

Amphiphilic Cyclooligomers of Diallyldimethylammonium Chloride, Diallyloctadecylammonium Chloride, and Sulfur Dioxide

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ABSTRACT: A hydrophilic monomer (diallyldimethylammonium chloride), a hydrophobic monomer (diallyloctadecylammonium chloride), and sulfur dioxide are cyclooligomerized in dimethylsulfoxide using azobisisobutyronitrile as the initiator to afford water-soluble cationic polyelectrolytes having a five-membered cyclic structure on the polymeric backbone. The molecular weights of the polymers containing varying amounts of the hydrophobic monomer (0–7.5 mol %) are determined by light-scattering experiments. The solution properties of the series of cationic polyelectrolytes are investigated by viscometric techniques. A polymer concentration (C_{HA}^*) of <1 g/dL is required for the manifestation of hydrophobic associations in these terpoly-

mers containing C_{18} hydrophobic pendants. This is a notable improvement over the C_{HA}^* values (ca. 15–17 g/dL) for the associating cyclooligomers having a pendant length of C10 to C14. The polymer solutions exhibit a sharp increase in viscosity with increasing polymer concentrations in salt-free as well as salt-added solutions. The presence of sodium chloride is shown to enhance the hydrophobic association tremendously. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1298–1306, 2005

Key words: association; cyclooligomerization; copolymerization; ionic polymers; diallylammonium monomers

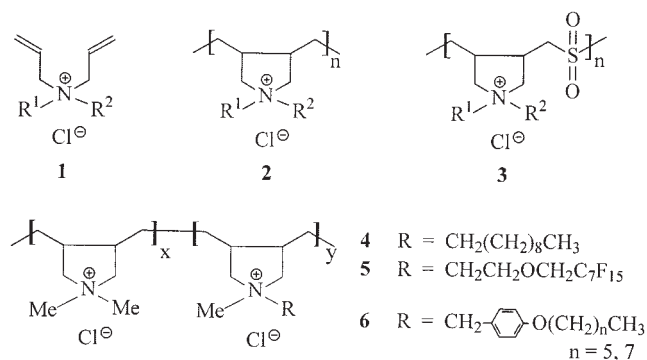
INTRODUCTION

The copolymerization of a water-soluble monomer with a few mole percents of a hydrophobic comonomer in a homogeneous solution in mixed solvents gives polymers with random distributions of the hydrophobes as isolated units. However, the micellar systems¹ involving a hydrophilic monomer (~3 wt %) in a continuous water phase and a hydrophobic monomer inside the micelles ensure a random distribution of the hydrophobes as small blocks in the hydrophilic polymer chains.^{2–6} The concentration-dependent intermolecular associations in the microblocky copolymers lead to superior viscosity behavior in comparison to the random copolymers, which largely exhibit intramolecular associative behavior.^{7–11} Above a certain polymer concentration (concentration required for hydrophobic associations, C_{HA}^*) in aqueous solution, a reversible formation of 3-dimensional physical crosslinks of polymer chains by intermolecular associations of the hydrophobic groups leads to a tremendous enhancement of the viscosity. The shear thinning or thixotropy behavior associated with the reversible

nature of these physical crosslinks led to their applications in water-borne coatings, paints, cosmetics, and enhanced oil recovery.^{12–16} In contrast to polymers containing neutral hydrophilic acrylamide and a neutral hydrophobic derivative of acrylamide, the presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a variety of behaviors.¹⁷ Ion-containing polyacrylamides usually require a higher hydrophobe content or the presence of an added salt in order to manifest effective interchain associations.^{18–20}

Butler's cyclooligomerization technique²¹ has been utilized for the conversion of diallylammonium salts **1** to an array of water-soluble cationic polyelectrolytes **2**^{22–26} and sulfur dioxide copolymers **3**^{27–29} of tremendous scientific and technological interest (Scheme 1). There are a few reports^{30–32} that describe the synthesis of associating ionic copolymers **4–6** by Butler's cyclooligomerization technique. A micellar process is not available in the cyclooligomerization technique, which uses monomer concentrations of 50–65 wt % to obtain polymers with high conversion and high molecular weight and low residual double bonds.³³ Cyclooligomerization of hydrophilic and hydrophobic diallyl monomers in such high concentrations has been reported to yield random rather than microblocky copolymers.³² At the same concentration, the viscosity of copolymers **4** and **5** were found to be significantly

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Scheme 1 Butler's cyclopolymerization technique²¹ for the conversion of diallylammonium salts **1** to an array of water-soluble cationic polyelectrolytes **2** and sulfur dioxide copolymers **3**.

higher compared to that of their homopolymers ($y = 0$). However, copolymers **4** and **5** with a hydrophobe content of 8.22 mol % were found to have an undesirable fairly high C_{HA}^* (15–17 wt %) compared to the hydrophobically associating nonionic copolymers of acrylamide ($C_{HA}^* < 1$ wt %).

Electrostatic repulsions between the polymer chains with similar charges may not permit the macromolecules to approach close enough to manifest interchain association by the hydrophobic pendants, especially when the pendants are not long enough. Note that the lengths of the hydrophobic pendants in copolymers **4**, **5**, and **6** are equivalent to 10, 11, and 14 CC bonds, respectively. (The length of the benzene ring is considered as equivalent to 4 CC bonds.) It is expected that an increase in the pendant length would lead to an efficient and increased association from a distance far enough that would minimize interchain repulsion between the like charges. In our continuing study of ionic polymers, we report the synthesis and solution properties of amphiphilic terpolymers **9** derived from cyclo-terpolymerization of hydrophilic monomer (M_1) **7**/hydrophobic comonomer (M_2) **8**/sulfur dioxide (Scheme 2). This work provides an opportunity to study the effect of the hydrophobic octadecyl pendant on the C_{HA}^* as well as on the overall viscosity behavior of this new class of associating terpolymers.

EXPERIMENTAL

Physical methods

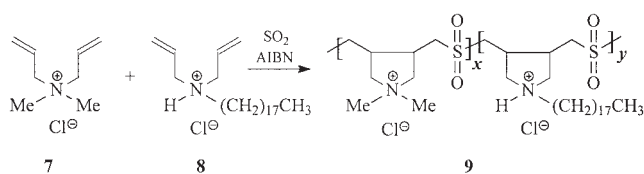
The melting points were recorded in a calibrated Electrothermal-IA9100 digital melting point apparatus using heating rates of 1°C/min in the vicinity of the melting points. Elemental analysis was carried out on a EuroVector elemental analyzer (model EA3000). IR spectra were recorded on a Perkin-Elmer 16F PC FTIR spectrometer. The ¹H- and ¹³C-NMR spectra of the polymers were measured in D₂O using dioxane as

internal standard on a Jeol LA 500-MHz spectrometer. Viscosity measurements were performed with an Ubbelohde viscometer (viscometer constant = 0.005718 cSt/s at all temperatures). A digital Brookfield rotational viscometer with UL adaptor accessories or SC4-18 spindle accessories was used to measure the apparent viscosities at various shear rates and temperatures.

The molecular weights of the samples were determined by light-scattering experiments at 21°C. Solutions of cationic polyelectrolyte **9** containing no hydrophobe ($y = 0$, polymer concentration = 0.03–0.1 g/dL) were prepared in 0.5M 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 with pore sizes of 0.2 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 experiments were performed using a DAWN EOS light-scattering instrument (Wyatt Technology Corporation). The system light source was a linearly polarized gallium arsenide laser. The laser was positioned so that the incident beam was vertically polarized. An RFM-340 refractometer (Bellingham & Stanley) was used to measure the differential refractive indices (dn/dc) of different polyelectrolyte solutions. The molecular weight determination of the hydrophobically modified polymers was complicated because of hydrophobic associations. As a result, we expect that the light-scattering measurements lead to an apparent weight, rather than a true molecular weight.

Materials

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



Scheme 2 The synthesis and solution properties of amphiphilic terpolymers **9** derived from cyclo-terpolymerization of hydrophilic monomer (M_1) **7**/hydrophobic comonomer (M_2) **8**/sulfur dioxide.

TABLE I
Terpolymerization of Monomers 7(M_1)/8(M_2)/SO₂

Entry no.	Sample	M_1 (mmol)	M_2 (mmol)	Feed ^a M_1/M_2	Polymer ^a M_1/M_2	Yield (%)	Intrinsic viscosity ^b (dL g ⁻¹)
1	M_2 -0	25.0	0	100:0	100:0	88.9	0.6625
2	M_2 -1.5	24.625	0.375	98.5:1.5	98.8:1.2	86.3	0.7062
3	M_2 -3.5	24.125	0.875	96.5:3.5	96.3:3.7	89.6	0.9735
4	M_2 -5.0	23.75	1.25	95:5	95.3:4.7	89.5	0.3754 ^c
5	M_2 -7.5	23.125	1.875	92.5:7.5	92.7:7.3	90.2	0.1879 ^c

The polymerization reactions were carried out in DMSO (6.5 g) containing 25 mmol each of ($M_1 + M_2$) and SO₂ in the presence of AIBN (125 mg) at 58°C for 24 h.

^a Mol% in the feed and polymer as determined by ¹H-NMR.

^b Obtained by extrapolation of the linear parts of the curves usually in the 0.25–0.031% range of polymer solution in 0.1N NaCl at 30°C as measured with an Ubbelohde viscometer ($K = 0.005718$).

^c Cloudy solution throughout the concentration range.

ylsulfoxide was dried over calcium hydride overnight and then distilled under reduced pressure at a boiling point of 64–65°C (4 mmHg). All glassware was cleaned using deionized water. Diallyldimethylammonium chloride (7) was prepared as described by Negi et al.³⁴ by reacting dimethyl allylamine with allyl chloride. Diallyloctadecylammonium chloride (8) was prepared by neutralizing diallyloctadecylamine with dry HCl using procedures described in the literature.^{30,34,35}

General procedure for terpolymerization of 7/8/SO₂

All polymerizations were carried out using the conditions described in Table I. In a typical experiment, SO₂ was absorbed in a solution of monomers 7/8 (i.e., M_1/M_2) in dimethylsulfoxide in a 25-cm³ round-bottomed flask. The required amount of initiator (AIBN, listed in Table I) was then added under N₂ and the closed flask was stirred using a magnetic stir bar at 58°C for 24 h. The movement of the stir bar was stopped after 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 filtered and dried under a vacuum at 50°C to a constant weight. All polymers, except M_2 -0, were

found to be soluble in methanol. The hygroscopic white terpolymers were stored in a desiccator. The elemental analyses (Table II) ascertained the mole ratio of ($M_1 + M_2$)/ M_3 (SO₂) as 1:1. The IR spectra, ¹³C-NMR spectra, and elemental analyses of the terpolymers closely resembled those of copolymer M_2 -0 as reported by two groups.^{28,36} The ¹H-NMR spectra for M_2 -0 and M_2 -3.5 are shown in Figure 1. The onset of thermal decomposition of the polymers (closed capillary) was found to be in the range of 235–250°C (decomposed, turned brown, and charred at 280°C).

RESULTS AND DISCUSSION

Synthesis of terpolymers and physical characterization

Monomers 7(M_1)/8(M_2)/SO₂ were cycloterpolymerized using AIBN as the initiator to give cationic poly-electrolyte 9 in excellent yields (Scheme 2). The results of the polymerization, carried out under similar conditions, and the intrinsic viscosities of the resultant polymers in dilute solutions are given in Table I. Entry 1 in Table I describes copolymer M_2 -0, indicating the absence of hydrophobic monomer 8 (M_2). Entries 2–5 describe the incorporation of octadecyl monomer 8 in the range of 1.5–7.5 mol %. Terpolymer M_2 -5 (entry 4), for instance, indicates the incorporation of 5 mol % hydrophobic octadecyl monomer 8.

TABLE II
Elemental analyses of 9.1H₂O (C₈H₁₈ClNO₃S)_x(C₂₄H₅₀ClNO₃S)_{1-x}

Polymers	Carbon ^a	Hydrogen ^a	Nitrogen ^a	Sulfur ^a
M_2 -0	38.93 (39.42)	7.31 (7.44)	6.02 (5.75)	12.99 (13.15)
M_2 -1.5	39.20 (39.75)	7.39 (7.49)	5.94 (5.71)	12.68 (13.06)
M_2 -3.5	39.93 (40.20)	7.66 (7.56)	5.86 (5.65)	12.98 (12.93)
M_2 -5.0	40.24 (40.53)	7.69 (7.61)	5.79 (5.61)	12.41 (12.84)
M_2 -7.5	41.31 (41.08)	7.80 (7.69)	5.81 (5.54)	12.37 (12.68)

^a Found (calculated) values.

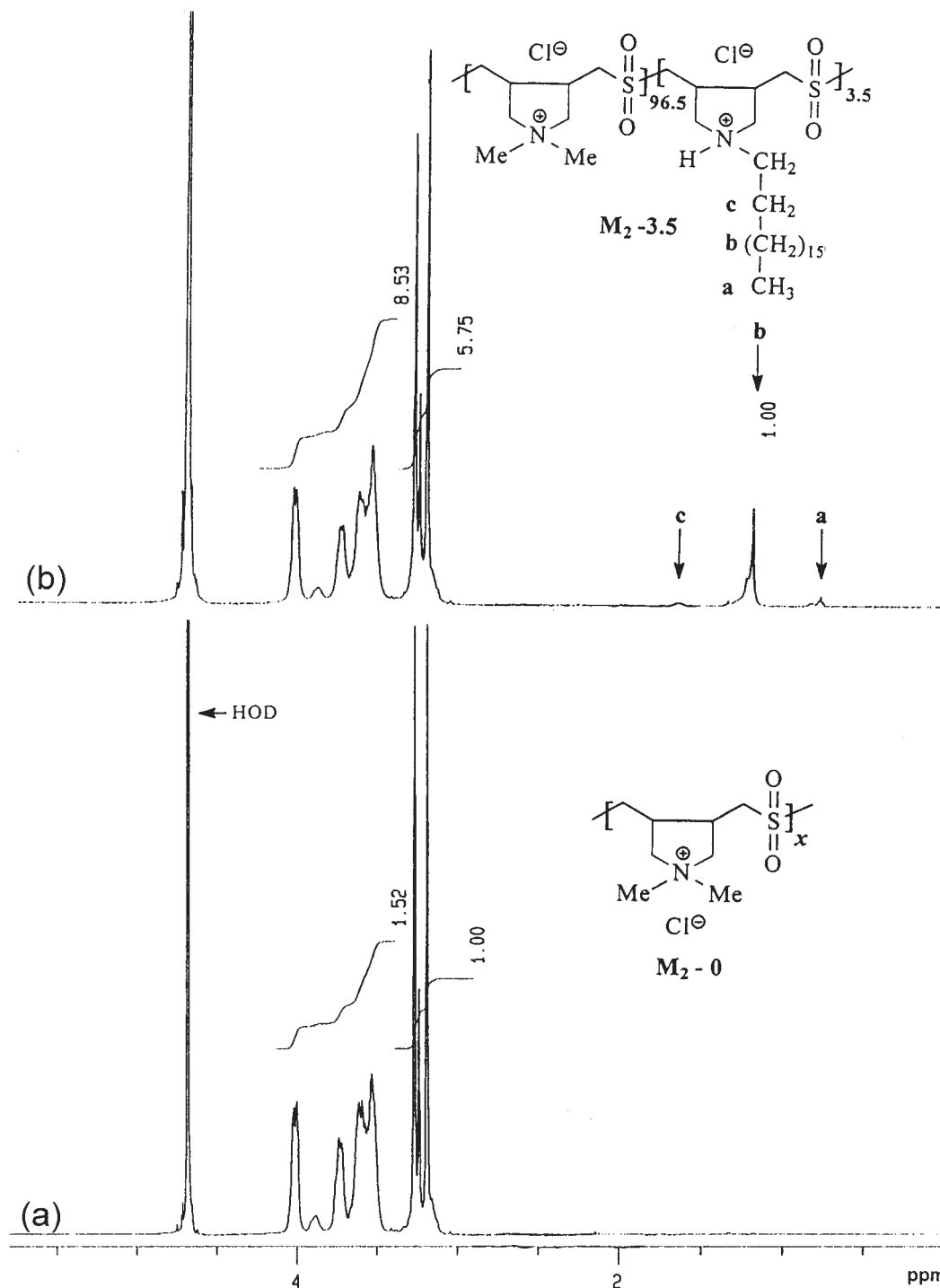


Figure 1 ¹H-NMR spectra of (a) M₂-0 and (b) M₂-3.5 in D₂O.

The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of copolymer M₂-0 as reported previously.^{28,36} Figure 1(a,b) displays the ¹H-NMR spectra of M₂-0 and M₂-3.5. The incorporation of the hydrophobic monomers was calculated using ¹H-NMR integration of the signals around δ 0.72 (for methyl protons of the hydrophobic pendants) and 1.08–1.20 ppm [for (CH₂)₁₅ of octadecyl pendants].

Hydrophobe incorporations were found to match closely with the feed ratio. This is expected because the polymers are obtained at high conversions. The sulfur analyses (Table II) ascertained the mole ratio of (M₁ + M₂) and SO₂ as 1:1.

The weight-average molecular weight (M_w) and root mean square radius (r_g) of the polymers are given in Table III. The polymers of higher hydrophobe con-

TABLE III
Light Scattering Measurements for Cationic Polyelectrolytes 9

Entry no.	Sample	$M_w \times 10^{-5}$ (g mol ⁻¹)	r_g (nm)	A_2 (mol mL g ⁻²)	Solvent
1	M_2-0	1.06	23.9	1.77×10^{-3}	0.5N NaCl
2	$M_2-1.5$	1.01	27.3	1.19×10^{-2}	Methanol
3	$M_2-3.5$	1.32	34.0	1.16×10^{-2}	Methanol
4	$M_2-5.0$	1.23	30.1	1.36×10^{-2}	Methanol
5	$M_2-7.5$	1.33	35.0	2.13×10^{-2}	Methanol

r_g , root mean square radius.

tents (e.g., $M_2-3.5$, -5 , -7.5) were insoluble in 0.5N NaCl but soluble in methanol; as such, their molecular weights were determined in this solvent. The copolymers, prepared under similar copolymerization conditions (initiator and monomer concentrations, reaction conversions, temperature, duration, etc.), are expected to have similar molecular weights. The M_w values for the polymers vary from $(1.06 \text{ to } 1.33) \times 10^5$ g/mol; these similar molecular weights allow meaningful assessments of the effects of hydrophobic association on the solution behavior. Note that polymers $M_2-3.5$, M_2-5 , and $M_2-7.5$ have somewhat higher M_w and r_g values than M_2-0 and $M_2-1.5$, and this could be attributed to the inability of the solvent methanol to disrupt hydrophobic associations completely.

Solubility and viscosity measurements

All of the synthesized polymers were found to be soluble in salt-free water. Whereas hydrophobe-free copolymer M_2-0 was insoluble in methanol, the terpolymers readily dissolved in methanol. The polymers were found to have different degrees of salt tolerance. Terpolymer $M_2-7.5$ was insoluble in 0.03N

NaCl, whereas M_2-5 remained soluble in 0.08N NaCl but cloudy in 0.1N NaCl. The presence of a lesser amount of hydrophobe makes the polymer more salt tolerant. Thus, $M_2-3.5$ remained soluble in 0.15N NaCl but cloudy in 0.2N NaCl, but terpolymer $M_2-1.5$ and copolymer M_2-0 gave clear solutions in 1N NaCl. (Concentrations $>1N$ were not tested.)

The viscosity of the solutions having a 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 vs. C) in the concentration range of 0.25–0.031 g/dL in 0.1N NaCl permitted us to determine the intrinsic viscosity $[\eta]$ values of the polymers (Table I). However, M_2-5 and $M_2-7.5$ polymers gave cloudy solutions in 0.1N NaCl and thus resulted in low values for the intrinsic viscosities.

Figures 2 and 3 display the variation of the viscosity with the concentration of M_2-5 and $M_2-7.5$, respectively, at various shear rates in salt-free water at 30°C. The hydrophobic associations began to manifest at around 1 g/dL C_{HA}^* of the polymers; at 2 g/dL the polymer solution looked like a gel. The associative

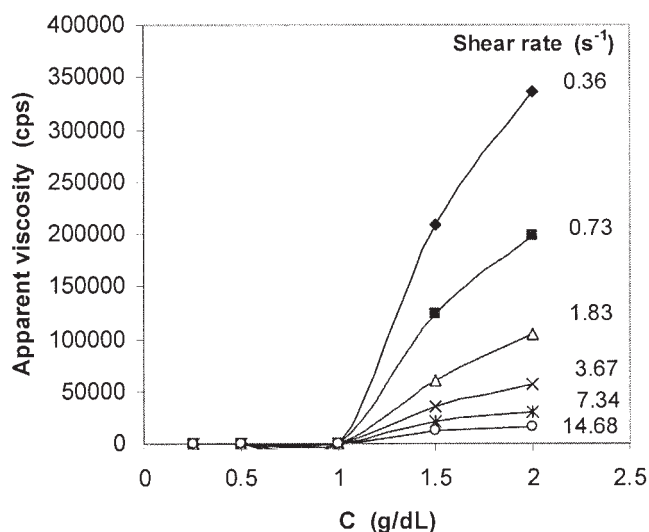


Figure 2 The variation of the viscosity with the concentration of M_2-5 at various shear rates in salt-free water at 30°C.

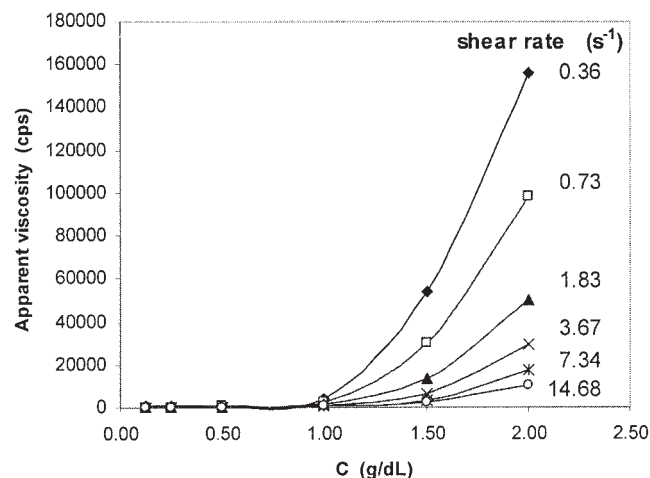


Figure 3 The variation of the viscosity with the concentration of $M_2-7.5$ at various shear rates in salt-free water at 30°C.

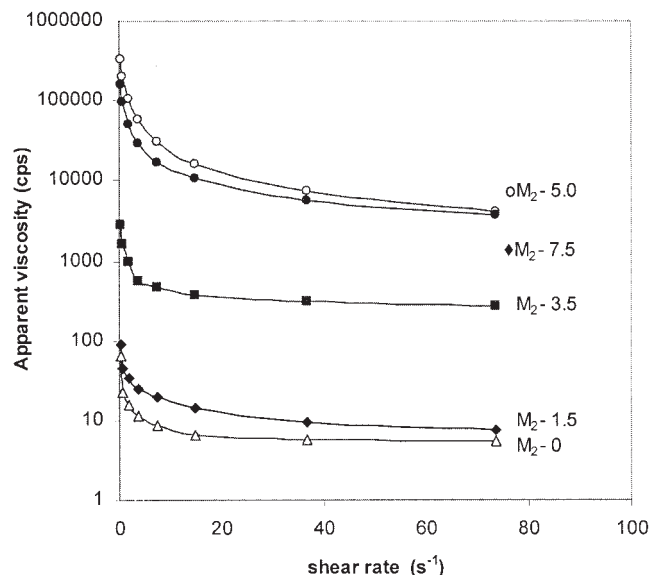


Figure 4 The variation of the viscosity of 2% solutions of M_2 -0, -1.5, -3.5, -5, and -7.5 at various shear rates in salt-free water at 30°C.

behavior of the polymers is more pronounced in the lower shear rate range, as expected, because higher shear rates lead to disruptions of hydrophobic associations. A rise in the polymer concentration from 1 to 1.5 g/dL results in an ~ 1000 -fold increase in sample viscosity of M_2 -5 at a shear rate of 1.83 s^{-1} , whereas the corresponding increase in M_2 -7.5 is 10-fold only. Interchain bridging (open associations) is thus found to be more effective for M_2 -5, whereas a mixture of inter- and intrachain associations makes the viscosity increment less dramatic in M_2 -7.5. Polymers with higher hydrophobe content are known to demonstrate higher degrees of intramolecular association.³²

Figure 4 displays the variation of the viscosity of 2 g/dL solutions of M_2 -0, -1.5, -3.5, -5, and -7.5 at various shear rates in salt-free water at 30°C. The semilog plots reveal the increase in viscosity values with the increase in the amount of hydrophobe incorporated in the polymers, except in the case of M_2 -7.5, which is found to be less viscous than M_2 -5. The data in the Figure 4 reveal the ratio of viscosity of M_2 -0, -1.5, -3.5, -5, and 7.5 at a shear rate of 1.83 s^{-1} as 1:2.2:6:2:6710, respectively. The M_2 -5 polymer is thus found to have higher viscosity than its M_2 -0 counterpart by a factor of 6710; the tremendous increase in the viscosity value must be attributed to the intermolecular hydrophobic associations between the polymer chains. A further increase in hydrophobe concentration to 7.5 mol % resulted in a decrease in the viscosity. This is consistent with studies indicating that random copolymers with higher proportions of hydrophobes form mainly intramolecular hydrophobic associations.³² Both M_2 -5 and M_2 -7.5 are expected to form intramo-

lecular as well as intermolecular hydrophobic associations; however, the contribution of each type of association depends on the concentration of the polymer in solution and the amount of hydrophobes. Whereas intramolecular associations are preferred in dilute solutions in which internal micellizations lead to decreased hydrodynamic volume and viscosity, the intermolecular associations are manifested in solutions having polymer concentrations greater than C_{HA}^* . The viscosity value increases continually from M_2 -0, reaches the maximum at M_2 -5, and then declines at M_2 -7.5 where the intramolecular association starts to assert its significance.

The variation of the viscosity of a 2% solution of M_2 -1.5 with the shear rates at various concentrations of NaCl at 30°C is displayed in Figure 5. The positive charges in the polymer chains are shielded by chloride ions. The decreased repulsion between the charges in the polymer chains leads to compaction of the polymer coil; as a result, the viscosity is expected to decrease with increasing concentration of added NaCl. By contrast, the presence of NaCl makes the aqueous system more hostile to the hydrophobes, thus forcing them to associate intermolecularly. In the case of M_2 -1.5, the decrease of the viscosity values with increasing concentration of NaCl implies the greater significance of polymer compaction by shielding than the hydrophobic associations in an environment increasingly hostile to the hydrophobes. As revealed by the plots in Figure 5, the effect of added salt is not so significant because of the opposing effects of shielding and hydrophobic associations on the viscosity. The ineffective associations of hydrophobic groups in this case could be discussed in terms of critical micelle

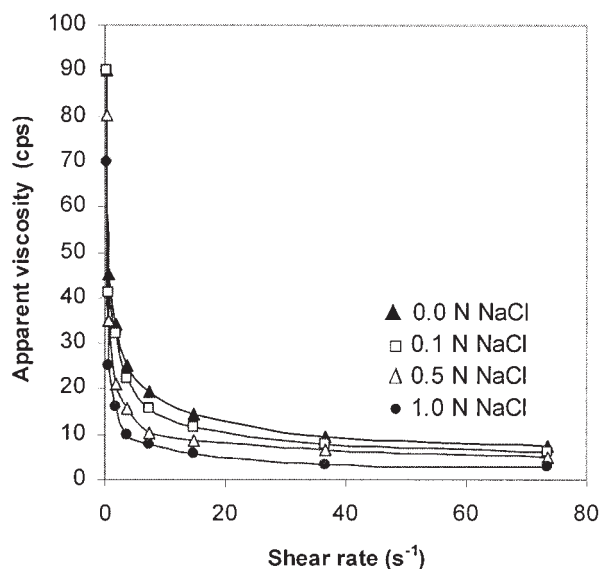


Figure 5 The variation of the viscosity of a 2% solution of M_2 -1.5 with the shear rates at various concentrations of NaCl at 30°C.

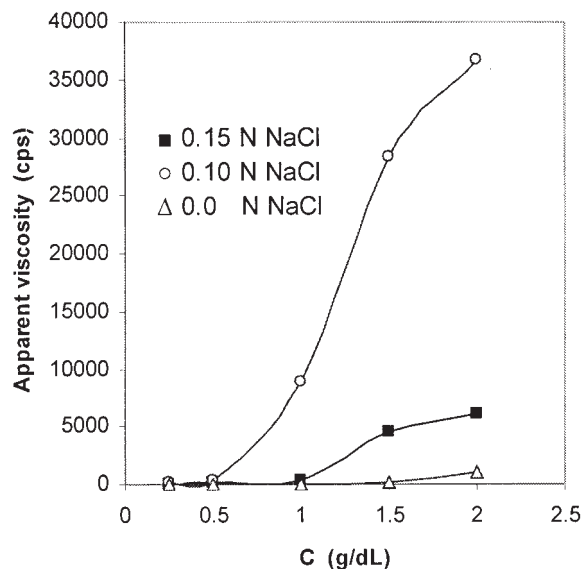


Figure 6 The variation of the viscosity with the concentration of $M_2-3.5$ at a shear rate of 1.83 s^{-1} in various NaCl solutions at 30°C .

concentration similar to that for small-molecule surfactants. At low hydrophobe incorporation (1.5 mol %) and polymer concentration (2 g/dL), an insufficient number of hydrophobic groups are present on any individual polymer chain to form a stable ensemble.

The effect of added NaCl on the viscosity of $M_2-3.5$ was found to be quite dramatic as displayed in Figure 6, which shows the viscosity versus concentration profiles for $M_2-3.5$ at a shear rate of 1.83 s^{-1} in various NaCl solutions at 30°C . In the presence of added salt, the increase in viscosity correlates well with the known effects of NaCl on hydrophobic association.³⁷ The association concentrations C_{HA}^* in salt-free and 0.1 and 0.15N NaCl solutions were found to be around 1.5, 0.5, and 1.0 g/dL, respectively. The viscosity at a polymer concentration of 1.5 g/dL is about 175 times larger in 0.1N NaCl compared to the value obtained in salt-free water. A further increase in the NaCl concentration to 0.15N leads to a decrease in viscosity values, which nevertheless remained higher than that in salt-free water. This behavior at higher salt concentration could be caused by the salting-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreases, and the polymer chains are unable to manifest effective intermolecular associations and tend to precipitate.

Figure 7 shows the viscosity versus shear rate profiles for $M_2-3.5$ at various concentrations in 0.1N NaCl at 30°C . The viscosity is sharply decreased at higher shear rates, which is a typical shear thinning behavior. However, at the low shear rates, the hydrophobically associating polymers exhibited a sharp increase in viscosity with increasing polymer concentration. This observation is similar to that frequently observed for

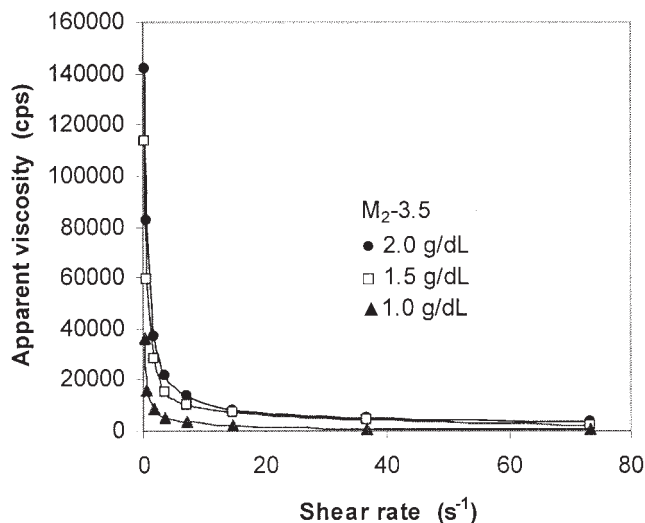


Figure 7 The variation of the viscosity with the shear rates at various concentrations of $M_2-3.5$ in 0.1N NaCl at 30°C .

hydrophobically modified associative polymers. 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.^{3,8,18,38-40}

The effect of added NaCl is again demonstrated in Figure 8, which shows the variation of the viscosity with the NaCl concentration of a 2 g/dL solution of M_2-5 at various shear rates at 30°C . The viscosity reaches the maximum at a salt concentration of 0.03N. The viscosity remains similar in salt-free and 0.05N NaCl solutions, whereas it decreases in 0.08N solutions.

Figure 9 displays the effect of temperature on the solution viscosity of a 2 g/dL solution of $M_2-3.5$ in

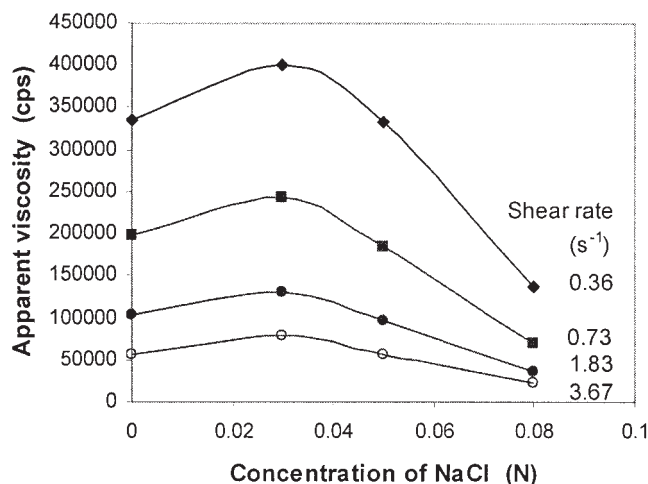


Figure 8 The variation of the viscosity with the NaCl concentration of a 2% solution of M_2-5 at various shear rates at 30°C .

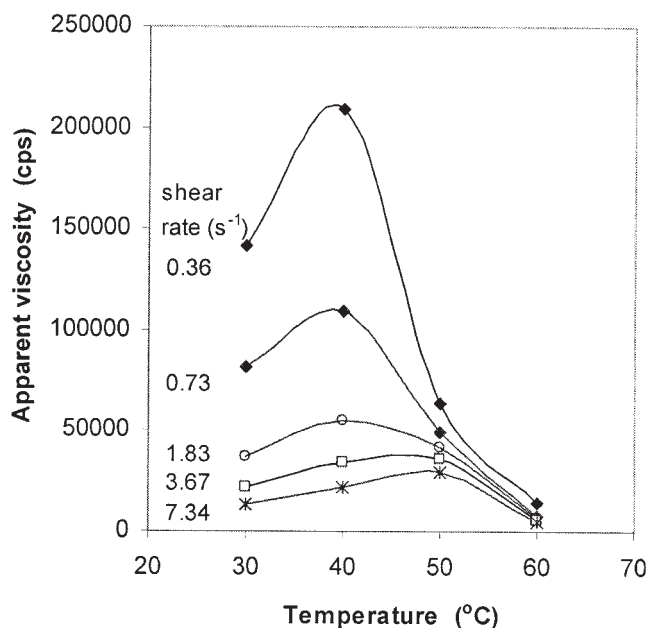


Figure 9 The variation of the viscosity of a 2% solution of $M_2-3.5$ at various shear rates and temperatures in 0.1N NaCl.

0.1N NaCl. As is evident from the figure, the viscosity reaches a maximum at 40°C at the lower shear rates ($0.36-1.83 \text{ s}^{-1}$) that are employed. At higher shear rates the viscosity reaches the maximum at 50°C and then decreases as the temperature is further increased. The increase in viscosity observed upon heating is consistent with an entropy driven increase in hydrophobic bonding.^{41,42} At higher temperatures the viscosity decreases, presumably as a result of changes in the hydration spheres of the hydrophobic groups or in the structure of water itself. The lowering of the solution viscosity with increasing temperature was reported for hydrophobically associating water-soluble polymers.^{8,40,43,44} This effect could 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 loss of interchain liaisons and/or an increase in polymer solubility as the temperature increases.

CONCLUSIONS

Hydrophobe incorporation considerably enhanced the viscosity values in the terpolymers. A typical polyelectrolyte is an extended chain with the ionic atmosphere projecting out radially.¹⁸ In earlier works³⁰⁻³² the electrostatic repulsive forces between the polymer chains did not permit them to move to a safer distance required for the pendants of 10, 11, and 14 CC bonds in copolymers 4-6 to manifest interchain bridging (associations) in the semidilute regime. The shorter pendant lengths may be the reason for the lower degree of

association and very high C_{HA}^* values of 15-17 g/dL for cyclopolymers 4 and 5.³¹ Such very high concentrations of polymers demand the presence of equivalent amounts of chloride counterions that can effectively shield the positive charges on the chains, thereby allowing them to approach close enough for interchain bridging. In contrast, the octadecyl pendants ($C_{18}H_{37}$) in terpolymers 9 can associate intermolecularly (at a polymer concentration of $\sim 1 \text{ g/dL}$) because the extended length of the pendants allows them to mingle with each other without exposing the chains to the adverse effects of electrostatic repulsions. Increasing the pendant length to C_{18} has thus drastically decreased the value of C_{HA}^* . The low C_{HA}^* ($\sim 1 \text{ g/dL}$) observed for the C_{18} polymer series is indeed a notable improvement over the C_{HA}^* values for the reported associating cyclopolymers.³¹

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