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The Effects of Zwitterionic and Anionic Charge Densities in Polymer Chains on the Viscosity Behavior of a pH-Responsive Hydrophobically Modified Ionic Polymer

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ABSTRACT: Sulfur dioxide, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride, and the hydrophobic monomer *N,N*-diallyl-*N*-octadecylammonium chloride were cyclocopolymerized in dimethyl sulfoxide using azobisisobutyronitrile (AIBN) as the initiator to afford water-soluble cationic polyelectrolytes (CPE) having a five-membered cyclic structure on the polymeric backbone. The CPE on acidic hydrolysis of the pendent ester groups gave the corresponding cationic acid salts (CAS), which, on treatment with sodium hydroxide, were converted to polybetaines (PB) and anionic polyelectrolytes (APE), as well as polymers PB/APE containing various proportions of zwitterionic (PB) and anionic fractions (APE) in the polymer chain. The solution properties of the CPE, APE, and PB/APE systems containing varying amounts of the hydrophobic monomers in the range 0–4 mol % were investigated by viscometric techniques. Treating the pH-responsive CAS polymers **4** with different equivalents of NaOH varied the zwitterionic and anionic charge densities in the polymer chain. It was found that the PB/APE polymer with a ratio of 33 : 67 for the zwitterionic and anionic fractions in the polymer chain, respectively, gave the highest viscosity value. The polymers showed that concentration (C^*_{HA}) of around 1 g/dL was required for the manifestation of significant hydrophobic associations. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1404–1411, 2005

**Key words:** associating ionic polymers; cyclopolymerization; hydrophobic association

INTRODUCTION

The cyclopolymerization of N,*N*-diallyl quaternary ammonium salts[1–3] as well as their cocyclopolymers with sulfur dioxide[4,5] led to the synthesis of an array of water-soluble cationic polyelectrolytes of tremendous scientific and technological interest.[6,7] The development in the cyclopolymerization process has in recent years entered a new stage that deals with synthesis of pH-responsive ionic polymers. The uses of structurally modified monomers have provided entries into the zwitterionic polymers[8–13] via cyclopolymerization reactions. Quaternary ammonium salts-derived cyclopolymers[8–13] with an anionic pendant show pH-responsive solution behavior due to the incorporation of the pH-triggerable CO_2^- functionality. Amine salts (e.g., **1**, Scheme 1) containing an *N*-H moiety and having a carboxy group in the pendant have been cyclopolymerized to polybetaines (PB) (e.g., **5** via **3**, x = 0) that show pH-responsive solution behavior in a wider spectrum of the pH scale due to the incorporation of two pH-triggerable functionalities (CO_2^- and the *N*-H).[14–16] One of the most gratifying aspects of the anionic polyelectrolyte (APE) **7** (y = 0) is its almost zero solubility[14] in water below pH ~ 7 (which leads to the formation of **4** and **5**) in the presence or absence of salt. This property makes it a suitable candidate for applications in protein purification in two-phase aqueous polymer systems[17] since it will permit its effective removal from solution by precipitation at lower pH values. The aqueous two-phase polymer system containing APE **7** (y = 0) and polyethyleneglycol has been tested for protein separation in our laboratory. The results are indeed very promising.[17]

We have recently reported[18] the synthesis of hydrophobically modified terpolymers of hydrophilic monomer **1**, hydrophobic monomer **2**, and sulfur dioxide (Scheme 1). The hydrophobe incorporation has considerably enhanced the viscosity values in the C_{18} polymer series, whereas the presence of even a large amount of C_{12} (0–10 mol%) hydrophobe 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.[19] The electrostatic repulsive forces between the chains do not permit them to move to the safe distance required for the dodecyl pendents ($C_{12}H_{25}$) to manifest interchain associations. The low C^*_{HA} (~ 1 g/dL) observed for the C_{18} polymer series
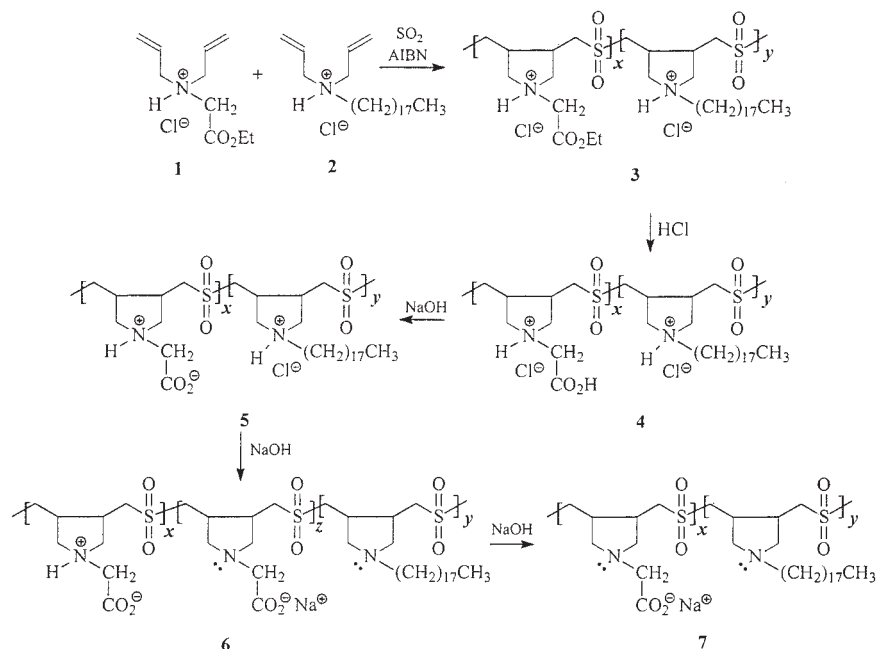
Scheme 1

is indeed a notable improvement over the C^*_{HA} of 15–17 g/dL for similar cyclopolymers having $\sim C_{11}$ pendents.[20] The octadecyl pendents ($C_{18}H_{37}$) can associate intermolecularly because the extended length of the pendents allows them to mingle with each other without exposing the chains to experiencing the adverse effect of electrostatic repulsions.

In our continuing studies of zwitterionic polymers, we now report the synthesis and comparative solution properties of the cationic polyelectrolyte (CPE) **3**, pH-responsive anionic polyelectrolyte (APE) **7,** and its corresponding polymer **6** containing varying proportions of polybetaine (PB), APE, and hydrophobe in a ratio of x : z : y, respectively.

EXPERIMENTAL

Physical methods

Elemental analyses were carried out in a Carlo–Erba elemental analyzer Model 1102. IR spectra were recorded on a Perkin–Elmer 16F PC FTIR spectrometer. ^{1}H NMR spectra of the polymers were measured in D_2O on a JEOL LA 500 MHz spectrometer. Viscosity measurements were made with a Ubbelohde viscometer (having viscometer constant of 0.005718 cSt/s at all temperatures) using CO_2-free water under N_2 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 to remove the dissolved gases. A Digital Brookfield rotational viscometer with UL adaptor accessories or SC4–18 spin-

dle 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 CPE **3** and APE **7** (polymer concentration range: 0.03–0.1 g/dL) were prepared in 0.5N NaCl solution; the presence of salt allows the screening of the charges 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 APEs in this solvent. Millipore disposable filters of pore size 0.02 μm were used to remove dust particles from the solutions of polyelectrolyte and the solvent (water). Corrections were made for the concentration of the polymer solution after filtration to account for the polymer screened by the filtration media. Measurements were performed on each solution immediately after filtration. Static light scattering (SLS) experiments were performed using a DAWN EOS light-scattering instrument (Wyatt Technology Corp., CA). The system light source was a linearly polarized gallium arsenide (GaAs) laser. The laser was positioned so that the incident beam was vertically polarized. An RFM-340 Refractometer (Bellingham and Stanley, UK) was used to measure the differential refractive indices (dn/dc) of different polyelectrolyte solutions. Molecular weight determination of the hydrophobically modified polymers was complicated owing to hydrophobic associations and, as a result, we can expect that the light scattering measurements lead to an apparent weight, $\bar{M}_{w,app}$, rather than a true molecular weight.

TABLE I
Terpolymerization[a] of the Monomers 1(M_1)/2(M_2)/SO$_2$ and Intrinsic Viscosity of the Resultant Cationic
Polyelectrolytes (CPE) 3

Entry no.	Sample CPE (3)	M_1 (mmol)	M_2 (mmol)	Time (h)	AIBN (g)	Temp (°C)	Feed[b] ($M_1 + M_2$)	Polymer[b] ($M_1 + M_2$)	Yield (%)	Intrinsic viscosity[c] (dL/g)	
										0.05 N	0.10 N
1	M_2-0	40.0	0	24	0.200	56.5	100 : 0	100 : 0	86.4	0.794	0.564
2	M_2-2.5	39.0	1.0	24	0.200	56.5	97.5 : 2.5	97.4 : 2.6	85.0	0.855	0.434
3	M_2-4	38.4	1.6	24	0.200	56.5	96 : 4	95.7 : 4.3	80.5	0.869	cloudy
4	M_2-4	38.4	1.6	24	0.100	56.5	96 : 4	96.1 : 3.9	54.4	0.206	cloudy
5	M_2-4	38.4	1.6	70	0.200	50.0	96 : 4	95.8 : 4.2	60.7	0.687	cloudy

[a] Polymerization reactions were carried out in DMSO (10.5 g) containing 40 mmol each of ($M_1 + M_2$) and SO$_2$ in the presence of AIBN.

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

[c] Obtained by extrapolation of the linear parts of the curves usually in the range 0.25–0.0625 g/dL polymer solution in 0.05 and 0.1 N NaCl at 30°C (measured with a Ubbelohde viscometer (K = 0.005718)).

[d] Cloudy solution throughout the concentration range.

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 was cleaned using deionized water. N,N-diallyl-N-carboethoxymethylammonium chloride (1) was prepared as described in a previous report.[14] N,N-Diallyl-N-dodecylammonium chloride (2) was prepared as before.[18]

General procedure for the terpolymerization of 1/2/SO$_2$

All the polymerizations were carried out using conditions as described in Table I using similar procedures as reported before.[18] The elemental analyses ascertained the mole ratio of (M_1+M_2) : M_3(SO$_2$) as 1 : 1 as reported before for all the copolymers.[18] The NMR and IR spectra and elemental analyses of the terpolymers closely resembled those of the copolymer M_2-0 as reported before.[14] The ^{1}H NMR spectra were used to determine the ratio of the M_1 and M_2 incorporated in the polymer as described before.[18]

General procedure for the acidic hydrolysis of the CPE 3

All the CPE 3 (Table I) were hydrolyzed in 6N HCl at 50°C in well over 90% isolated yields as reported before.[18] The polymer cationic acid salts (CAS) 4 gave satisfactory elemental analyses. The elemental analyses supported the presence of 1 mol of water per mole of the repeating units. The ^{1}H NMR spectra supported

the ratio of the M_1 and M_2 incorporated in the polymer as similar to the feed ratio.

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

The CAS terpolymers 4 were converted to the corresponding PB/APE 6 (x = z = 0.48; y = 0.04) by adding 1.5 equivalents of aqueous NaOH, and the resultant solutions were used for viscosity measurement in NaCl. Thus, a stock solution for the above PB/APE 6-M_2-4 was prepared by dissolving 0.500 g (1.773 mmol) of CAS 4 M_2-4 (it contains 4 mol % of the hydrophobe, derived from CPE 3-M_2-4, entry 3, Table I) in NaOH solution containing 2.624 (i.e., 1.773 + 1.773 × 0.96 × 0.5) mmol of NaOH (12.0 cm^3 of 0.2183N NaOH was used for the purpose). The release of 1.773 mmol of NaCl thus made the system 0.1478N NaCl. The solution was then diluted to 17.7 cm^3 with deionized distilled water to make the solution 0.1N NaCl. Further dilution with 0.1N NaCl to 25 cm^3 made the concentration of CAS 4 M_2-4 in the presence of 1.5 equivalents of NaOH as 2 g/dL in 0.1N NaCl. [CAS (4.1H$_2$O) and APE (7.2H$_2$O) have very similar molar masses of 273.73 and 277.27, for the repeating units, respectively.]

Likewise, the stock solutions of 2 g/dL of the CAS 4 M_2-4 in the presence of 1.67, 1.80, and 2.00 equivalents of NaOH were prepared by treating 0.500 g (1.773 mmol) of CAS 4 M_2-4 as above with (1.773 + 1.773 × 0.96 × 0.67), (1.773 + 1.773 × 0.96 × 0.80), and (1.773 + 1.773 × 0.96 × 1) equivalents of NaOH to obtain stock solution of APE/PB 6 (x = 0.32; z = 0.64; y = 0.04), APE/PB 6 (x = 0.19; z = 0.77; y = 0.04), and APE 7 (x = 0.96; y = 0.04), respectively.

Stock solutions of CAS 4-M_2-2.5 (derived from CPE 3-M_2-2.5, entry 2, Table I) in the presence of various

equivalents of NaOH were prepared in the similar way.

RESULTS AND DISCUSSION

Synthesis of the terpolymers and physical characterization

The hydrophilic monomer **1** (M_1), hydrophobic monomer **2** (M_2), and SO_2 were cyclocopolymerized using AIBN as the initiator to give the cationic polyelectrolytes (CPE) **3** in excellent yields (Scheme 1). The results of the cyclocopolymerization, carried out under various conditions, and the intrinsic viscosities of the resultant polymers in dilute solutions are given in Table I. Entry 1 in Table I describes the copolymer M_2-0, indicating the absence of the hydrophobic monomer **2**. Entries 2–5 describe the incorporation of the octadecyl monomer **2** in mol % of 2.5 and 4.0. The CPE terpolymer M_2-2.5 (entry 2), for instance, indicates the incorporation of 2.5 mol % hydrophobic monomer **2**. The use of 5 mg of initiator per mmol of the monomers (M_1+M_2) gave the polymer with the highest yield and intrinsic viscosity (entry 3, Table I); the decrease in the initiator concentration (entry 4) or temperature (entry 5) drastically reduced both the yields and viscosity values. Sulfur analyses ascertained the mole ratio of (M_1+M_2) : SO_2 as 1 : 1. The incorporation of the hydrophobic monomers was calculated using ^{1}H NMR integration as described.[18] While the hydrophobe incorporations were expected to match closely with the feed ratio for the polymers obtained at high conversions (entries 2 and 3, Table I), we were gratified to observe the similar matching for the polymers at moderate conversions (entries 4 and 5). The absence of compositional drifts thus could be attributed to the similar reactivity ratios for the hydrophilic **(1)** and hydrophobic monomer **(2)** as a result of having similar steric environments in the immediate vicinity around the nitrogen centers.

The CPE **3** (entries 1–3, Table I) were hydrolyzed in 6N HCl to produce the water-insoluble cationic acid salts (CAS) **4**, which, on treatment with 1.5, 1.67, 1.80, and 2.0 equivalents of NaOH, afforded the solution of PB/APE **6** and APE **7** in approximate PB/APE ratios of 50 : 50, 33 : 67, 20 : 80, and ∼ 0 : 100, respectively. CAS **4** as well as PB **5** (obtained by treating CAS **4** with 1 equivalent of NaOH) was found to be insoluble in salt-free or salt-added solution.[14] Critical NaOH equivalent required for the solubility of CAS **4** was around 1.25; this amount of NaOH would result in the formation of PB/APE **6** with an x : z ratio of approximately 75 : 25 (Scheme 1).

The APE **7** (derived from CPE **3**) is found to have higher viscosity than the corresponding CPE **3**; it is to be noted that both have a similar degree of polymerization and charge (albeit of opposite sign) (Tables I

TABLE II
Intrinsic Viscosity of the Polyelectrolytes and Apparent Molecular Weight of the Cationic and Anionic Polyelectrolytes

	Intrinsic viscosity[a] (dL/g)		
Sample	0.05 N NaCl	0.10 N NaCl	$10^{-5} \bar{M}_{w,app}$
3, CPE-M_2-0[b]	0.794	0.564	1.75
3, CPE-M_2-2.5[c]	0.855	0.434	2.30
7, APE-M_2-0[d]	1.75	1.25	2.38
7, APE-M_2-2.5[e]	1.59	1.15	3.54
7, APE-M_2-4[f]	1.79	1.28	3.66

[a] Obtained by extrapolation of the linear parts of the curves usually in the range 0.25–0.0625 polymer solution in 0.05 and 0.1 N NaCl at 30°C (measured with a Ubbelohde viscometer (K = 0.005718)).

[b,c] CPE 3 Samples from entries 1 and 2, respectively, Table 1.

[d,e,f] Obtained by hydrolysis of the corresponding CPE 3 in entries 3, 4, and 5, respectively, Table 1.

and II). Even though the CPE **3** have smaller distances between the neighboring positive charges, the widely separated but highly exposed anionic pendents in APE **7** 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 nitrogens in the CPE; 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 apparent molecular weights $\bar{M}_{w,app}$ of the polymers are given in Table II. The polymers CPE **3**-M_2-4 (entries 3–5, Table I) of higher hydrophobe content were insoluble in 0.5N NaCl, and as such their molecular weights were not determined. The $\bar{M}_{w,app}$ for the APE **7** were found to be higher than that of the CPE **3**. Intrinsic viscosity values also revealed the same trend. It should also be noted that the $\bar{M}_{w,app}$ of the polymers containing hydrophobe is higher compared to hydrophobe-free samples. The incorporation of the hydrophobes along the backbone seems to result in higher molecular weights. This could be attributed to the partial aggregation of the hydrophobically modified polymers, as inferred from the negative value of the second virial coefficient. For all the APE, Zimm plots showed significant curvature, indicating that the negative charges on the polymer backbone are not neutralized effectively. This is expected because the sodium ions are unable to screen the charges on the carboxylate (CO_2^- groups), whereas the chloride ions are able to screen the positive charges on the CPE. The copolymers (entries 1–3, Table I) prepared under similar copolymerization conditions (initiator and monomer concentrations, reaction conversions, temperature, duration, etc.) are expected to have similar molecular weights. The rather similar values of the
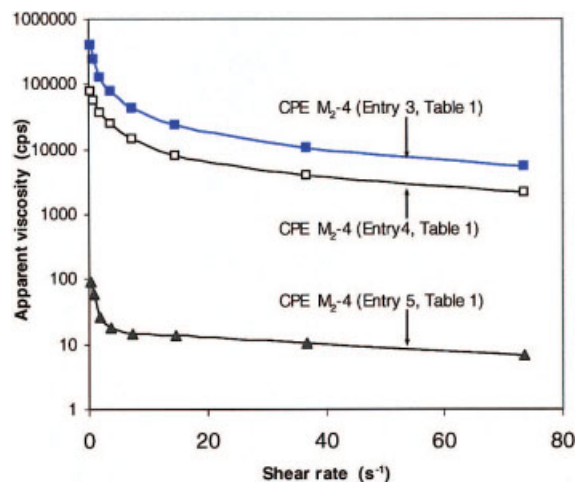
Figure 1 Variation of viscosity with shear rates of a 2 g/dL solution CPE-M_2-4 samples from entries 3, 4, and 5 (Table I) in salt-free water at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

intrinsic viscosity for CPE samples (entries 1–3, Table I) seem to confirm that their $\bar{M}_w$ should be close, contrary to the findings from light scattering experiments. The similar molecular weights should allow meaningful assessments of the effects of hydrophobic association on the solution behavior.

Viscosity measurements

The CPE **3** as well as the corresponding APE **7** having 2.5 or higher mol % of the hydrophobe **2** has been shown to manifest hydrophobic association at a concentration (C^*_{HA}) of less than 1 g/dL[18] in salt (NaCl)-free as well as salt-added solutions. Variation of viscosity with shear rates of various CPE **3**-M_2-4 samples (entries 3–5, Table I) at a concentration of 2 g/dL in salt-free water is shown in Figure 1. Even though all three samples are shown to have 4 mol % hydrophobes, the sample from entry 3 has the highest viscosity as a result of the most effective hydrophobic associations owing to its highest molecular weight. The average number of hydrophobe per polymer chain is the lowest in the case of the sample from entry 5 and, as such, a much higher concentration of the polymer will be required for the formation of 3-dimensional physical crosslinks.

The viscosity behavior of the PB/APE **6**-M_2-4 (derived from entry 3, Table I) having various compositions of PB (x) and APE (z) fractions in the dilute solution regime in 0.1N NaCl is displayed in Figure 2. The viscosity values were found to increase with the increase in the APE fraction (z). This is expected since the decrease in the polybetaine fraction (x) provokes an extension of the polymer backbone as a result of increased repulsion among the charged COO⁻
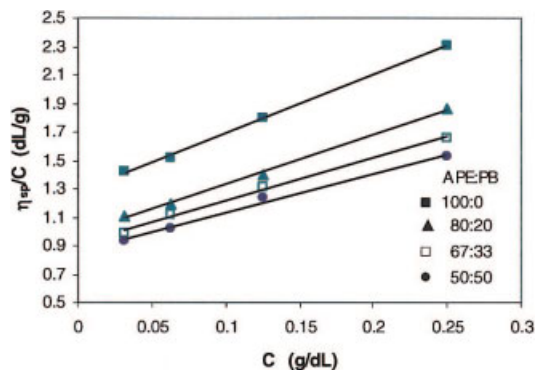

Figure 2 The viscosity behavior of the APE/PB **6**-M_2-4 (derived from entry 3, Table I) in 0.1N NaCl at 30°C with a Ubbelohde viscometer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]

groups. The polybetaine fraction tends to compact the polymer coil as a result of internal neutralization of the charges.

Variation of viscosity of a 2 g/dL solution of CAS **4**-M_2-2.5 at various shear rates in the presence of various equivalents of NaOH in 0.1N NaCl is shown in Figure 3. The viscosity attains its maximum value in the presence of 1.67 equivalent of NaOH, and decreases upon further addition of NaOH. Addition of 1.67 equivalent of NaOH will transform the CAS **4**-M_2-2.5 to its corresponding PB/APE **6**, having an approximate composition of 33 : 67 for the zwitterionic (x) and anionic (z) parts, respectively. As mentioned earlier, CAS **4** as well as PB **5** (obtained from CAS **4** on treatment with 1 equivalent of NaOH) are insoluble in water. Internal neutralization of the charges in polybetaines is known to lead the polymer backbone to adapt collapsed coil conformation as a result of intra- and interchain interactions.[21,22] When the net charge
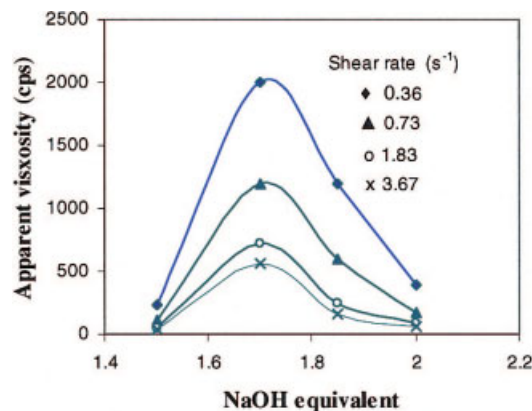

Figure 3 Variation of viscosity of a 2 g/dL solution of CAS **4**-M_2-2.5 at various shear rates in the presence of various equivalents of NaOH in 0.1N NaCl at 30°C. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
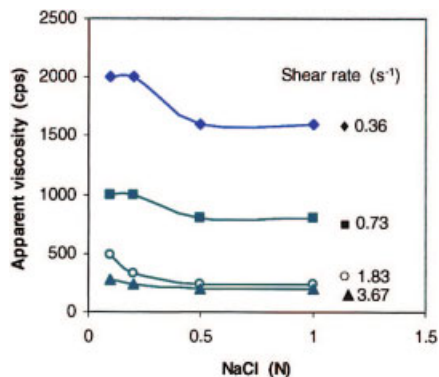
Figure 4 Variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-2.5 at various shear rates and NaCl concentration in the presence of 1.67 equivalents of NaOH at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-4 at various shear rates in 0.1N NaCl in the presence of 1.50 and 1.67 equivalents of NaOH at 30°C. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

of an ionic polymer approaches zero, attraction between oppositely charged units leads to a globule-like conformation, and most often to insolubility in pure water. While the presence of ionic sites of similar charges (CO$_2^-$ groups in the APE fraction) along the hydrophilic backbone can lead to a better solubility in water and a stronger thickening efficiency due to coil expansion, intermolecular electrostatic repulsions lead to a lowering of the degree of hydrophobic association. At an x/z ratio of 33 : 67, the combined effects of the coil expansion and hydrophobic association was found to lead to a maximum viscosity value (Fig. 3). At lower x/z ratios, the effect of coil expansion due to a higher APE fraction is more than counterbalanced by the lower degree of intermolecular hydrophobic associations; whereas at higher x/z ratios, the coil contraction becomes the predominant effect.

Figure 4 shows the viscosity of a 2 g/dL solution of CAS **4**-M$_2$-2.5 versus NaCl concentration at various shear rates in the presence of 1.67 equivalent of NaOH. The positive charges in the polymer chains are shielded by chloride ions. The decreased repulsion between the charges in the polymer chains lead to a compaction of the polymer coil, and as a result the viscosity is expected to decrease with increasing concentration of the added NaCl. The presence of NaCl, on the other hand, makes the aqueous system more hostile to the hydrophobes, thus forcing them to associate intermolecularly. In the case of M$_2$-2.5, the decrease of 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 4, the effect of added salt is not so significant owing to the opposing effects of shielding and hydrophobic associations on the viscosity.

Figures 5 and 6 display the variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-4 (derived from entry
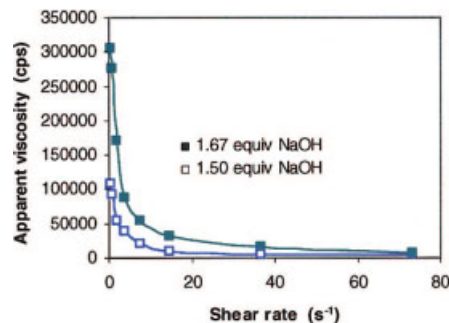
3, Table I) at various shear rates in 0.1N NaCl in the presence of 1.50, 1.67, 1.80, and 2.0 equivalents of NaOH at 30°C. While the viscosity decreases with increasing shear rates in the presence of 1.50 and 1.67 equivalents of NaOH (Fig. 5), in the lower shear rate range viscosity remains more or less constant or even increases in the presence of 1.8 and 2.0 equivalents of NaOH (Fig. 6). At lower x/z ratios, the effect of interchain repulsions due to a higher proportion of negatively charged APE fraction allows the hydrophobes to take part at least to some extent in intramolecular associations. With the increase in shear rates, the intramolecular associations are disrupted with the simultaneous increase in intermolecular associations. Further increase in the shear rates disrupts the intermolecular associations, thus leading to a decrease in the viscosity values. The viscosity is enhanced tremendously in the presence of 1.67 equivalents of NaOH (Fig. 7), as was the case with polymer sample CAS **4**-M$_2$-2.5 (Fig. 3).

Figure 8 shows the viscosity versus shear rate profiles for a 2 g/dL solution of CAS **4**-M$_2$-4 (entry 3,
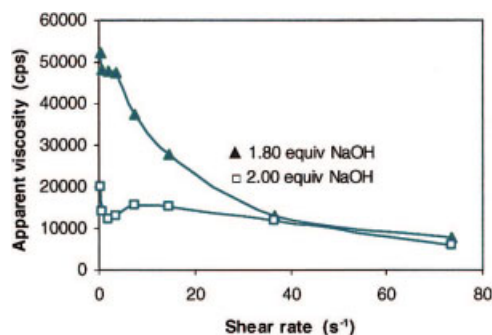

Figure 6 Variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-4 at various shear rates in 0.1N NaCl in the presence of 1.80 and 2.0 equivalents of NaOH at 30°C. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
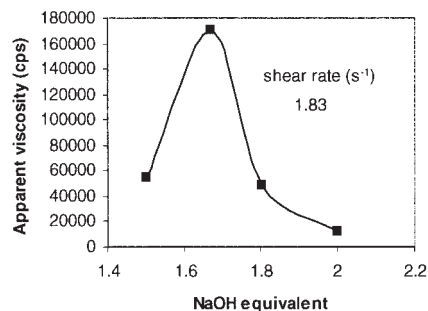
Figure 7 Variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-4 at a shear rate of 1.83 s^{-1} in the presence of various equivalents of NaOH in 0.1N NaCl at 30°C.

Table I) with NaCl concentrations at various shear rates in the presence of 1.67 equivalents of NaOH. The viscosity decreases with increasing concentration of NaCl. One would think *a priori* that the presence of salts would favor intermolecular hydrophobic associations. However, upon adding salt, there is a screening of the charges that induces chain contraction, leading to a decrease in the distance between the hydrophobes in a chain, thus presumably favoring hydrophobic intramolecular associations.

Figure 9 displays the variation of viscosity with concentration of CAS **4**-M$_2$-4 in the presence of 1.67 equivalents of NaOH. As evident from the Figure, the critical association concentration (C*$_{HA}$) was found to be around a polymer concentration of 1g/dL; changing the polymer concentration from 1 g/dL to 2 g/dL resulted in an increase of viscosity by a factor of 378 at a shear rate of 0.73 s^{-1}.

CONCLUSIONS

This work involved an interesting class of interconvertible polymers. Since the CAS **4**, PB **5**, and APE **7**
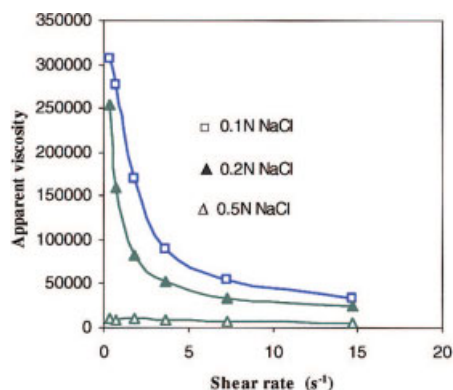

Figure 8 Variation of viscosity of a 2 g/dL solution of CAS **4**-M$_2$-4 with NaCl concentrations at various shear rates in the presence of 1.67 equivalents of NaOH at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
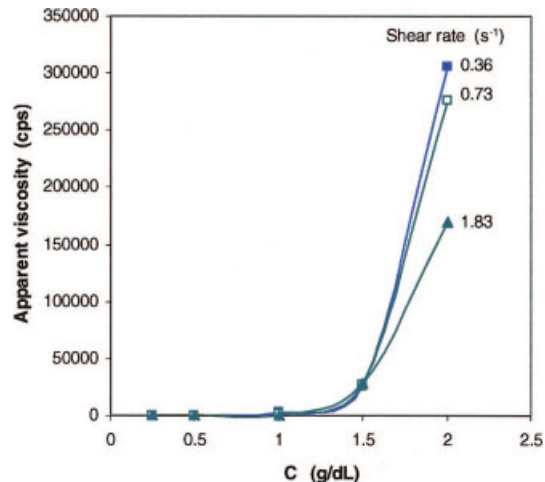

Figure 9 Variation of viscosity with concentration of CAS **4**-M$_2$-4 in the presence of 1.67 equivalents of NaOH at various shear rates in 0.1N NaCl at 30°C. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

are derived from the same CPE **3**, they all have identical degrees of polymerization, thus allowing a meaningful assessment of their solution properties. The hydrophobe incorporation has considerably enhanced the viscosity values for the polymers presented here. The viscosity of the pH-responsive polymers PB/APE **6** was found to be highest for the polymer chain containing zwitterionic and anionic charge densities in a ratio of 33 : 67, respectively. The work demonstrated the balance of zwitterionic and anionic charge densities required for the enhancement in the viscosity values of the ionic polymers. The pH-induced change in the conformation of PB/APE **6** can be manipulated judiciously in the effective use of this hydrophobically modified polymer in protein separation.[17]

References

1. Butler, G. B. J Polym Sci 1996, 34, 913.
2. Butler, G. B. Cyclopolymerization and Cyclocopolymerization; Marcel Dekker: New York, 1992.
3. McCormick, C. L. J Polym Sci 1996, 34, 911.
4. Harada, S.; Katayama, M. Makromol Chem 1966, 90, 177.
5. Harada, S.; Arai, K. Makromol Chem 1967, 107, 64.
6. Ottenbrite, R. M.; Ryan, Jr., W. S. Ind Eng Chem Prod Res Dev 1980, 19, 528.
7. Chem Economics Handbook; Stanford Research Institute: Menlo Park, CA, 1983; pp 581–1011I, 581–5022L, 581–1012D.
8. Thomas, D. B.; Armentrout, R. S.; McCormick, C. L. Polym Prepr (Am Chem Soc Div Polym Chem) 1999, 40, 275.
9. Ali, S. A.; Rasheed, A.; Wazeer, M. I. M. Polymer 1999, 40, 2439.
10. Ali, S. A.; Rasheed, A. Polymer 1999, 40, 6849.
11. Ali, M. M.; Perzanowski, H. P.; Ali, S. A. Polymer 2000, 41, 5591.
12. Ali, S. A.; Ali, Aal-e. Polymer 2001, 42, 7961.

13. Thomas, D. B.; Vasilieva, Y. A.; Armentrout, R. S.; McCormick, C. L. Macromolecules 2003, 36, 9710.
14. Al-Muallem, H. A.; Wazeer, M. I. M.; Ali, S. A. Polymer 2002, 43, 1041.
15. Al-Muallem, H. A.; Wazeer, M. I. M.; Ali, S. A. Polymer 2002, 43, 4285.
16. Ali, S. A.; Al-Muallem, H. A.; Wazeer, M. I. M. J Polym Sci Polym Chem Ed 2002, 40, 2464.
17. Waziri, S. M.; Abu-Sharkh, B. F.; Ali, S. A. Biotechnol Prog 2004, 20, 526.
18. Umar, Y.; Al-Muallem, H. A.; Abu-Sharkh, B. F., Ali, S. A. Polymer 2004, 45, 3651.
19. McCormick, C. L.; Middleton J. C.; Cummins, D. F. Macromolecules 1992, 25, 1201.
20. Gopalkrishnan, F. S.; Butler, G. B.; Hogen-Esch, T. E.; Zhang, N. Z. In: Shalaby, W.; McCormick, C. L.; Butler, G. B, Eds. Water-Soluble Polymers, ACS Symposium Series 467; ACS: Washington, DC, 1991; p 175.
21. Schultz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, H.; Gardner, R. T. Polymer 1986, 27, 1734.
22. Salamone, J. C.; Volksen, W.; Israel, S. C.; Olson, A. P.; Raia, D. C. Polymer 1977, 18, 1058.