

Electrolyte- and pH-Responsive Polyampholytes with Potential as Viscosity-Control Agents in Enhanced Petroleum Recovery

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ABSTRACT: Low-charge-density amphoteric copolymers and terpolymers composed of AM, the cationic comonomer (3-acrylamidopropyl)trimethyl ammonium chloride, and amino acid derived monomers (e.g., *N*-acryloyl valine, *N*-acryloyl alanine, and *N*-acryloyl aspartate) have been prepared via free-radical polymerization in aqueous media. These terpolymers with random charge distributions have been compared to terpolymers of like compositions containing the anionic comonomer sodium 3-acrylamido-3-methylbutanoate. Terpolymer compositions determined by ^{13}C - and ^1H -NMR spectroscopy, terpolymer molecular weights and polydispersity indices obtained via size exclusion chromatography/multi-angle laser light scattering, and hydrodynamic dimensions determined via dynamic light scattering have allowed a direct comparison of the fundamental parameters affecting the behavioral characteristics. The solution properties of low-charge-density amphoteric copolymers and terpolymers have been studied as functions of the solution pH, ionic strength, and polymer concentration. The low-charge-density terpolymers display excellent solubility in deionized water with no phase separation. The charge-balanced terpolymers exhibit antipolyelectrolyte behavior at pH values greater than or equal to 6.5 ± 0.2 . As the solution pH decreases, these charge-balanced terpolymers become

increasingly cationic because of the protonation of the anionic repeat units. The aqueous solution behavior (i.e., globule-to-coil transition at the isoelectric point in the presence of salt and globule elongation with increasing charge asymmetry) of the terpolymers in the dilute regime correlates well with that predicted by the polyampholyte solution theories. An examination of the comonomer charge density, hydrogen-bonding ability, and spacer group (e.g., the moiety separating the ionic group from the polymer chain) indicates that conformational restrictions of the sodium 3-acrylamido-3-methylbutanoate and *N*-acryloyl valine segments result in increased chain stiffness and higher solution viscosities in deionized water and brine solutions. On the other hand, the terpolymers with *N*-acryloyl alanine and *N*-acryloyl aspartate segments are more responsive to changes in the salt concentration. An assessment of the effects of the terpolymer structure on the viscosity under specified conditions of the ionic strength and pH from these studies should allow for rational design of optimized systems for enhanced petroleum recovery. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2812–2821, 2007

Key words: radical polymerization; rheology; solution properties; stimuli-sensitive polymers; structure-property relations; water-soluble polymers

INTRODUCTION

Polyampholytes are polymers that possess both anionic and cationic functional groups and fall under the class of polyzwitterions. Polyampholytes and the complex solution properties that they possess are of particular interest in the development of rheological modi-

fiers.^{1–7} In the dilute regime, ampholytic terpolymers characteristically exhibit unique globule-to-coil transitions, with increasing electrolyte concentrations resulting in larger hydrodynamic volumes and subsequent increases in the solution viscosity. This phenomenon is often called the *antipolyelectrolyte effect*. To fully understand the solubility and solution properties of ampholytic terpolymers, a general understanding of the complex associations that govern these properties, such as polymer–solvent and polymer–polymer interactions, must be known.^{4,8–18} Of fundamental importance are the electrostatic interactions that occur among the charged repeating units of the polyampholyte chain. Factors such as the charge density, charge asymmetry (e.g., degree of charge balance), charge spacing and distribution, and solution ionic strength are critical parameters. Even though the solution behavior of polyampholytes is typically dominated by electrostatic effects, other interactions along the polyampholyte backbone and with the solvent must be

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considered.⁹ Factors such as hydrophobic substitution, steric hindrance/chain stiffening due to bulky pendant groups, and hydrogen bonding along the backbone or with pendant groups must be taken into account when we examine polyampholyte behavior in aqueous solutions.

Of the previously mentioned polyampholyte characteristics, unique salt-responsive behavior is the focus of study in academic laboratories as well as industrial laboratories. Synthetic polyampholytes based on polyacrylamide (PAM) are excellent prospects for electrolyte-tolerant rheology modifiers, drag-reducing agents, and flocculants because of their ability to sustain high solution viscosities under saline conditions and exhibit stimuli-responsive behavior.^{4,19–23} PAM polyampholytes that contain low charge densities and incorporate large concentrations of acrylamide (AM) are often preferred because long runs of hydrophilic AM repeat units increase the terpolymer solubility at low ionic strengths. The overall performance of low-charge-density polyampholyte terpolymers as viscosifying agents is typically greater than that of high-charge-density ampholytic copolymers.^{19–23} Sulfonate anions and quaternary ammonium cations are the most commonly reported ionic functional groups for most PAM-based polyampholyte systems, and these are known to be insensitive to changes in the solution pH.^{23–26} Such non-pH-responsive systems are often called *quenched polyampholytes*, and their degree of exhibited polyampholyte or polyelectrolyte character is solely determined by the ratio of anionic-to-cationic monomer incorporation.^{23–26} However, when polyampholytes are prepared with comonomers bearing weak acid and/or weak base functionality (e.g., carboxylic acids and tertiary amines), the degree of polyampholyte or polyelectrolyte behavior exhibited in aqueous solutions is governed not only by the ratio of anionic-to-cationic comonomer content but also by the solution pH.^{27–29} Changes in solution pH can elicit either polyampholyte or polyelectrolyte solution behavior, thus allowing the production of functional terpolymers with pH-triggerable solution properties. Such pH-responsive ampholytic systems are called *annealed polyampholytes*.¹⁰ These polyampholytes are well-suited for a range of applications in which pH-triggerable changes in the solution viscosity might be useful, such as smart polymers for enhanced oil recovery (EOR) or formulations for coatings and personal care products.

To date, our synthetic research efforts have been focused on the development of stimuli-responsive, water-soluble polymers designed for use in EOR applications.^{27–38} These model systems are structurally tailored for potential applications as viscosifiers and/or mobility-control agents for secondary and tertiary EOR methods, drilling mud additives, cement additives, and hydraulic fracturing and acidifying

aids. The goal of previous synthetic work has been to design novel polymers that exhibit large dilute solution viscosities in the presence of the adverse conditions normally encountered in oil reservoirs (e.g., high salt concentrations, the presence of multivalent ions, and elevated temperatures). The polymers are also designed to have triggerable properties that can be elicited by external stimuli such as changes in the pH and/or salt concentration.

Chemical processes, mainly polymer flooding and surfactant polymer injection, have been the focus of attention of longstanding research in the field of polymer science in relation to EOR. Polymer flooding is based on the principle of improving (decreasing) the mobility difference between injected and in-place reservoir fluids to reduce channeling effects. Mobility control must be maintained within the flood, and the displacing phase should have a mobility equal to or lower than the mobility of the oil phase. This mobility ratio (M) is normally expressed as follows:

$$M = \frac{\lambda_w}{\lambda_o} = \frac{\frac{k_{iw}}{\mu_w}}{\frac{k_{io}}{\mu_o}} \quad (1)$$

where λ_w and λ_o represent the mobility of the water and oil, respectively; k represents the permeability to each phase; and μ is the viscosity.³⁹ When M is 1 or slightly less, the displacement of the oil by the water phase will occur in a pistonlike fashion. By contrast, if M is greater than 1, the more mobile water phase will finger through the oil, causing a breakthrough and poor recovery.⁴⁰ On the basis of the principle of the mobility ratio, water-soluble polymers can be used to increase the viscosity of the water phase while reducing the permeability of water to the porous rock and thereby creating a more efficient and uniform front to displace oil from the reservoir.^{39,40}

Previous studies in our group have shown that copolymers of AM with low molar fractions of sodium 3-acrylamido-3-methylbutanoate (AMBA) are exceptional viscosifiers compared with conventional anionic PAMs that contain acrylate functionalities.³⁵ Unlike hydrolyzed PAMs, these AMBA copolymers are able to maintain their viscosity in highly saline media in the presence of divalent cations (e.g., Ca^{2+} and Mg^{2+}) and at elevated temperatures. Under these conditions, solutions of conventional anionic PAMs typically lose viscosity, and precipitation of the polymer may occur.^{34,35}

In this work, we examine the effects of structure on the dilute solution behavior of terpolymers prepared from AMBA and the amino acid derived monomers *N*-acryloyl valine (AVA), *N*-acryloyl alanine (AAL), and *N*-acryloyl aspartate (AAS). These amphoteric monomers differ in the placement of the carboxylate functionality and spacer group (e.g., the moiety sepa-

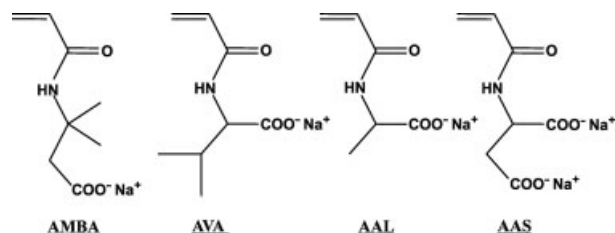


Figure 1 AMBA, AVA, AAL, and AAS monomers.

rating the ionic group from the polymer chain; Fig. 1). However, the conformation-dependent intramolecular and intermolecular associations for respective polyampholyte terpolymers might be expected to be substantially different. The choice of monomers was based on the favorable performance of AMBA in harsh conditions, as shown by previous studies,^{34,35,38} and the fact that these amino acid derivatives can be synthesized in a facile, cost-efficient manner from readily available, naturally occurring starting materials. The terpolymers were synthesized with the goal of creating a well-characterized series of model high-molecular-weight, low-charge-density polyampholytes for the examination of their stimuli-responsive solution behavior.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich (St. Louis, MO) and used as received unless otherwise noted. AM was recrystallized three times from acetone and dried *in vacuo* before use (mp = 83.5°C). 2,2'-Azabis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044) was a donation from Wako Pure Chemical Industries, Ltd. (Richmond, VA), and was used as received. HCl and NaOH solutions (0.100 ± 0.005M) were purchased from Fisher Scientific (Pittsburg, PA). Deionized (DI) water was obtained from a Barnstead NANOPure reverse osmosis/filtration unit (resistivity = 18.0 MΩ) (Dubuque, IA). The AMBA monomer and resultant terpolymers were synthesized in a manner previously reported for similar systems.^{30–32,34,35}

Synthesis of the amino acid monomers

AVA, AAL, and AAS were synthesized from the naturally occurring amino acids valine, alanine, and aspartic acid with a modified literature procedure.⁴¹ A 0.5 molar portion of the amino acid of choice and 1.0 mol of NaOH were placed in a 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer and dissolved in 200 mL of DI water. The solution was then cooled to ~5°C. To the solution, 0.5 mol of acryloyl chloride was added dropwise, the temperature being kept below 8°C. After the complete addi-

tion of acid chloride, the solution was allowed to react for 2 h. The mixture was then neutralized with 85 mL of concentrated HCl, and this resulted in the formation of a white precipitate. The precipitate was collected via vacuum filtration, recrystallized from water, dried, and stored under N₂.

AVA

mp: 83.5°C (lit. 83–85°C).⁴¹ ¹H-NMR (D₂O, 25°C, 300 MHz): CH₂CHCO 5.71 (d), CH₂CHCO 6.22 (m), HNCH(COOH)CH 4.15 (d), HNCH(COOH)CH 2.01 (m), CHCH(CH₃)₂ 0.98 (d).

AAL

mp: 69.5°C (lit. 69–71°C).⁴¹ ¹H-NMR (D₂O, 25°C, 300 MHz): CH₂CHCO 5.71 (d), CH₂CHCO 6.22 (m), HNCH(COOH)CH₂ 4.63 (d), HNCH(COOH)CH₃ 1.41 (d).

AAS

mp: 117°C (lit. 116–119°C).⁴¹ ¹H-NMR (D₂O, 25°C, 300 MHz): CH₂CHCO 5.71 (d), CH₂CHCO 6.22 (m), HNCH(COOH)CH₂ 4.45 (m), HNCH(COOH)CH₂ 2.17 (d).

Synthesis of low-charge-density, amphoteric polyampholyte terpolymers

Low-charge-density terpolymers of AM, (3-acrylamidopropyl)trimethyl ammonium chloride (APTAC), AMBA, and the amino acid derived monomers (AVA, AAL, and AAS) were synthesized via conventional free-radical polymerization in 0.5M NaCl. Sodium formate (NaOOCH) was added as a chain-transfer agent to control the polymer molecular weight, suppress gel effects, and avert excessive broadening of the molecular weight distribution (MWD).⁴² The monomer concentration was maintained at 0.46M, and the monomer/NaOOCH concentration ratio was held constant at 32 to produce terpolymer samples with weight-average molecular weights (*M_w*'s) ranging from 1 to 2 × 10⁶ g/mol. The monomer-to-initiator ratio was held at 1000:1, and the reaction solution pH was adjusted to 8.0 ± 0.5 to ensure neutralization of the amino acid monomer to the sodium salt form. Described next is a typical polymerization procedure for AM₉₀-AVA₅-APTAC₅.

To a 1.0-L, three-necked, round-bottom flask equipped with a mechanical stirrer and an N₂ inlet were added DI water (750 mL) and NaCl (21.9 g, 0.375 mol). The flask was placed in a 30°C temperature bath, and the contents were sparged with N₂ for 30 min. AM (21.88 g, 0.308 mol), AVA (2.93 g, 0.017 mol), APTAC (4.70 g of a 75 wt % APTAC solution in water, 0.017 mol), NaOH (0.70 g, 0.017 mol), and NaOOCH (0.73 g, 0.011 mol) were added to the flask,

TABLE I
Properties of the Amphoteric Polyampholyte Terpolymers

| Entry | Polymer ^a | AM (mol %) ^b | Anionic monomer (mol %) ^b | APTAC (mol %) ^b | M_w (10^6 g/mol) ^c | PDI ^c | h_d (nm) ^d |
|-------|--|-------------------------|--------------------------------------|----------------------------|------------------------------------|------------------|-------------------------|
| 1C | AM ₉₀ -AVA ₅ -TAC ₅ | 90.7 | 5.0 | 4.3 | 1.5 | 1.52 | 43.1 |
| 2C | AM ₉₀ -AAL ₅ -TAC ₅ | 90.2 | 5.1 | 4.7 | 1.1 | 1.59 | 43.8 |
| 3C | AM _{92.5} -AAS _{2.5} -TAC ₅ | 92.7 | 2.7 | 4.6 | 1.1 | 1.40 | 38.9 |
| 4C | AM ₉₀ -AMB ₅ -TAC ₅ | 91.4 | 4.6 | 4.3 | 1.5 | 1.51 | 43.9 |

^a The subscripts refer to the molar percentages of the monomers in the reaction medium.

^b Determined via inverse-gated decoupled ¹³C- and ¹H-NMR spectroscopy.

^c Determined via aqueous SEC-MALLS in a 0.1M NaCl phosphate buffer (pH 7).

^d Determined via aqueous DLS in a 0.1M NaCl phosphate buffer (pH 7).

and the solution was allowed to stir for 20 min under N₂ sparging. The pH of the resulting monomer solution was then adjusted to 8.0 ± 0.5 before the polymerization was initiated. The water-soluble azo initiator VA-044 (110.5 mg, 0.377 mmol, dissolved in 10 mL of degassed DI water) was then added to the flask by syringe. The polymerization was allowed to proceed under N₂ for 6.5 h. After the completion of the reaction, the contents of the flask were discharged to Spectra-Por No. 4 dialysis tubing (molecular weight cutoff = 12–14,000 g/mol) and dialyzed for 1 week, with the dialysis water being changed every 24–48 h. The pH of the dialysate was maintained for ~ 7.5 to ensure that the AVA repeat units remained ionized. The purified terpolymer was isolated from water via lyophilization to yield a white solid. Terpolymers of AAL and AAS were prepared in a similar fashion. Physical data are listed in Table I.

Terpolymer characterization

NMR spectroscopy

Terpolymer samples for NMR spectroscopy analysis were prepared as 5–10 wt % solutions in D₂O containing 0.5M NaCl. All NMR experiments were performed at the ambient temperature ($25.0 \pm 1.0^\circ\text{C}$). ¹³C-NMR spectra were obtained with a Varian Unity Inova 500-MHz NMR spectrometer (Palo Alto, CA) with a standard 5-mm two-channel probe. For the quantitative determination of the terpolymer composition, a gated decoupled pulse sequence with a 6–7-s relaxation delay was used to suppress nuclear Overhauser effects. Typically, 10,000–15,000 scans were accumulated for ¹³C spectra. All shifts were referenced automatically by the acquisition software (VNMR version 6.1C, Palo Alto, CA) with the resonance frequency of D₂O. The error associated with the use of ¹³C-NMR spectroscopy integration for individual values of termonomer incorporation was generally $\pm 5\%$ of the calculated value. ¹H-NMR spectra were obtained at 300 MHz with a Varian Mercury Plus spectrometer. Typical acquisition parameters were a relaxation delay of 0.05 s, a 7.1- μs pulse

corresponding to a 90° flip angle, and an acquisition time of 2 s. Data analysis was performed with MestRe-C (version 2.3a) spectral analysis software (Departamento de Química Orgánica, Universidad de Santiago de Compostela, Santiago, Chile).

Size exclusion chromatography/multi-angle laser light scattering (SEC-MALLS)

Aqueous size exclusion chromatography (SEC) was employed to determine the terpolymer molecular weight and polydispersity index (PDI). The SEC system comprised an Agilent 1100 series isocratic pump (Santa Clara, CA) with a vacuum degasser, a Rheodyne (Rohmet Park, CA) 7725i manual injector with a 100- μL injection loop, two Viscogel columns (GPW_{XL}-5000 and 6000 and a GPW_{XL} guard column from Viscotek, Houston, TX) connected in series, a Dawn EOS 18-angle laser light scattering detector (Wyatt Technologies, Santa Barbara, CA), and an Optilab DSP interferometric refractometer (Wyatt Technologies). Data acquisition and analysis were performed with Astra version 4.90.07 chromatography software (Wyatt Technologies). SEC analysis was conducted at the ambient temperature ($25.0^\circ\text{C} \pm 1.0^\circ\text{C}$). The eluent for the copolymers and terpolymers was a 0.1- μm -filtered 0.1M NaCl phosphate buffer (pH 7; 25 mM NaH₂PO₄ and 25 mM Na₂HPO₄). Refractive-index increments (dn/dc) of the terpolymers were determined with the refractometer in the offline mode at the ambient temperature. The associated error of offline dn/dc determination was typically ± 2 –3%. The reported SEC-MALLS data are the averages of three separate injections; the error associated with the individual values of M_w determined via SEC-MALLS was typically $\pm 2\%$.

Dynamic light scattering (DLS)

DLS studies of the polyelectrolyte copolymers and polyampholyte terpolymers at a concentration of 0.10 g/dL in a 0.1- μm -filtered 0.1M NaCl phosphate buffer (pH 7; 25 mM NaH₂PO₄ and 25 mM Na₂HPO₄) were conducted with a Malvern Instruments (Malvern Worcs, UK) Zetasizer Nano series instrument

equipped with a 22-mW He–Ne laser operating at 632.8 nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple-tau digital correlator electronic system. Hydrodynamic diameter (h_d) calculations were determined with Dispersion Technology software (version 4.00) (Malvern Worcs, UK).

Intrinsic viscosity determination

Stock solutions were prepared by the dissolution of vacuum-oven-dried terpolymer samples in a 0.1- μ m-filtered 0.1M NaCl phosphate buffer (pH 7; 25 mM NaH_2PO_4 and 25 mM Na_2HPO_4) and were allowed to age 72 h while being agitated gently on an orbital shaker. Subsequent dilutions of the stock solutions were made and allowed to age for 24 h on an orbital shaker before analysis. The apparent viscosities of the dilute terpolymer solutions were determined with a Contraves LS-30 low-shear rheometer (London, UK) with a 2T cup and bob geometry operating at 5.96 s^{-1} and 25.0°C . Initial experiments at various shear rates in the dilute regime showed the fluids to be non-shear-thinning (i.e., Newtonian fluids). Therefore, the apparent viscosities determined at 5.96 s^{-1} are considered to be zero-shear apparent viscosities. Apparent viscosity measurements were repeatable with a precision of $\pm 1\%$. Intrinsic viscosities were determined through the plotting of the reduced viscosity versus the concentration and extrapolation to a zero concentration. The determinations of the intrinsic viscosity were repeatable within $\pm 2\%$.

Potentiometric titration

The pH measurements for potentiometric titrations were conducted at $25.0 \pm 0.5^\circ\text{C}$ with an Orion 900A pH meter (Boston, MA) with a Ross Sure-Flow 8175 pH electrode (Boston, MA). The meter was calibrated via a two-point calibration method. Terpolymer concentrations for titration were 0.50 g/dL. Minimal volume variation during the titration was achieved by the addition of microliter aliquots of the titrant. Terpolymer solutions were adjusted to pH ~ 10 with concentrated NaOH to ensure the complete neutralization of all the carboxylic acid groups and then back-titrated with a 0.1M HCl standard solution.

Dilute solution viscometry

Stock solutions were prepared by the previously mentioned procedure with DI water or saline media. The adjustment of the pH was achieved via the addition of microliter aliquots of NaOH or HCl. The adjustment of the pH was performed on the same day as rheological analysis to prevent acid- and/or base-catalyzed

hydrolysis of the AM repeat units upon aging at pH extremes. The solution pH was measured before sample analysis with an Orion 900A pH meter with a Ross Sure-Flow 8175 pH electrode.

The apparent viscosities of the pH-adjusted samples were obtained by the previously mentioned procedure. The measurements of the apparent viscosity were repeatable with a precision of $\pm 1\%$. The specific viscosity (η_{sp}) was calculated from the apparent viscosity as follows:

$$\eta_{\text{sp}} = \left(\frac{\eta_{\text{app}} - \eta_o}{\eta_o} \right) \quad (2)$$

where η_{app} is the apparent viscosity (cP) and η_o is the solvent viscosity (cP). The reduced viscosity (dL/g) was calculated by the division of η_{sp} by the polymer concentration (g/dL).

RESULTS AND DISCUSSION

Polyampholyte terpolymer synthesis

The synthesized terpolymers are shown in Table I. An entry number is provided for each polymer for ease of reference. Our goal was to synthesize low-charge-density polyampholytes with high solubility (i.e., terpolymer compositions containing a minimum of 90% AM) and beneficial viscosifying properties, as reported in previous work with similar systems.^{4,35,36,38} The high levels of AM promote the solubility of the polyampholyte terpolymers, even in the absence of added electrolytes, because of the extremely hydrophilic nature of the nonionic monomer. APTAC, a quaternary ammonium acrylamido monomer, was employed as the cationic species in the series.

The first column of Table I lists the amphoteric terpolymers synthesized for this study. 1C–3C^{36,37} are the nearly charge-balanced polyampholytes containing the amino acid derived monomers AVA, AAL, and AAS; 4C^{30–32} is the nearly charge-balanced polyampholyte containing the AMBA monomer. The terpolymers were synthesized with 5.0 mol % of each anionic monomer and 5.0 mol % APTAC in the feed. Because there are two carboxy groups on the AAS repeating units, the charge density is twice that of the molar percentage monomer incorporation; therefore, the molar percentage monomer incorporation is different for 3C and its counterparts in Table I. Polymerizations were allowed to proceed for 6–7.5 h to obtain conversions of $\sim 75\%$.

The synthesis of the polymers was conducted under conditions expected to yield model terpolymers with homogeneous compositions, random charge distributions, and PDIs less than 2.0. A polymerization medium with 0.5M NaCl was used to ensure the random distribution of the charged groups along the polyam-

TABLE II
 pK_a Values, Charge Densities, and Charge Asymmetries of the Amphoteric Polyampholytes

| Entry | Polymer ^a | Apparent pK_a of the COOH group ^b | Charge density (mol %) ^c | Charge asymmetry ^c |
|-------|--|--|-------------------------------------|-------------------------------|
| 1C | AM ₉₀ -AVA ₅ -TAC ₅ | 5.61 | 9.3 | 1.13 |
| 2C | AM ₉₀ -AAL ₅ -TAC ₅ | 4.22 | 9.8 | 3.10 |
| 3C | AM _{92.5} -AAS _{2.5} -TAC ₅ | 4.11 | 7.8 | 1.24 |
| 4C | AM ₉₀ -AMB ₅ -TAC ₅ | 5.91 | 8.9 | 1.92 |

^a The subscripts refer to the molar percentages of the monomers in the reaction medium.

^b Determined in DI water at 25°C.

^c Determined with eq. 3 under the assumption of complete ionization of the amino acid repeat units.

pholyte terpolymer chain. The added electrolyte effectively screens electronic interactions of the charged monomers, thus reducing the tendency for monomer incorporation into the terpolymer chain as alternating pairs.⁴³ Sodium formate is highly effective in suppressing broad MWDs and controlling the molecular weight of the free-radical polymerization of acrylamido monomer systems and was used as a conventional chain-transfer agent.⁴² In addition to the use of sodium formate to control the molecular weight, the polymerizations were conducted at 30°C to minimize chain branching and hydrolysis reactions that have been reported at higher temperatures.^{44,45}

SEC-MALLS and DLS analysis

M_w and PDI data for 1C–4C were obtained by aqueous SEC-MALLS and refractive-index detection. The aqueous buffer solution containing 25 mM NaH₂PO₄ and 25 mM Na₂HPO₄ phosphate with 0.1M NaCl allowed solubility and sufficient screening of charges on the polyampholytes for optimal SEC analysis. This solvent was also employed for the determination of intrinsic viscosities via dilute solution viscometry and h_d values by DLS of the series. The M_w , PDI, and h_d values for the copolymer and terpolymer series are listed in Table I. The M_w values of the terpolymers range from 1.1 to 1.5 × 10⁶ g/mol, and the h_d values are in the range of 39–44 nm. It is apparent from the data that the use of sodium formate as a chain-transfer agent yielded the desired results because all polymers had similar M_w values and exhibited PDI values ranging from 1.5 to 1.6.

Determination of the pK_a , charge density, and charge asymmetry

Potentiometric titrations of the copolymers and terpolymers were performed at a concentration of 0.05 g/dL to determine the pK_a value of the amphoteric repeat unit and the resulting charge density and charge asymmetry (Equation 3). The charge density is typically defined as the total number of anionic and cationic

groups incorporated into a given polymer, and the charge asymmetry indicates the degree of charge imbalance present in a polyampholyte.⁹ Equation (3) is used to determine the charge asymmetry, σN , of a given polyampholyte. For a polyampholyte consisting of N repeat units containing a fraction of positive repeat units, f_+ , and a fraction of negative repeat units, f_- , σN is defined such that $N_+ = f_+ \times N$ is the number of positive (cationic) repeat units and $N_- = f_- \times N$ is the number of negative (anionic) repeat units present in the ampholytic terpolymer. Charge densities and charge asymmetries (assuming 100% neutralization of the –COOH repeat units to the carboxylate form) of 1C–4C are given in Table II. The values for the charge asymmetries of the polyampholytes obviously change as the solution pH is lowered because of the protonation of the –COOH repeat units, as the values for N_- are pH-dependent (Fig. 2):

$$\sigma N = \frac{(N_+ - N_-)^2}{N_+ + N_-} \quad (3)$$

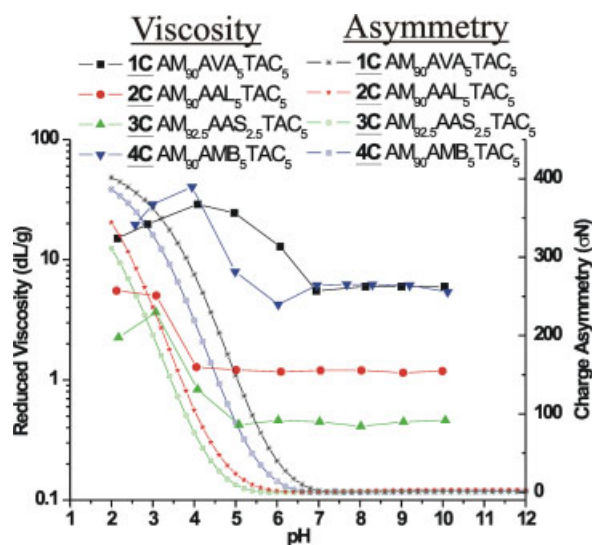


Figure 2 Charge asymmetry and reduced viscosity as functions of the solution pH for the polyampholyte terpolymers in DI water. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pH-responsive solution viscometry

In the absence of electrolytes

The charge asymmetry values (smooth, fitted curves) and reduced solution viscosities (point-to-point curves) as functions of the pH for the terpolymer series in DI water at dilute concentrations (0.1 g/dL) are shown in Figure 2. Under these conditions (absence of electrolytes), terpolymer conformations are most sensitive to changes in the pH because electrostatic interactions are operative in the absence of charge screening. The magnitude of the response is affected by the nature of the anionic comonomer and its concentration with respect to the APTAC units in the terpolymer. At a low pH, the AVA, AAL, AAS, and AMBA units are in their protonated state, and any uncompensated APTAC cationic repeat units impart asymmetry and thus polyelectrolyte characteristics as reflected by increased values in the reduced viscosity. Polymers 1C–4C with balanced molar compositions of amphoteric COOH functional groups and cationic APTAC groups behave as cationic polyelectrolytes at low pHs. With increasing pH, carboxylate anions begin to compensate for cationic groups, and a viscosity minimum is reached when the terpolymers become charge-balanced polyampholytes (lowest charge asymmetry). The lowest values of the viscosity are expected in DI water for these conformations that allow the highest degree of cation/anion pairing and minimal hydration of the associated mer units.

The overall aqueous solution behavior of terpolymers 1C–4C matches qualitatively that predicted from simple calculations of charge asymmetry based on the terpolymer compositions and pH conditions at low ionic strengths. However, a close examination of Figure 2 reveals quite significant differences in the solution behavior as the different anionic mer units are incorporated. This behavior can be rationalized only in terms of differences in the chain conformation because the molecular weights and terpolymer compositions are similar. The most dramatic changes in the solution viscosity occur for AAS terpolymers, followed by AAL, AMBA, and AVA terpolymers, respectively. For the stoichiometrically balanced systems at pH values above the pK_a of the respective carboxy groups, Figure 2 shows that, despite charge asymmetries of 1, the viscosity values are much higher for 4C and 1C, followed by 2C and 3C. Even at the isoelectric point (IEP), the AMBA- and AVA-containing terpolymers, 4C and 1C, have significantly higher viscosities than 2C, whereas the more conformationally responsive terpolymer, 3C, has the lowest value.

A second feature observed in the plots of the reduced viscosity versus the pH in Figure 2 is the dramatically higher pK_a for the carboxylic acid units in the AMBA and AVA repeats versus those of AAL and AAS in these terpolymer systems. Similar effects have

been observed by our group^{29,31,35} and others^{9,10} for the carboxylic acid units in constrained hydrogen-bonded or hydrophobic environments. The lower viscosity values for AMBA- and AVA-containing terpolymers below pH 4 may also be attributed to intrachain hydrogen bonding, which is gradually broken with increases in the solution pH.

Because the terpolymers of this study contain amphoteric units AVA, AAL, AAS, and AMBA, it may be anticipated that conformational restrictions differing with each of these would affect the extent and nature of ion pairing above and below the IEP. For amphoteric polyampholytes, uncompensated charges would be expected to stretch collapsed globules into more extended states. Theoretical models of this type have been proposed by Dobrynin and Rubinstein.⁹ In addition, Kantor and Kardar^{11–18} have suggested a pearl necklace model with theoretically predicted behavior similar to that observed in our experimental work. It is logical that the extended state would occur when all cationic and anionic interactions have been disrupted and uncompensated like-charge interactions have been maximized. In an aqueous solution at a relatively low ionic strength, the data suggest that chain-stiffening effects, which reduce the number of available conformational states, decrease in the order of AVA \approx AMBA > AAL > AAS.

Salt-responsive behavior at the IEP

The reduced viscosities of the charge-balanced polyampholyte terpolymers as a function of the NaCl concentration are shown in Figure 3. Classic antipolyelectrolyte behavior is exhibited by all systems at their respective IEPs and is demonstrated by the increase in the viscosity with an increase in the NaCl concentration. The increases in the hydrodynamic volume and coil expansion (indicated by the increase in the viscosity) are due to shielding of charges on the polyampholyte chain by the small-molecule electrolytes; the magnitude of the change in the viscosity follows the order of AVA \approx AMB > AAL > AAS.

A detailed examination of Figure 3 reveals that the reduced viscosities of 1C and 4C are greater than those of 2C and 3C throughout the NaCl concentration regime. Upon further inspection, it can be seen that differences in the molecular weight, PDI, and degree of polymerization of the terpolymer systems are not large enough to account for the trend, but at elevated ionic strengths, the electrostatic interactions of the polymer chain are greatly diminished (because of charge screening), thus indicating the increased effect of the polymer–solvent interactions of the uncharged portion of the terpolymers. Therefore, it is postulated that increased polymer chain stiffness due to the hydrogen-bonding ability of the AMB and AVA seg-

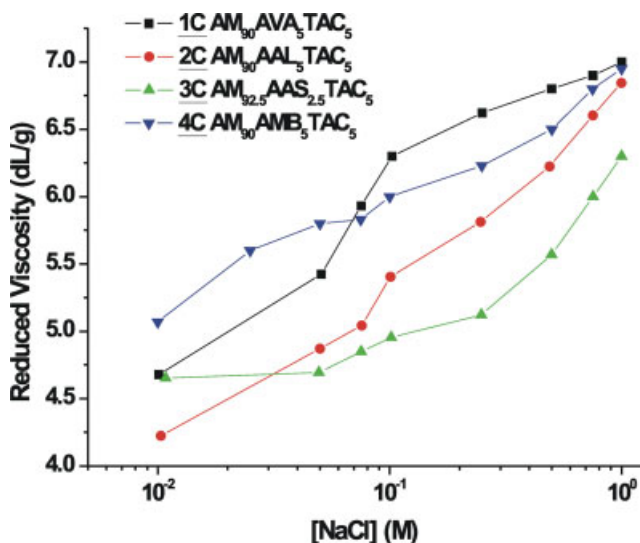


Figure 3 Reduced viscosity of the polyampholyte terpolymers as a function of the NaCl concentration at pH 6.5 ± 0.2 (polymer concentration = 0.1 g/dL). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ments with neighboring AM repeat units results in higher solution viscosities of 1C and 4C. Thus, it can be concluded that the observed salt response at [NaCl] > 0.1M results from the composite effects of decreasing polymer–solvent interactions and increasing chain stiffness due to intramolecular hydrogen bonding.

Combined pH- and salt-responsive behavior

As a means of observing the combined pH- and salt-responsive behavior of the polyampholyte terpolymer series in dilute solutions, the reduced viscosities of the polyampholyte terpolymer solutions (concentration = 0.1 g/dL) were measured as functions of the pH and NaCl concentration. Figure 4 represents three-dimensional (3D) plots of the combined pH- and salt-responsive characteristics of the polyampholyte terpolymers. These serve as phase diagrams that map the viscosity response to variations in the solution pH and salt concentration. Such diagrams are of great practical value in tailoring terpolymer structures for optimal behavior in oil-recovery operations; for exam-

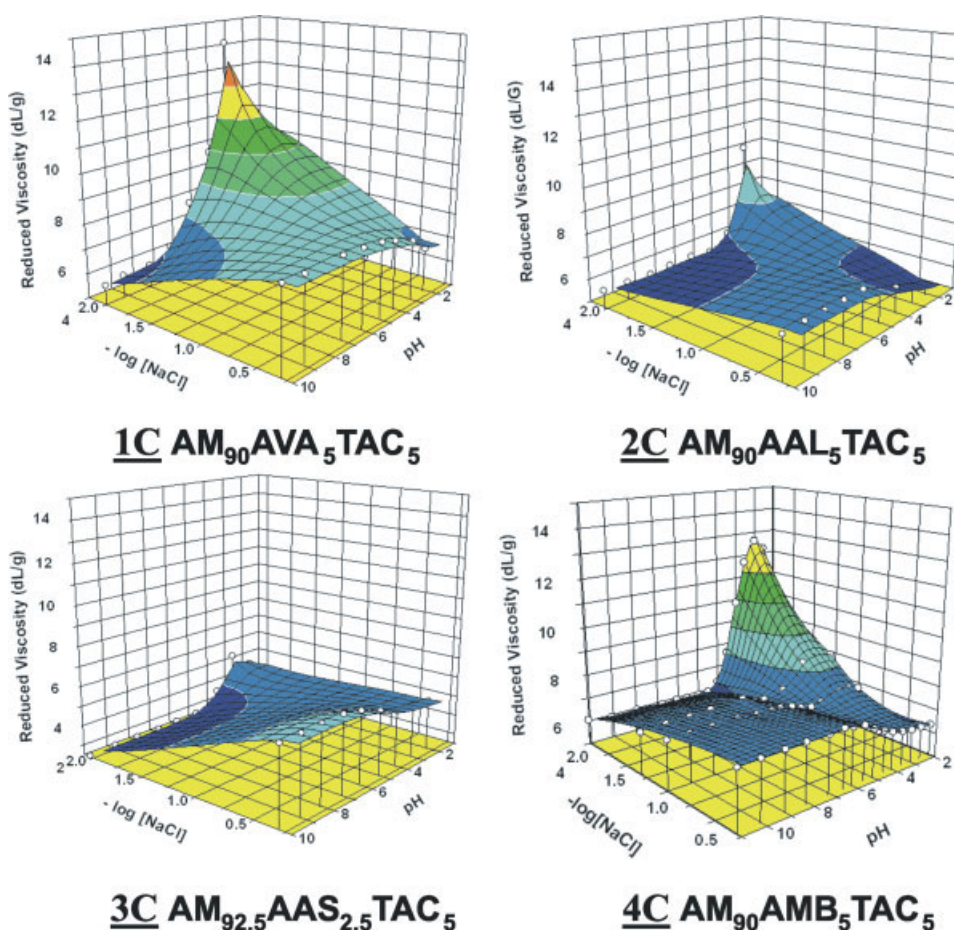


Figure 4 3D plots of the reduced viscosity as a function of the NaCl concentration and solution pH for terpolymers 1C–4C at a concentration of 0.1 g/dL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

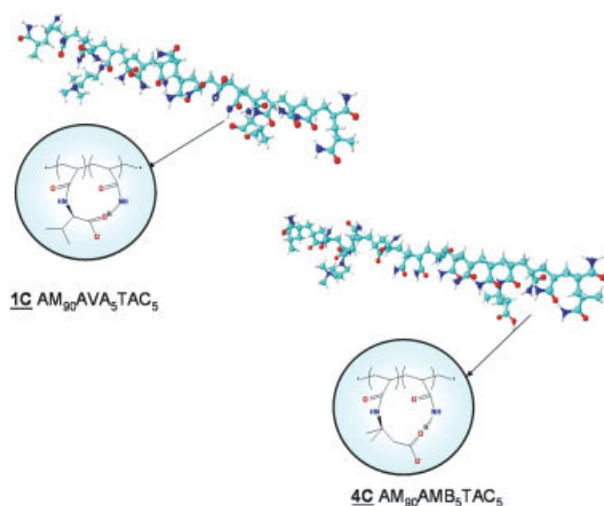


Figure 5 Postulated hydrogen-bonding ability of AVA and AMBA repeat units with AM in terpolymers 1C and 4C, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ple, the structure can be targeted for a specific viscosity for mobility control in EOR with known values of reservoir salinity and pH.

In Figure 4, four distinct regions can be observed in the 3D viscosity/NaCl concentration/pH plots for each of the stoichiometrically balanced terpolymers (1C–4C):

1. At pH values less than 4 and a low NaCl concentration, a maximum can be observed, corresponding to coil expansion due to unscreened electrostatic repulsions of uncompensated cationic charges.
2. At a high pH and low NaCl concentration, a polyampholyte valley can be observed, indicating coil collapse due to unscreened electrostatic attractions.
3. At a low pH and high NaCl concentration, a polyelectrolyte valley can be observed as the electrostatic repulsions among cationic groups are screened at higher ionic strengths, leading to coil contraction.
4. At a high pH and high NaCl concentration, a polyampholyte plateau can be observed, as the increased ionic strength screens electrostatic attractions between cation/anion complexes, allowing coil expansion.

Although the contours of the 3D plots for 1C–4C are very similar, there exist differences in the magnitudes of the solution viscosity responses. We attribute the differences to the effects of terpolymer microstructures that result in increased chain stiffness due to the hydrogen-bonding ability of the AVA and AMBA repeat units (Fig. 5) that limit the conformational mobility of 1C and 4C while in aqueous solutions.

From the solution property profiles shown in Figures 2 and 3, it can be said that all the terpolymers examined possess pH-responsive aqueous solution behavior. Although 2C and 3C display the most responsive behavior in the absence of electrolytes because of their increased conformational mobility, their ability to maintain viscosity under brine conditions is substantially less than that of 1C and 4C. The AVA and AMBA monomers are isomers and display similar solution behavior under both DI water and brine conditions. The increased chain stiffness of 1C and 4C allows for the preservation of high solution viscosities through the entire pH and ionic strength ranges presented in this study with no phase separation.

Each particular terpolymer offers advantages in applications such as EOR. For example, the more conformationally responsive 2C and 3C at their IEPs can elicit low solution viscosities in DI water, which should aid in their injection into porous media with less shear degradation because of low hydrodynamic volumes. Once in the well, the screening of the electrostatic interactions by *in situ* electrolytes would result in globule-to-coil transitions causing subsequent increases in the solution viscosity and increased mobility control in secondary and tertiary EOR processes. However, terpolymers 1C and 4C display more restricted chain conformations in DI water, larger hydrodynamic volumes, and greater solution viscosities. Such behavior is less advantageous to the injection process, but once in the porous media of the well, the viscosity of the terpolymer solutions at or above the IEP is higher than that of 2C or 3C. This would result in better control of the water-flood process for EOR.

CONCLUSIONS

A series of model low-charge-density polyampholyte terpolymers composed of AM, APTAC, and AMBA and the amino acid derived monomers AVA, AAL, and AAS were synthesized via conventional free-radical polymerization in aqueous media. The reaction conditions were selected to yield terpolymers with random charge distributions, homogeneous compositions, and uniform molecular weights and MWDs. Compositional analysis by ^1H - and ^{13}C -NMR revealed reasonable agreement between the monomer feed compositions and final terpolymer compositions. The terpolymers were characterized extensively via SEC-MALLS and DLS analysis in a 0.1M NaCl phosphate buffer (pH 7) at 25°C. SEC-MALLS analysis showed that the use of NaOOCH as a conventional chain-transfer agent allowed the control of the terpolymer molecular weight and suppressed excessively broad MWDs, whereas DLS provided h_d values for each polymer. These polymerization conditions were of vital importance in developing a model terpolymer series that allows comparisons of relevant solution prop-

erties within the series. Potentiometric titration studies provided apparent pK_a values of the terpolymers from which charge density and charge asymmetry values were calculated. The aqueous solution properties of the series are dependent on the terpolymer composition (e.g., the level of the ionic comonomer content and ratio of anionic monomers to cationic monomers). The terpolymers with low charge densities and/or large charge asymmetries exhibit excellent solubility in DI water. An examination of the pH- and salt-responsive dilute solution viscosity profiles for the amphoteric series revealed that polyampholyte or polyelectrolyte behavior can be elicited simply by changes in the solution pH and/or electrolyte concentration. The extent of this viscosity response is dependent on the terpolymer charge density, microstructure, and charge asymmetry. At a low ionic strength, the dilute solution viscosity is governed predominantly by electrostatic interactions. By contrast, at a high ionic strength, electrostatic interactions are eliminated because of charge screening. Other factors such as intramolecular hydrogen bonding, terpolymer chain stiffness, and backbone hydrophobicity also affect the solution properties. The terpolymers' unique solution properties should offer advantages for utilization in applications such as mobility-control agents and channel blockers for EOR. The enhanced viscosities of the responsive polyampholytes may also offer opportunities for developing more effective drilling mud additives, cementing systems, and hydraulic fracturing and acidifying fluids.

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