymer, and as such, it was converted into PB/APE **13** containing various proportions of PB and APE fractions by treatment with NaOH.

The NMR and IR spectra of the terpolymers closely resembled those of copolymer M$_2$-(0) as reported.[26] Figure 1(a–d) displays the ^{1}H-NMR spectra of APE **14**–M$_2$-(0.25), APE **14**–M$_2$-(0), CPE **11**–M$_2$-(0.25), and CPE **11**–M$_2$-(0) in D$_2$O, respectively. A comparison of the proton spectra of the polymers

CPE **11** showed that the **CH$_3$**—CH$_2$OC and the CH$_3$**CH$_2$**—OC protons, which appeared at δ values of 1.19 ppm (t) and 4.21 ppm, respectively, were absent in the spectra [Fig. 1(c,d)] of APE **14**, which thus indicated the complete removal of the ester groups by hydrolysis. The incorporation of the hydrophobic monomers was calculated with ^{1}H-NMR integration of the signals around δ0.71 (for methyl protons of the hydrophobic pendants) and 1.0–1.65 ppm [for methyl protons of the ester groups and (CH$_2$)$_6$ of the octyl pendants]. The aromatic protons of the CPE **11a** polymers appeared at δ6.46 ppm. Hydrophobe incorporations were found to be less than the feed ratio (Table I). The sulfur analyses ascertained the molar ratio of (M$_1$ + M$_2$)/SO$_2$ as 1 : 1.

The polymerization reactions under entries 4–8 in Table I gave an appreciable quantity of the water-insoluble polyhydrophobe **15**. Figure 2(a,b) displays the ^{1}H-NMR spectra of **15** and the dendritic monomer **9**. A careful analysis of the ^{1}H-NMR spectrum revealed the presence of 60 H between δ values of 0.60–1.90 ppm, whereas the signals at δ 2.00–5.30 ppm were integrated for 24 H as expected. A strong band in the Fourier transform infrared spectrum of polymer **15** at 1303 cm^{-1} was assigned to the antisymmetric vibration of the SO$_2$ unit, whereas the corresponding symmetric vibration expected to appear around 1125 cm^{-1} was presumably buried under a very strong and relatively broad absorption at 1164 cm^{-1}. A relatively weak peak at 1744 cm^{-1}, attributed to the ester functionality, indicated the incorporation of a few molar percentage of hydrophilic monomer **10**. Hydrophobe **9** was found to be
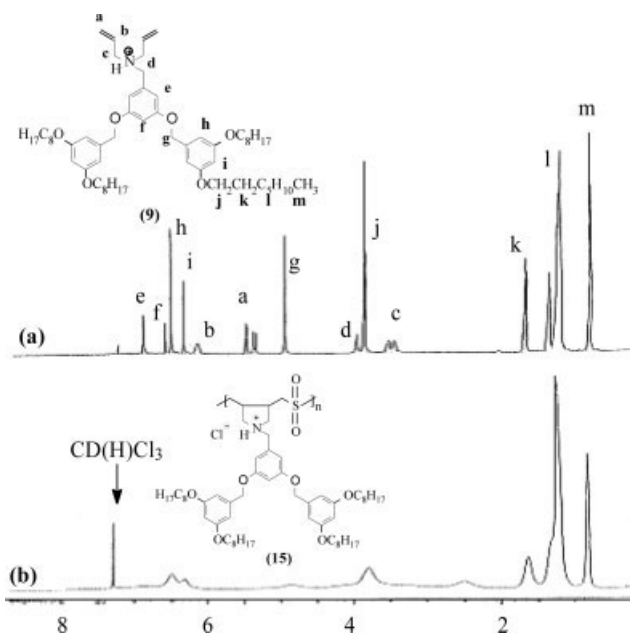

Figure 2 ^{1}H-NMR spectra of (a) hydrophobic monomer **9** and (b) hydrophobe/SO$_2$ copolymer **15** in CDCl$_3$.
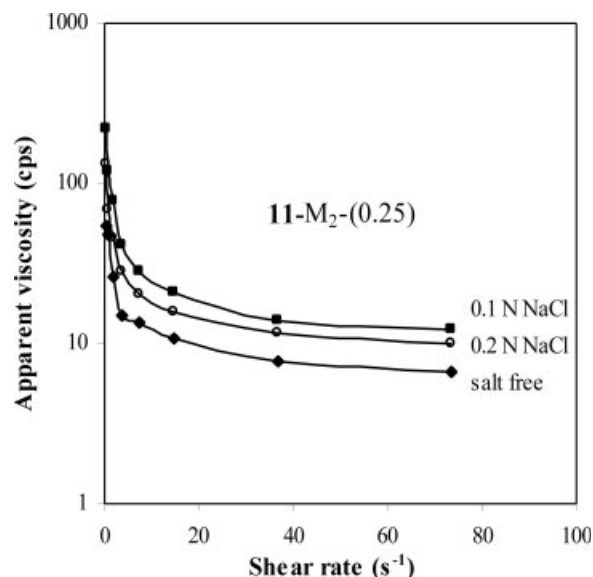
Figure 3 Variation of the viscosity of a 2-g/dL solution of 11–M$_2$-(0.25) with the shear rate at various concentrations of NaCl at 30°C.

partially soluble in the DMSO/SO$_2$ system, and as such, whereas the soluble portion of the hydrophobe took part in the terpolymerization process to yield CPE **11,** the DMSO-insoluble portion underwent copolymerization to give **15**.

Solubility, viscosity measurements, and solution properties

All CPEs **11** and their corresponding APEs **14** were soluble in salt free water and in 0.1N NaCl (Table I). The aqueous solution of the polymers reflected their amphiphilic nature by displaying a high foaming ability even at the dilute polymer concentrations.

The extrapolation of the linear part of the viscosity plots in the concentration range 0.250–0.0312 g/dL permitted us to determine the [η]'s for the polymers in 0.1N NaCl (Table I). The [η] values of CPEs **11** (all the entries except entry 8 in Table I) were found to be more or less similar, which thereby indicated the similar degree of polymerization for the polymers. This was expected because the polymerizations were carried out under similar conditions. The hydrophobe was found to be soluble in the lower concentration range (entries 2 and 3, Table I), whereas at higher concentration ranges, it was partially soluble. The temperature and amount of DMSO were varied in the hope of achieving a higher incorporation of the hydrophobe in the terpolymer. A comparison of the polymers obtained under entries 5–8 (Table I; all having 1.5 mol % hydrophobe **9** in the feed) revealed that the highest incorporation of 0.93 mol % of the hydrophobe was achieved under entry 5. Both increasing the tempera-

ture to 65°C (entries 6 and 7) and varying the amount of DMSO (entries 7 and 8) led to a lower incorporation of the hydrophobe. Polymer **11** under entry 7 has the lowest molar percentage of hydrophobe incorporated because the decreased amount of DMSO made the hydrophobe least soluble in the polymerization system and, as such, gave rise to the highest amount of polydendrimer **15**. Increasing the amount of DMSO led to CPE **11** with the lowest [η] and yield (entry 8). The [η] values of APE **14** (all entries except entry 8), like their CPE counterparts, were also found to be more or less similar, as expected. The APEs were found to have higher viscosity values than the CPEs in 0.1N NaCl, even though they both had similar degrees of polymerization and charge (albeit of opposite sign). Although the added Cl$^-$ ions could effectively neutralize the positive charges in the polymer backbone of CPE **11,** the Na$^+$ ions were less effective in neutralizing the negative charges in APE **13** because the Na$^+$ ions had a larger hydration shell[27] and, thus, were unable to approach the CO$_2^-$ moiety to a close proximity to neutralize the negative charges in the polymer backbone. As such, the APEs were expected to have a more extended polymer backbone to relieve repulsion between the negative charges.

Figures 3 and 4 display the variation in the viscosity of a 2-g/dL solution of **11**–M$_2$-(0.25) and **11**–M$_2$-(0.35) with the shear rate in salt-free water and at various concentration of NaCl. At all the shear rates, the apparent viscosity values in 0.1N NaCl were found to be higher than in salt-free water. Although the viscosity value of **11**–M$_2$-(0.25) decreased in 0.2N NaCl as compared to the viscosity in 0.1N NaCl, it

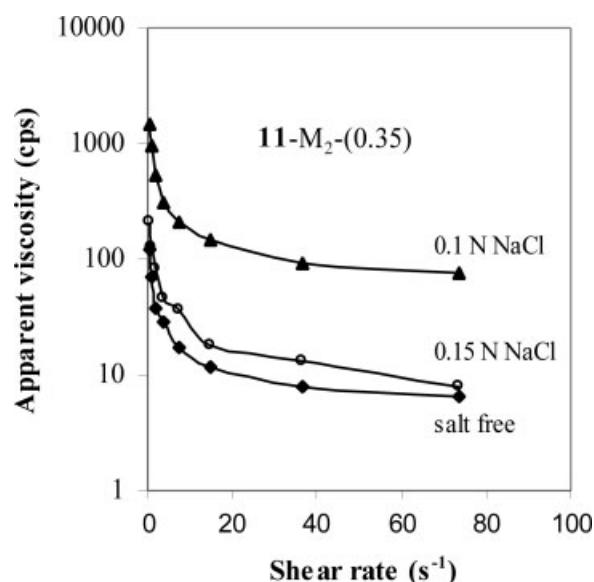**Figure 4** Variation of the viscosity of a 2-g/dL solution of **11**–M$_2$-(0.35) with the shear rate at various concentrations of NaCl at 30°C.
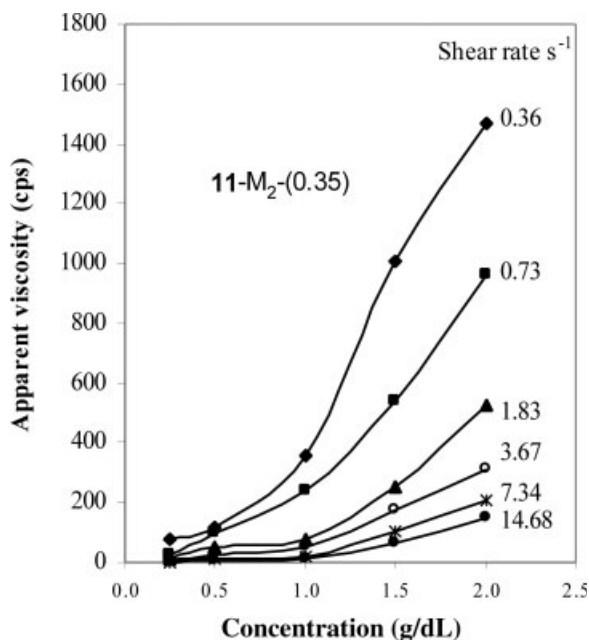
Figure 5 Apparent viscosity dependence on the concentration of a 2-g/dL solution of **11**–M$_2$-(0.35) at various shear rates in 0.1N NaCl at 30°C.
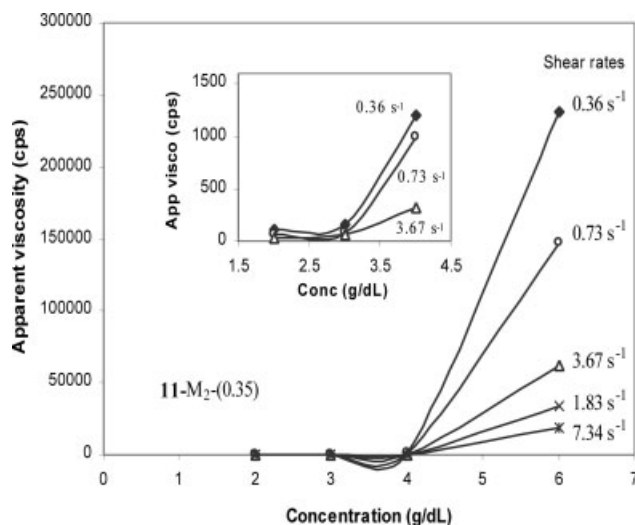

Figure 6 Variation of the viscosity with the concentration of CPE **11**–M$_2$-(0.35) at various shear rates in salt-free water at 30°C. (The inset shows the variation in the lower concentration range.)

still remained higher than that in salt-free water. The same trend was observed for the terpolymer **11**–M$_2$-(0.35), where the apparent viscosity values in salt-free water and 0.1 and 0.15N NaCl were found to be 120, 1470, and 208 cps, respectively, at a shear rate of 0.36 s^{-1}. In the presence of added salt, the increase in viscosity correlated well with the known effects of NaCl on hydrophobic association.[28] The presence of NaCl made the aqueous system more hostile to the hydrophobes, which, thus, forced them to associate intermolecularly. The increase in viscosity values implied a greater significance of hydrophobic associations than polymer compaction by the shielding of the positive charges in the polymer chains by chloride ions. The behavior at the higher salt concentrations could be attributed to the salting-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreased, and the polymer chains were unable to manifest effective intermolecular associations and tended to precipitate.

Figure 5 shows the variation of the viscosity with the concentration of **11**–M$_2$-(0.35) in 0.1N NaCl at 30°C. Hydrophobic associations, as indicated by the exponential increase in the viscosity values, began to manifest around a C_{HA}^* value of 1.5 g/dL for the polymer. Figures 6 and 7 display the variation of viscosity with the concentrations of **11**–M$_2$-(0.35) and **11**–M$_2$-(0.93), respectively, at various shear rates in salt-free water at 30°C. Hydrophobic associations began to manifest around C_{HA}^* values of 4.0 and 3 g/dL for polymers **11**–M$_2$-(0.35) and **11**–M$_2$-(0.93),

respectively. The strong interchain associations contributed significantly to the thickening.[8,23,29–31]

Figure 8 shows the variation of the viscosity with the shear rate profiles of 4-g/dL solutions of CPEs **11** in salt-free water at 30°C. At a shear rate of 0.36 s^{-1}, polymers **11**–M$_2$-(0), **11**–M$_2$-(0.35), **11**–M$_2$-(0.53), **11**–M$_2$-(0.65), and **11**–M$_2$-(0.93) had apparent viscosity values of 140, 1200, 180,000, 308,000, and 858,000 cps, respectively. This study clearly demonstrated the increase in the viscosity values with increasing incorporation of the hydrophobes; **11**–M$_2$-(0.93), having the highest amount of hydrophobe incorporated (i.e., 0.93 mol %), thus showed a tremendous
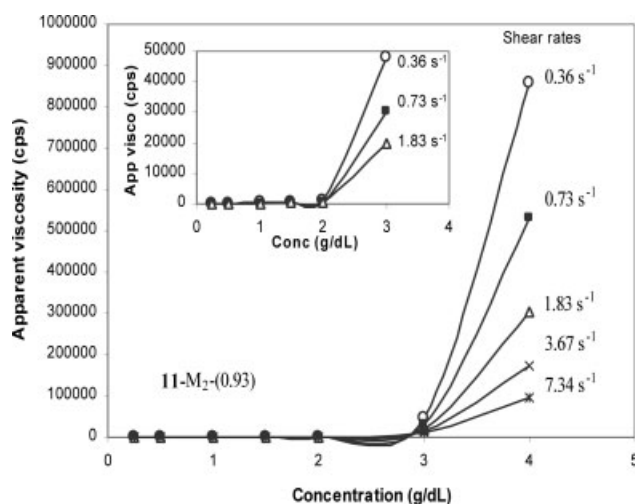

Figure 7 Variation of the viscosity with the concentration of CPE **11**–M$_2$-(0.93) at various shear rates in salt-free water at 30°C. (The inset shows the variation in the lower concentration range.)
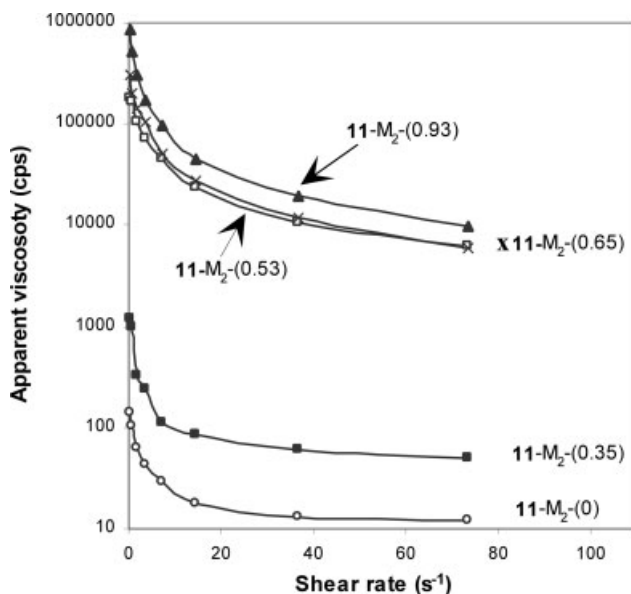
Figure 8 Variation of the viscosity with the shear rate of 4-g/dL solutions of CPE **11**–M$_2$-(0), CPE **11**–M$_2$-(0.35), CPE **11**–M$_2$-(0.53), CPE **11**–M$_2$-(0.65), and CPE **11**–M$_2$-(0.93) in salt-free water at 30°C.

increase in the viscosity values [by a factor of 715 over **11**–M$_2$-(0.35)].

Figure 9 displays the effect of temperature on the solution viscosity of a 4-g/dL solution of **11**–M$_2$-(0.53) at various shear rates in salt-free water. As evident from the figure, the viscosity increased as the temperature increased, reached a maximum at 30°C, and then decreased as the temperature was further increased. The lowering of solution viscosity with increasing temperature has been reported for hydrophobically associating water-soluble polymers,[8,31–33] presumably as a result of changes in the hydration spheres of the hydrophobic groups or in
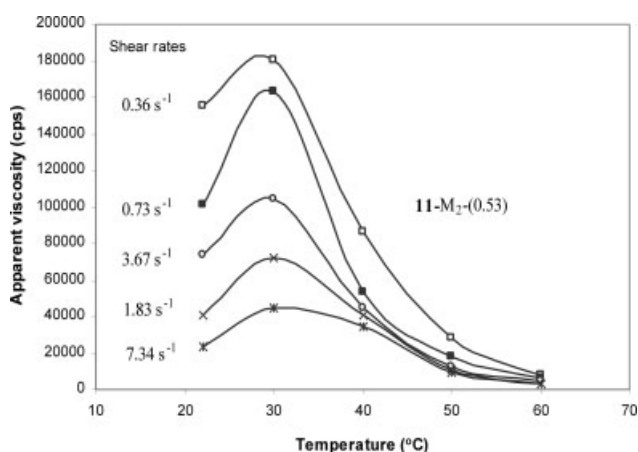
the structure of water itself. This effect could also be attributed to the weakening of the hydrophobic effect at elevated temperatures because of the increased mobility of the polymer chains, which gives rise to a loss of interchain liaisons and/or an increase in polymer solubility as the temperature increases. The viscosity increases observed upon heating to 30°C were consistent with an entropy-driven increase in hydrophobic bonding.[34,35]

The variation of the viscosity with the shear rate profile of a 4-g/dL solution of CAS **12**–M$_2$-(0.93) in the presence of various equivalents of NaOH in 0.14N NaCl is shown in Figure 10. The viscosity values increased continuously with the increase in NaOH concentration. For instance, in the case of **12**–M$_2$-(0.93), the addition of 1.50, 1.64, 1.73, 1.82, 1.90, and 2.0 equiv of NaOH led to apparent viscosity values of 1500, 37,992, 222,000, 400,000, 456,000, and 484,000 cps, respectively, at a shear rate of 0.36 s^{-1}. As a result of the internal neutralization of the charges, PBs are known to adapt collapsed coil conformations because of intrachain and interchain interactions,[27,36] and as expected, PB **13** ($z = 0$), obtained after addition of 1 equiv of NaOH, was found to be insoluble in water. It was only after the addition of 1.5 equiv of NaOH that PB/APE **13** ($x = z = 0.5$) became soluble. With the further addition of NaOH, the increasing number of CO$_2^-$ groups along the polymer chains led to a better solubility in water and a stronger thickening efficiency because of coil expansion. However, the increasing interchain electrostatic repulsions with the increase in the number of CO$_2^-$ groups did not lead to a lowering of the degree of hydrophobic association, as is evident from the figures. This was because the extended length of the pendants of the hydrophobes allowed
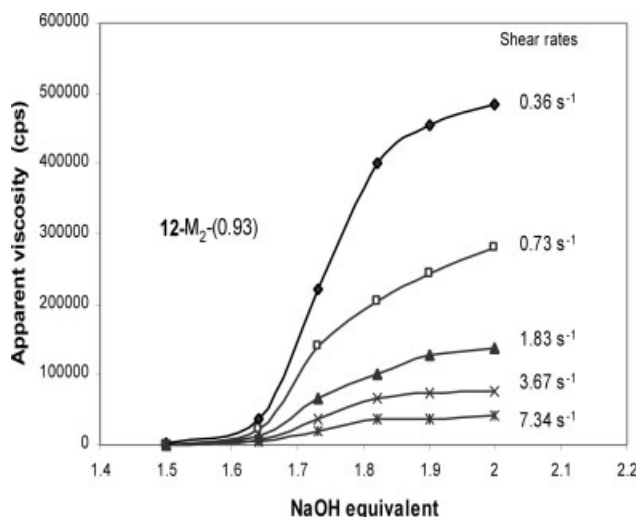

Figure 9 Variation of the viscosity of a 4-g/dL solution of **11**–M$_2$-(0.53) at various shear rates and temperatures in salt-free water at 30°C.

Figure 10 Variation of the viscosity with the shear rate of a 4-g/dL solution of CAS **12**–M$_2$-(0.93) in the presence of various equivalents of NaOH in 0.14N NaCl at 30°C.
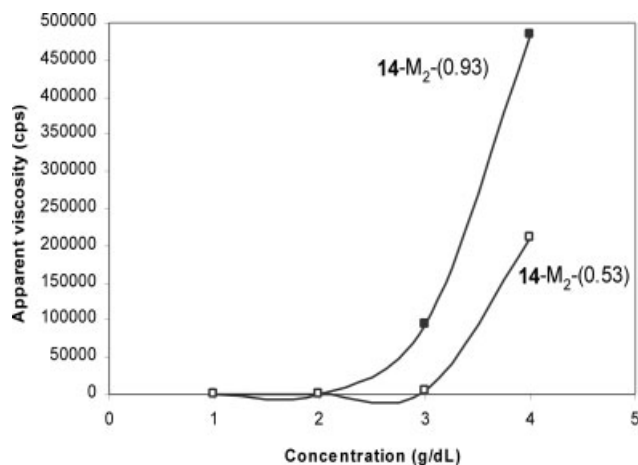
Figure 11 Variation of the viscosity with the concentrations of APE **14**–M$_2$-(0.53) and APE **14**–M$_2$-(0.93) at various shear rates in 0.14N NaCl at 30°C.

Figure 12 Variation of the viscosity with the CTAB concentration of a 2-g/dL solution of CPE **11**–M$_2$-(0.93) at different shear rates at 30°C in salt-free water.

them to mingle with each other without exposing the chains to experience the adverse effect of electrostatic repulsions.[37] Figure 11 displays the variation of viscosity with the concentrations of APE **14**–M$_2$-(0.53) and **14**–M$_2$-(0.93), respectively, at a shear rate of 0.36 s^{-1} in 0.14N NaCl at 30°C. Hydrophobic associations began to manifest around a C_{HA}* value of 2.0 g/dL for the polymer.

Polymer surfactant interactions

An interesting feature of amphiphilic polyelectrolytes with poor water solubility is that redissolution is greatly facilitated by the addition of surfactants, which indicates the existence of surfactant/copolymer interactions such that surfactant micelles provide the solublization of the hydrophobic moieties of the amphiphilic polyelectrolyte. The interactions are driven by electrostatic attraction and/or association of the hydrophobic groups on the polymers and those of the surfactant molecules. The polymer surfactant interaction was examined with viscometric measurements on terpolymer **11**–M$_2$-(0.93) (entry 5, Table I) in the presence of a cationic cetyltrimethylammonium bromide (CTAB) surfactant. Figure 12 illustrates the viscosity behavior of a 2-g/dL solution of CPE **11**–M$_2$-(0.93) in the presence of the cationic surfactant CTAB at various shear rates. On the addition of CTAB above its critical micelle concentration of 9.2 × 10^{-4} M, the solution of CPE **11**–M$_2$-(0.93) became more viscous, which indicated the existence of surfactant/terpolymer interactions. The terpolymer was sufficiently hydrophobic to overcome competitive ionic repulsion effects, which promoted the bridging micelle formation. This interaction of CPE with a surfactant of like charge (CTAB) is rather unusual, but 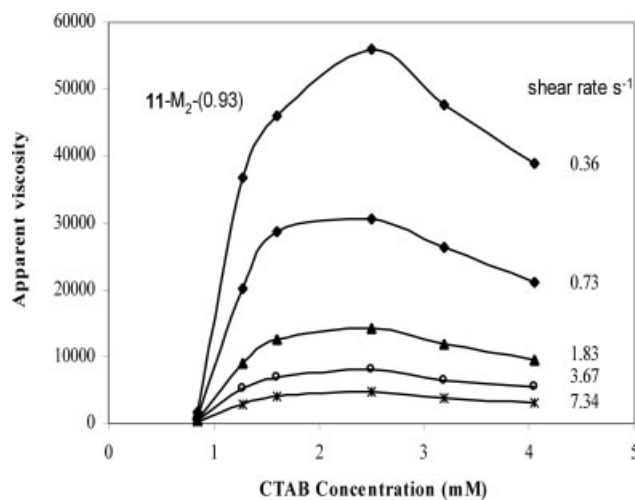it is not unique. An interaction in aqueous solutions of hydrophobically modified polyelectrolytes with surfactants of the same charges has been recently reported.[38] On further increase in the CTAB concentration, the viscosity continued to increase, which suggested gradual polymer restructuring and the formation of mixed micelle domains that contained hydrophobic groups belonging to two or more distinct polymer chains. The addition of surfactants to hydrophobically modified polymers solutions can increase the viscosity of the polymer solutions, provided comicellization between the polymer and surfactant provides bridging between the polymer chains (Fig. 13).[39] A further increase in the concentration of CTAB led to the formation of more micelles, the number of micelles per polymer-bound hydrophobe increased, and this eventfully disfavored comicellar bridging.
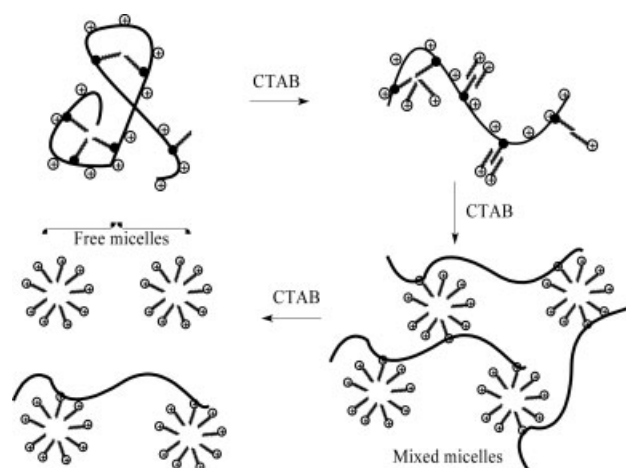

Figure 13 Effect of CTAB on the structural reformation of a CPE.

CONCLUSIONS

A new dendritic diallylammonium hydrophobic monomer (**9**) was synthesized in excellent yield. We were unable to incorporate a higher molar percentage of hydrophobe **9** in terpolymer CPE **11** because of the solubility problem of the hydrophobe in the polymerization medium. It is our continuing goal to search for a suitable reaction medium that would permit us to achieve an incorporation of 2–3 mol % of the hydrophobe. Nonetheless, the incorporation of 0.93 mol % of microblock **9** tremendously enhanced the solution viscosity of polymer **11**–M$_2$-(0.93). The manifestation of a low $C_{HA}*$ was indeed a notable improvement over the reported $C_{HA}*$ values of associating ionic cyclopolymers.[19] In the absence of a micellar process, this direct solution polymerization work has paved the way to the prevention of costly micellar processes that involve the utilization and subsequent removal of surfactants. This study involved an interesting class of interconvertible polymers—CAS **12**, PB PB/APE **13**, and APE **14**—all derived from the same CPE **11** and having identical degrees of polymerization, which thus allowed a meaningful assessment of their solution properties. The addition of small amounts of CTAB to a solution (2 g/dL) of **11**–M$_2$-(0.93) made the solution more viscous and indicated polymer–surfactant interactions. The shear thinning or thixotropy behavior associated with the reversible nature of these physical crosslinks may lead to their application in waterborne coatings, paints, cosmetics, and enhanced oil recovery. The pH-induced change in the conformation of PB/APE **13** can be manipulated judiciously in the effective use of these hydrophobically modified polymers in protein partitioning in aqueous two-phase polymer systems.[40]

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