

# Hydrophobically Modified Acrylamide-Based Polybetaines. I. Synthesis, Characterization, and Stimuli-Responsive Solution Behavior

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**ABSTRACT:** Acrylamide-based, hydrophobically modified (HM) polybetaines containing *N*-butylphenylacrylamide (BPAM) and varying amounts of the sulfobetaine monomer 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS) or the carboxybetaine monomer 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (AMPDAB) were synthesized by micellar copolymerization. The corresponding control (co)polymers lacking BPAM or betaine comonomers were also prepared. The terpolymers were characterized by  $^{13}\text{C}$ -NMR and UV spectroscopy, classical light scattering, and potentiometric titration. Low charge density polymers contained 3.9–8.6 mol % betaine, whereas the high charge density systems contained 17–25 mol % betaine; the HM polymers contained up to 1.0 mol % BPAM as the hydrophobe. The weight-average molecular weights of the polymers ranged from  $4.19 \times 10^5$  to  $1.29 \times 10^6$  g/mol, and most HM polymers exhibited

negative second virial coefficients. The  $\text{p}K_a$  of the carboxybetaine moieties was found to increase with increasing levels of hydrophobic and betaine comonomer incorporation. The response of aqueous polymer solutions to various external stimuli, including changes in solution pH and electrolyte concentration, was investigated using rheological analysis. The solution behavior of the polymers was characteristic of HM polyacrylamides and acrylamide-based polyzwitterions. The high charge density HM polycarboxybetaine exhibited unusual solution behavior that can be explained in terms of electrostatic, hydrophobic, and hydrogen-bonding associations. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 647–657, 2004

**Key words:** amphiphilic polymers; polyzwitterions; micellar copolymerization; water-soluble polymers; viscosity

## INTRODUCTION

Zwitterionic polymers have been the subject of ongoing investigation in our laboratories because of their unique responsiveness to saline media.<sup>1</sup> Unlike polyelectrolytes (PEs), which bear *either* anionic or cationic charges, polyzwitterions (PZs) bear *both* anionic and cationic functionalities. PZs may be categorized as polyampholytes (anionic and cationic charges on *separate* repeat units) or polybetaines (anionic and cationic charges on the *same* repeat unit). In aqueous solution, PE coils generally contract with increasing ionic strength because of the screening of intramolecular repulsions between like charges along the polymer backbone.<sup>2</sup> This phenomenon, known as the PE effect, tends to impair the viscosity performance of PEs in applications in which the polymers encounter saline media. In con-

trast to PEs, PZ solutions exhibit “antipolyelectrolyte” behavior in which the polymer adopts a more expanded conformation with increasing ionic strength.<sup>3</sup> This effect is attributed to the screening of intramolecular attractions between the anionic and cationic moieties along or pendant to the polymer backbone by the small molecule electrolytes. The increase in hydrodynamic size is also accompanied by an increase in solution viscosity, making PZs ideal candidates for salt-tolerant viscosifiers.

Another area of academic and industrial endeavor is the synthesis of hydrophobically modified (HM) water-soluble polymers by micellar copolymerization and the study of their solution behavior in aqueous media. These hydrophilic copolymers contain small amounts (typically  $\leq 1$  mol %) of hydrophobic comonomers that enable viscosification through intermolecular hydrophobic associations.<sup>4–9</sup> Often referred to as associative thickeners (ATs), the HM copolymers exhibit greater thickening efficiencies and more complex rheological properties compared to those of their unmodified counterparts. Several polymer systems investigated by our group have proven to be effective ATs with pH- and shear-responsive behavior.<sup>10–16</sup> These systems have potential for application in areas such as enhanced oil recovery, drag reduction, and in

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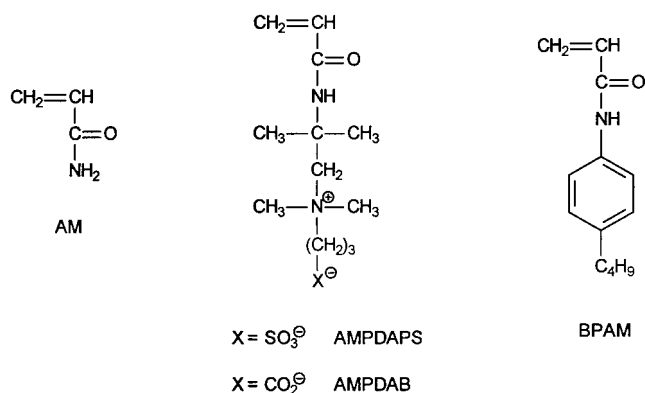
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the formulation of coatings, personal care products, and cosmetics.

Efforts have been made to produce associative PZs that combine the benefits of PZ salt tolerance and HM copolymer thickening efficiency. Salamone and coworkers<sup>17–24</sup> investigated unique HM polyampholytes that incorporated 2-methacryloyloxyethyl-*N*-alkyl-*N,N*-dimethylammonium bromide monomers that are cationic and hydrophobic in nature. In one study,<sup>22</sup> HM cationic monomers bearing alkyl chains of different lengths were used to prepare ion-pair comonomers (IPCs) with sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS). The resulting IPCs were copolymerized with acrylamide (AM) to yield HM polyampholytes; subsequent rheological studies revealed that the solution viscosities of the terpolymers were highly dependent on the level of IPC incorporation and on the length of the alkyl chains.<sup>21</sup> As a result of the hydrophobic modification, these polyampholytes were shown to maintain solution viscosity over wide ranges of salt concentration. Candau and coworkers<sup>25</sup> reported the micellar copolymerization of AM, NaAMPS, 3-(methacryloyloxyethyl)trimethylammonium chloride (MOETAC), and either *N,N*-dihexylacrylamide or *N*-ethylphenylacrylamide as the hydrophobic comonomer to yield HM polyampholytes. The resulting HM polyampholytes exhibited both salt- and shear-responsive rheological behavior. Winnik and Wiyazawa<sup>26,27</sup> prepared phosphorylcholine-based HM polybetaines by postpolymerization modification of HM poly(*N*-isopropylacrylamide) with pendant amine moieties, and the solution behavior of the HM polybetaines was examined in mixed aqueous–organic media. Because of high levels of phosphobetaine and hydrophobic comonomer incorporation and the random sequence of comonomer incorporation, the polymers tended to behave as polymeric micelles and were not examined as ATs.

In the study reported here, terpolymers composed of acrylamide (AM), either 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS) or 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (AMPDAB) and *N*-butylphenylacrylamide (BPAM) (Fig. 1) were synthesized using micellar copolymerization techniques to yield HM polybetaines. These HM polybetaines combine the unique attributes of both PZs and ATs. Additionally, the HM polycarboxybetaines are pH-responsive because of their carboxylic acid functionality, thus allowing the HM polycarboxybetaines to exhibit PE, PZ, or combined PE–PZ behavior in aqueous solution. The pH- and salt-responsive solution behavior of the terpolymers, in particular the rheological response, is interpreted in terms of polymer composition and microstructure.



**Figure 1** Monomers employed in synthesis of HM polybetaines by micellar copolymerization.

## EXPERIMENTAL

### Materials

AMPDAPS,<sup>28</sup> AMPDAB,<sup>29</sup> and BPAM<sup>7</sup> were prepared according to previously reported synthetic procedures. Triton X-100 was purchased from Bio-Rad Laboratories (Hercules, CA). All other chemicals were purchased from Aldrich Chemical (Milwaukee, WI) and used as received except where indicated. Potassium persulfate (KPS) was recrystallized twice from deionized (DI) water. DI water was obtained from a Barnstead NANOPure reverse osmosis/filtration unit (resistivity = 18.0 M $\Omega$ ) (Dubuque, IA).

### Terpolymer synthesis

To a 500-mL, three-neck round-bottom flask equipped with mechanical stirrer and N<sub>2</sub> inlet/outlet was added DI water (225 mL). The flask was immersed in a 50°C bath, and the contents were sparged with N<sub>2</sub> for 1 h. SDS (5.71 g, 0.020 mol) was added to the flask and allowed to dissolve, followed by the addition of BPAM (101.0 mg, 0.50 mmol). Solubilization of BPAM was complete after 45 min, as indicated by the transparent appearance of the reactor contents. AM (5.24 g, 0.074 mol) and AMPDAPS (7.24 g, 0.025 mol) were then added to the flask and the mixture was stirred for 10 min. KPS (8.9 mg, 0.033 mmol) dissolved in 5 mL of degassed DI water was then added to the flask by syringe. The polymerization was allowed to proceed under N<sub>2</sub> atmosphere for 4.5 h. The stirring speed was adjusted to maintain a shallow vortex in the reaction medium. Polymerization was terminated by precipitating the polymer in an excess of acetone. The precipitated polymer was redissolved in DI water, purified by dialysis against DI water using Spectra-Por No. 4 dialysis tubing (molecular weight cutoff = 12,000–14,000 g/mol) for 2 weeks, and isolated by lyophilization.

**TABLE I**  
Target Compositions of HM Polybetaines and Control Polymers

Sample ID	AM <sup>a</sup> (mol %)	AMPDAPS <sup>a</sup> (mol %)	AMPDAB <sup>a</sup> (mol %)	BPAM <sup>a</sup> (mol %)
HSB5	94.5	5	—	0.5
HSB25	74.5	25	—	0.5
SB5	95	5	—	—
HCB5	94.5	—	5	0.5
HCB25	74.5	—	25	0.5
CB5	95	—	5	—
HAM	99.5	—	—	0.5
PAM	100	—	—	—

<sup>a</sup> Indicates mol % monomer present in the feed ratio.

The HM polybetaine terpolymers were designated as either HSB# (sulfobetaine series) or HCB# (carboxybetaine series), where # indicates the mol % of betaine comonomer present in the feed. Copolymers lacking either BPAM or betaine comonomer were prepared for the purpose of performing comparative studies. For example, copolymers of AM and AMPDAPS or AMPDAB were synthesized using the same procedure outlined above, but in the absence of BPAM. These copolymers are designated SB# and CB#, respectively. A nonionic copolymer of AM and BPAM was prepared by micellar copolymerization using the above procedure and was designated HAM. A polyacrylamide homopolymer, designated PAM, was also synthesized under micellar conditions. The sample nomenclature and target compositions of the HM polybetaines and control polymers synthesized for this study are indicated in Table I.

### Instrumentation and analysis

#### UV-vis spectroscopy

UV spectra were obtained using a Hewlett-Packard Model 8452A photodiode-array spectrophotometer (Hewlett-Packard, Palo Alto, CA). The fixed resolution was 2 nm. The sample optical density was maintained below 1.0 and the model compound used was *N*-(4-butyl)phenylamidopropionic acid.<sup>7</sup>

#### <sup>13</sup>C-NMR and <sup>1</sup>H-NMR spectroscopy

<sup>13</sup>C-NMR and <sup>1</sup>H-NMR spectra were obtained with a Bruker AC 200 spectrometer (Bruker Instruments, Billerica, MA) and processed using software provided by the manufacturer. Betaine comonomer incorporation was determined by inverse-gated decoupled <sup>13</sup>C-NMR with a delay time of 6 s.

#### Compositional analysis

Terpolymer compositions were determined using results from inverse-gated decoupled <sup>13</sup>C-NMR and

UV-vis experiments. The representative relationships used to calculate the mol % of each monomer in the terpolymers are given by eqs. (1) and (2), as follows:

$$x = (C - z) - y \quad (1)$$

$$Y = \frac{\frac{y}{MW_y}}{\left(\frac{(C - z) - y}{MW_x}\right) + \left(\frac{y}{MW_y}\right) + \left(\frac{z}{MW_z}\right)} \quad (2)$$

where *C* is the total polymer concentration in the UV-vis sample solution (in g/dL); *x* is the AM concentration (in g/dL); *y* is the betaine monomer concentration (in g/dL); *Y* is the betaine comonomer incorporation [in mol % (from <sup>13</sup>C-NMR)]; *z* is the BPAM concentration [in g/dL (from UV-vis)]; and *MW<sub>x</sub>*, *MW<sub>y</sub>*, and *MW<sub>z</sub>* are the molecular weights of AM, the betaine comonomer (AMPDAPS or AMPDAB), and BPAM, respectively.

#### Classical light scattering

Classical light scattering (LS) measurements were performed on a Brookhaven Instruments BI-200SM automatic goniometer (Holtville, NY) equipped with a Spectra-Physics 127 laser (632.8 nm) and BI-2000 autocorrelator (Mountain View, CA). Berry plots were obtained using software provided by the manufacturer. Data points for classical LS analysis were taken at 60, 70, 90, 100, 110, and 135° and at 25°C. The polymers were examined in 0.5M NaCl and purified by extensive centrifugation in an Eppendorf 5415C ultracentrifuge (Brinkmann Instruments, Westbury, NY). Errors in reported molecular weights ranged from 0.4 to 5.8%. Refractive index increments were measured using a Chromatix KMX-16 laser differential refractometer (Thermo-Separation Products, Sunnyvale, CA) operating at 632.8 nm and 25°C.

#### Potentiometric titration

Potentiometric titrations were conducted using an Orion model 900A titration system (Thermo Electron, Waltham, MA) under an inert atmosphere. Titration samples were purged with N<sub>2</sub> until a constant pH was maintained. The experimental error associated with the titration was ±0.05 pH units.

#### Solution rheology

Polymer stock solutions were prepared by dissolving lyophilized polymer in DI water and allowing them to age 7 to 10 days while agitating gently on an orbital shaker. Stock solutions were diluted with DI water to the desired concentration and allowed to age for sev-

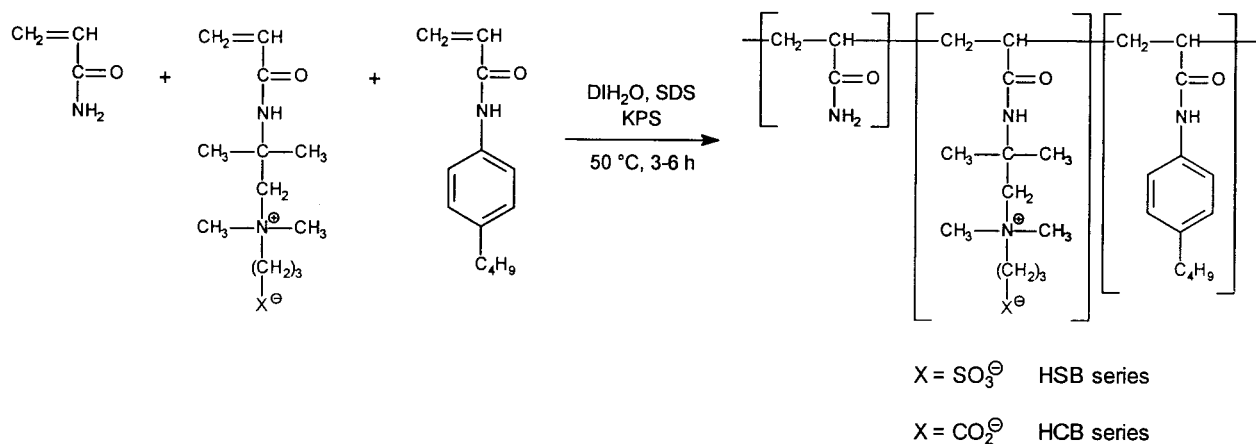


Figure 2 Synthesis of HM polybetaine terpolymers.

eral days on an orbital shaker before analysis. Solution viscosity measurements were performed using a Contraves LS-30 low-shear rheometer (Zurich, Switzerland). The measurements were conducted at 25°C at a shear rate of 5.96 s<sup>-1</sup>. Reported viscosities are the average of five measurements. The upper viscosity limit of the rheometer was taken as 125 cP.

## RESULTS AND DISCUSSION

### Polymer synthesis

AM-based HM polybetaine terpolymers were synthesized by micellar copolymerization using the feed ratios outlined in Table I (see Fig. 2). The terpolymers contain sulfobetaine (AMPDAPS) or carboxybetaine (AMPDAB) comonomers at low (5 mol %) and high (25 mol %) incorporations, and the single-tailed alkylaryl acrylamide monomer BPAM was used as the hydrophobic comonomer. The HM polysulfobetaine and HM polycarboxybetaine terpolymers were designated as the HSB# and HCB# series, respectively, where # indicates the targeted level of betaine comonomer incorporation. To enable comparative studies that distinguish the effects of betaine and hydrophobic comonomer incorporation, control (co)polymers CB5, SB5, HAM, and PAM (refer to Table I for target compositions) were synthesized.

The average number of BPAM monomers per micelle ( $N_{\text{H}}$ ) was calculated to be 1.65 using the following equation:

$$N_{\text{H}} = \frac{[\text{BPAM}] \times N_{\text{agg}}}{[\text{SDS}] - \text{cmc}_{\text{SDS}}} \quad (3)$$

in which [BPAM] is the concentration of BPAM (in mol/L),  $N_{\text{agg}}$  is the aggregation number of SDS ( $N_{\text{agg}} \approx 62$  for SDS), [SDS] is the concentration of SDS (in

mol/L), and  $\text{cmc}_{\text{SDS}}$  is the critical micelle concentration of SDS [in mol/L ( $8.1 \times 10^{-3}$  mol/L)].<sup>12</sup>

It was assumed that the presence of the betaine comonomers in the micellar polymerization medium did not significantly change the aggregation number of SDS during HM terpolymer synthesis. This is a reasonable assumption, given that the betaine monomers are entirely hydrophilic and lack amphiphilic character that would cause them to comicellize with SDS.

### Polymer characterization

#### Compositional analysis

Polymer compositions (Table II) were determined from the combined results of UV and inverse-gated decoupled <sup>13</sup>C-NMR spectroscopic analysis. The carbonyl region of a typical <sup>13</sup>C-NMR spectrum used to determine betaine comonomer incorporation is shown in Figure 3 (note that the carbonyl peak for BPAM is

TABLE II  
Compositional Data for the HM Polybetaine Terpolymers and the Control Samples

Sample ID	AM (mol %)	Betaine comonomer <sup>a</sup> (mol %)	BPAM <sup>b</sup> (mol %)
HSB5	95	4.1 <sup>c</sup>	0.88
HSB25	76	23 <sup>c</sup>	1.0
SB5	95	5.0 <sup>c</sup>	—
HCB5	96	3.6 <sup>d</sup>	0.64
HCB25	82	17 <sup>d</sup>	1.0
CB5	91	8.9 <sup>d</sup>	—
HAM	99.5	—	0.55

<sup>a</sup> Determined by inverse gated decoupled <sup>13</sup>C-NMR.

<sup>b</sup> Determined by UV-vis spectroscopy.

<sup>c</sup> AMPDAPS.

<sup>d</sup> AMPDAB.

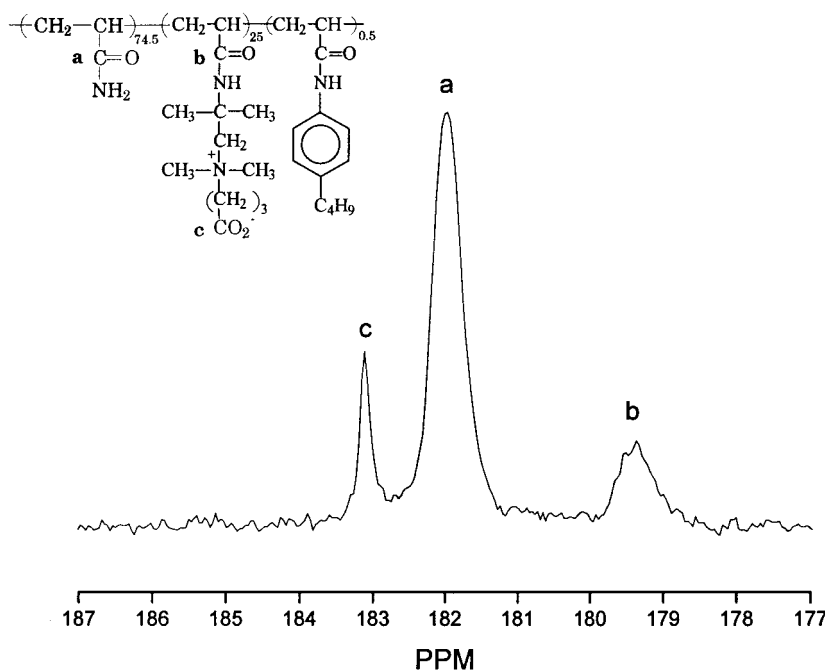


Figure 3 Carbonyl region of HCB25  $^{13}\text{C}$ -NMR spectrum.

undetectable because of low incorporation). The values for betaine comonomer incorporation agree reasonably well with the target values (Table I), given the margin of error (typically  $\geq 5\%$ ) associated with  $^{13}\text{C}$ -NMR as a quantitative analytical tool. Although polymerizations were halted at  $< 50\%$  conversion to avoid compositional drift, BPAM incorporation in the HM samples is consistently higher than the target value of 0.5 mol %. These results are consistent with those reported by Middleton and coworkers<sup>7</sup> for BPAM-modified AM copolymers that were synthesized under similar micellar conditions. Additionally, Candau and coworkers<sup>30</sup> reported copolymer drift and higher molar incorporations of hydrophobes with single tails.

#### Light scattering analysis

Classical light scattering data for the polymers synthesized in this study are given in Table III. Values of

TABLE III  
Classical Light-Scattering Data for the HM Polybetaines and the Control Samples

Sample ID	$M_w^a$ ( $10^6$ g/mol)	$A_2^a$ ( $\text{cm}^3 \text{ mol/g}$ ) <sup>-2</sup>
HSB5	0.827	$1.3 \times 10^{-3}$
HSB25	1.13	$-4.82 \times 10^{-5}$
SB5	0.819	$4.08 \times 10^{-4}$
HCB5	1.29	$-9.18 \times 10^{-5}$
HCB25	0.419	$-5.77 \times 10^{-3}$
CB5	1.16	$1.36 \times 10^{-4}$
HAM	0.806	$-2.52 \times 10^{-3}$
PAM	0.850	$4.2 \times 10^{-3}$

<sup>a</sup> Determined in 0.5M NaCl at 25°C.

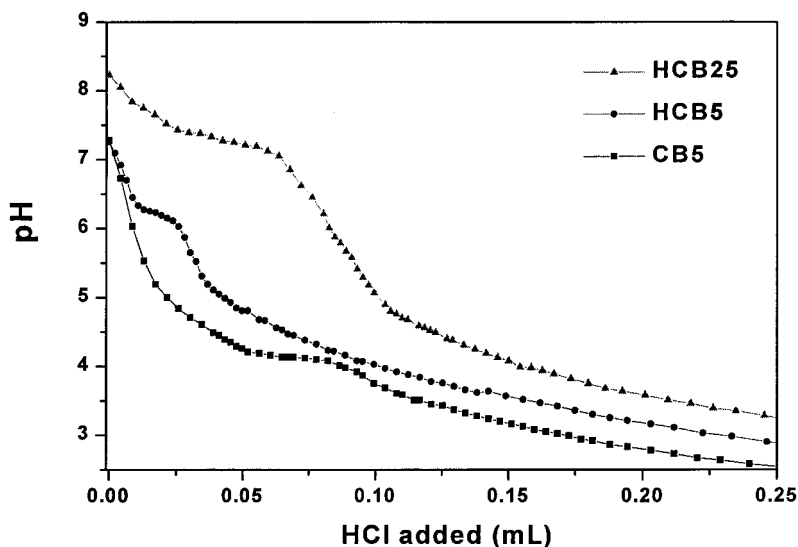
weight-average molecular weight ( $M_w$ ) range from  $4.19 \times 10^5$  g/mol (HCB25) to  $1.29 \times 10^6$  g/mol (HCB5). All HM polymers except HSB5 exhibit negative second virial coefficients ( $A_2$ ), a commonly observed phenomenon for associative polymers analyzed by classical light scattering in aqueous media.

#### Potentiometric titration

Potentiometric titrations were performed on the carboxybetaine polymers (Fig. 4). The  $\text{p}K_a$  values were found to increase with increasing BPAM incorporation. The  $\text{p}K_a$  of CB5 is 4.1, which is typical of carboxybetaines; however, the  $\text{p}K_a$  values of HCB5 and HCB25 are 6.2 and 7.2, respectively. It is reasonable that increasing hydrophobe incorporation increases  $\text{p}K_a$  values because of shifts in the Henderson–Hasselbach equilibrium as a consequence of restricted polymer conformation and local dielectric effects. These results indicate that both HCB5 and HCB25 possess some PE character at ambient pH.

#### Polymer solution rheological behavior

Overall, the polymer solutions exhibit behavior characteristic of HM- and/or PZ-type polymers, with the exception of HCB25, which has quite unusual behavior likely attributable to the high level of AMPDAB incorporation. Results from each rheological experiment are given in the following section along with possible explanations for the observed behavior based on the structure and composition of the polymers.



**Figure 4** Potentiometric titration curves for the HM carboxybetaine terpolymers (HCB25 and HCB5) and the carboxybetaine copolymer (CB5).

An important factor to consider when examining polymer solution behavior is the critical overlap concentration ( $c^*$ ) of the polymer solution. Below  $c^*$  (i.e., in the dilute regime), individual polymer chains are essentially isolated from each other, and the solution viscosity is dependent on the individual contributions of the solvated polymer coils. At  $c^*$ , polymers in solution become entangled, and the solution viscosity increases more rapidly with increasing polymer concentration. Above  $c^*$  (i.e., in the semidilute regime), the solution viscosity is dependent on the individual contributions of the polymer coils plus the entanglements between the network of overlapping coils. For solutions of associative (e.g., hydrophobically or electrostatically associating) polymers, network formation occurs at lower concentrations than for nonassociative polymers—due to the onset of intermolecular associations that occur before chain entanglement.<sup>31,32</sup> This network formation is accompanied by a dramatic increase in solution viscosity. Thus, associative polymers are typically more efficient thickeners than their unmodified counterparts because the formation of intermolecular hydrophobic junctions offers an additional viscosification mechanism above  $c^*$ .

Viscosity profiles of the HM sulfobetaine terpolymers and relevant control (co)polymers are shown in Figure 5. HSB5 exhibits the greatest increase in viscosity with increasing polymer concentration, followed by HAM, SB5, HSB25, and PAM. Based on these data, several comparisons can be made to rationalize structure–behavior relationships. Peiffer and Lundberg<sup>33</sup> reported that AM-based polyampholytes containing charge densities of less than 10 mol % mainly associate intermolecularly at concentrations of 1 to 3 g/dL, whereas polyampholytes with charge densities greater

than 10 mol % associate intramolecularly. These zwitterionic systems incorporated quaternary amines and sulfonate groups similar to those used in the AMPDAPS-containing samples. The viscosity data illustrated in Figure 5 appear to be consistent with those reported by Peiffer and Lundberg.<sup>33</sup> The terpolymer with low zwitterionic monomer incorporation, HSB5, attains higher viscosity compared to that of the terpolymer with higher zwitterionic incorporation, HSB25, despite its lower molecular weight and comparable hydrophobe incorporation. Interactions between sulfobetaine units are relatively strong and cause AM-based polymers containing large amounts ( $\geq 60$  mol %) of sulfobetaine comonomer to be insoluble in DI water.<sup>28</sup> It may be postulated that at 25 mol % sulfobetaine incorporation, zwitterions on the same chain are present in sufficient concentrations to severely restrict polymer conformation yet still allow formation of soluble, intramolecularly associated complexes.

A meaningful comparison may be made between SB5 and HAM because of similar molecular weight values. In the concentration range studied, HAM shows a sharp upturn in reduced viscosity as a function of polymer concentration, whereas SB5 does not; this provides evidence that HAM passes through  $c^*$  in this concentration range and that there are intermolecular associations of the BPAM moieties on the HAM chains. It is also reasonable to conclude that the hydrophobic association of BPAM moieties has a greater effect on the solution rheology of HSB5 than does the electrostatic association of AMPDAPS moieties.

The rheological behavior of the HM carboxybetaine terpolymers and relevant control (co)polymers was

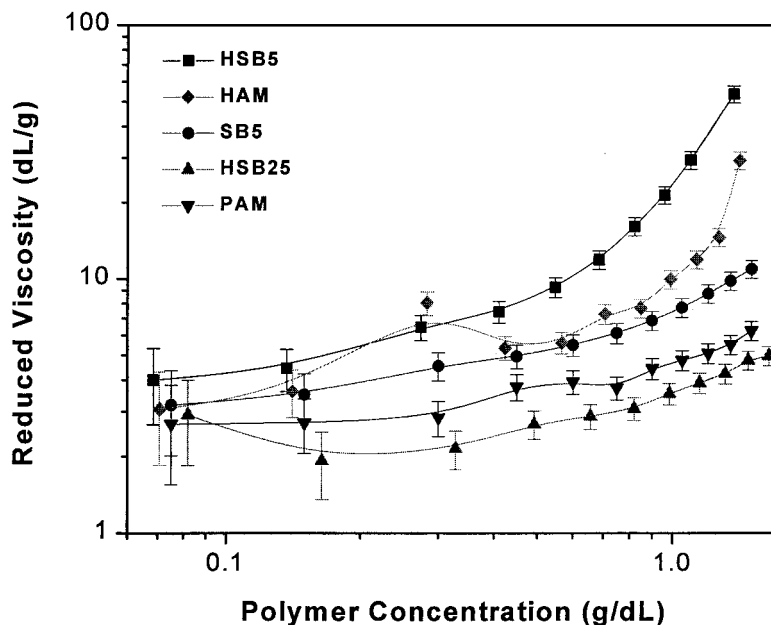


Figure 5 Viscosity profiles of HM sulfobetaine terpolymers and control polymers in DI water at ambient pH ( $7.5 \pm 0.5$ ).

also studied as a function of concentration at ambient pH (Fig. 6). HCB25 exhibits a much higher solution viscosity than that of the other carboxybetaine-containing polymers in DI water, despite its relatively low molecular weight. Because of the high viscosity of the HCB25 solutions in DI water, measurements were made at lower polymer concentrations than the other samples to prevent the upper viscosity limit of the LS-30 rheometer from being exceeded. After HCB25, HCB5 appears to be the most efficient thickener because of hydrophobic modification. Incorporation of

carboxybetaine moieties appears to have a substantial effect on viscosity enhancement, presumably attributable to the greater hydrophilicity of the carboxybetaine relative to that of the sulfobetaine.<sup>34,35</sup> CB5 is a more effective viscosifier than HAM, contrasting the behavior of SB5 and HAM mentioned earlier. The molecular weight of CB5 is  $1.16 \times 10^6$  g/mol, whereas that of HAM is  $8.06 \times 10^5$  g/mol. Although molecular weight differences may be partly responsible for this behavior, the increased hydrophilicity of CB5 most likely plays a more crucial role, allow-

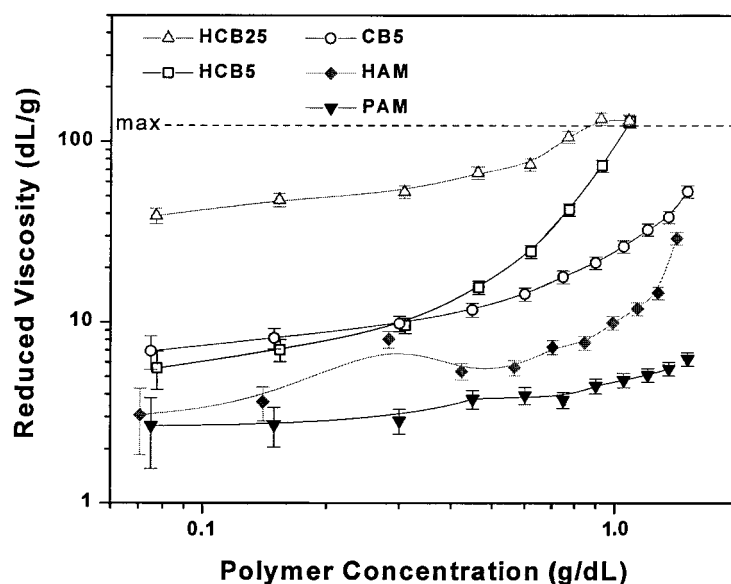
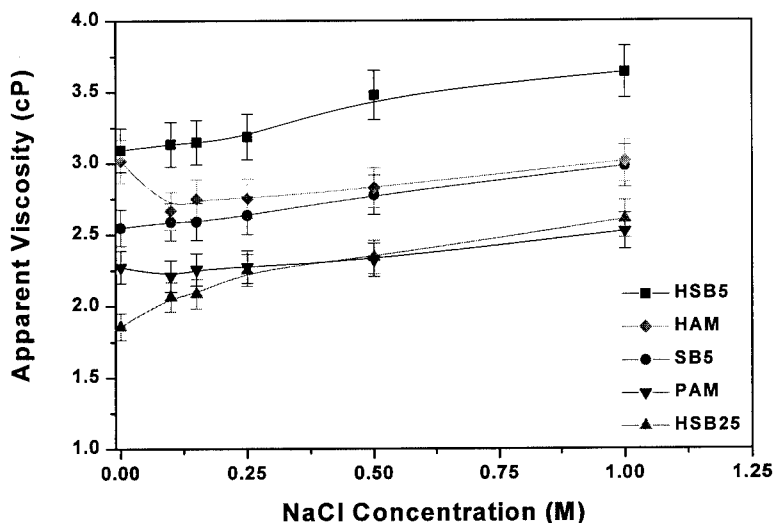


Figure 6 Viscosity profiles of HM carboxybetaine terpolymers and control polymers in DI water at ambient pH ( $7.5 \pm 0.5$ ).



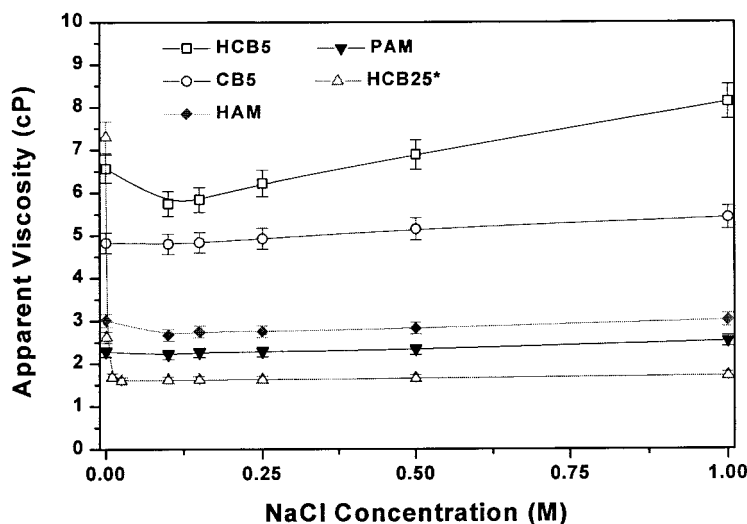
**Figure 7** Reduced viscosity as a function of NaCl concentration for the HM sulfobetaine terpolymers and control polymers. Polymer concentration = 0.4 g/dL, ambient pH ( $7.5 \pm 0.5$ ).

ing CB5 to adopt a more expanded conformation than that of HAM.

#### Effect of salt

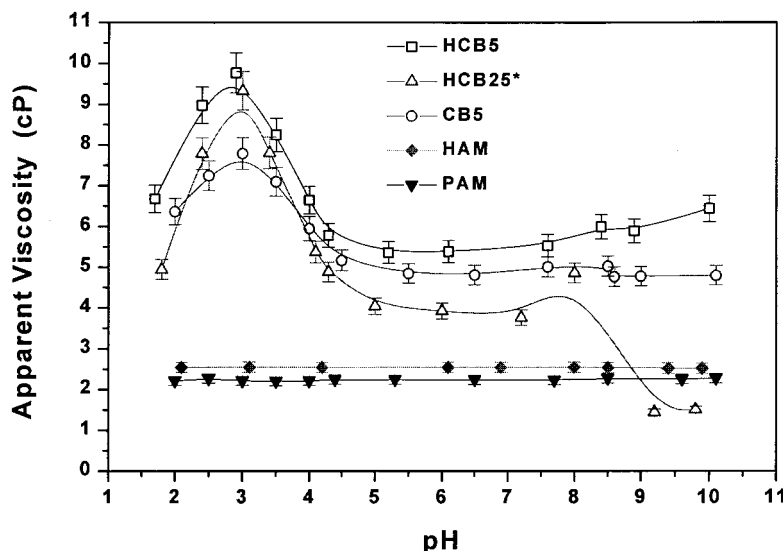
The effect of NaCl addition on the solution viscosity of the HM sulfobetaine terpolymers and relevant control (co)polymers was investigated (Fig. 7). HSB25, HSB5, and SB5 were found to respond to the addition of salt at a polymer concentration of 0.4 g/dL. The increase in viscosity at higher salt concentrations is consistent with the disruption of intramolecular zwitterionic associations attributed to shielding by the added ions. HAM exhibits a viscos-

ity decrease at low NaCl concentration as a consequence of increased intramolecular hydrophobic association in the presence of salt. Figure 8 depicts the effect of NaCl concentration on the viscosity behavior of the HM carboxybetaine terpolymers and relevant control (co)polymers. A very slight initial decrease in viscosity was observed for HCB5, followed by an increase. The initial decrease may be attributed to a slight PE effect, followed by typical PZ response to added electrolytes. The small PE effect is likely attributable to the relatively high  $pK_a$  ( $pK_a = 6.2$ ) of this polymer (Fig. 4). HCB25 demonstrates classical PE behavior in the presence of very low concentrations (e.g., 1 mM) of NaCl; the solution



**Figure 8** Apparent viscosity as a function of NaCl concentration for the HM carboxybetaine terpolymers and control polymers. Polymer concentration = 0.4 g/dL, except for HCB25, where polymer concentration = 0.1 g/dL, ambient pH ( $7.5 \pm 0.5$ ).





**Figure 9** Apparent viscosity as a function of pH for the HM carboxybetaine terpolymers and control polymers. Polymer concentration = 0.4 g/dL, except for HCB25, polymer concentration = 0.1 g/dL.

viscosity of HCB25 dramatically decreases and does not increase on further salt addition (i.e., an anti-polyelectrolyte effect was not observed).

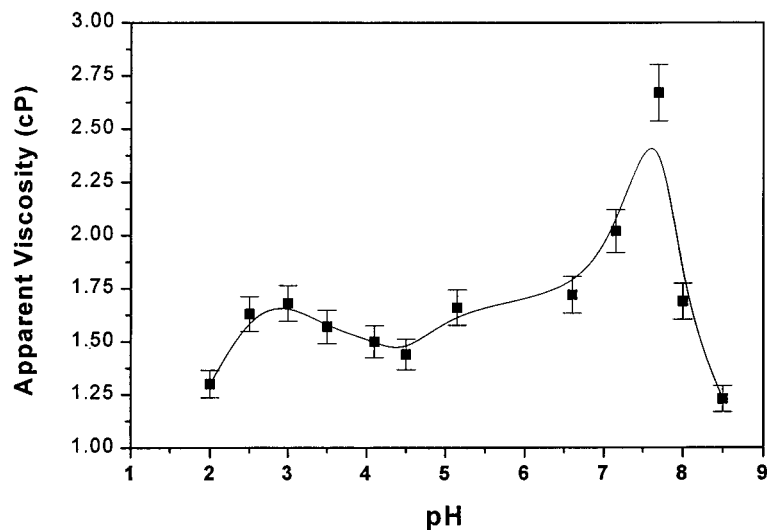
#### Effect of pH

The ambient pH of most polymer solutions in this study ranged from 7.0 to 7.5. Adjustment of pH was readily achieved by the addition of small aliquots of concentrated HCl or NaOH. No effect of pH on solution viscosity was detected for sulfobetaine-containing polymers. This was expected because of the very low  $pK_a$  ( $pK_a \approx -9$ ) of the sulfonate moiety.<sup>35</sup> As shown in Figure 9, a maximum in viscosity at  $pH \approx 3$  is apparent in all carboxybetaine polymers. This phenomenon was previously reported and is attributed to polycation formation as the pH is lowered, thus causing an increase in viscosity resulting from intramolecular charge–charge repulsion.<sup>29</sup> At pH values below 3, intramolecular association of the carboxylic acid groups and the excess ionic strength of the solutions become significant, inducing collapse of the PE coils and causing the observed decrease in viscosity.<sup>13,36</sup>

HCB25 solutions exhibit unusual (and unexpected) pH-responsive behavior. When HCB25 was dissolved in DI water, the solution pH was approximately 7.5. At pH 3, all three carboxybetaine-containing polymers exhibited a maximum in viscosity attributed to the polycation nature of the polymers because the carboxylate groups of the betaine are protonated. However, unlike HCB5 and CB5, HCB25 exhibited a reproducible maximum in viscosity at pH 7.5–8.0, followed by a sharp decline in solution viscosity at successively higher pH values (Fig. 9). An additional viscosity study as a function of pH was performed on HCB25 at

a lower polymer concentration (Fig. 10) to determine whether the unusual pH response was being caused by a pH-induced transition from dilute to semidilute conditions (i.e., pH-induced chain overlap). The relative size of the anomalous pH 7.5 peak increased, whereas the pH 3 peak maximum decreased.

Based on these experimental observations, the unusual behavior of HCB25 can be rationalized by considering the following conceptual model, which describes the associative nature of the polymer as a function of pH. Recall that the  $pK_a$  of HCB25 ( $pK_a = 7.2$ ) is higher than that of typical carboxybetaines ( $pK_a = 4$ ); thus most of the carboxybetaine units on this polymer will be protonated in the low-to-intermediate pH range (i.e., pH 2 through pH 7.5, the ambient solution pH of HCB25 in DI water). In this pH range, HCB25 behaves as a cationic PE, and intra- and intermolecular electrostatic associations between carboxybetaine units are not possible because those repeat units are not in their zwitterionic form. However, the carboxylic acids of the protonated betaine are capable of hydrogen-bonding associations with other betaine moieties, as well as with the pendant amide groups of the PAM backbone. (This phenomenon was previously observed in HM copolymers of AM with acrylic acid.<sup>13</sup>) In addition to hydrogen-bonding associations, the hydrophobic BPAM units are also capable of intra- and intermolecular association. At  $pH \geq 8.0$ , the carboxybetaine moieties become fully ionized, and electrostatic associations between the zwitterionic species are possible. Under these conditions, the carboxylic acid groups are deprotonated and unable to form hydrogen bonds. The ability of the BPAM units to associate is assumed to remain unchanged above pH 8.0.



**Figure 10** Apparent viscosity of HCB25 as a function of pH in DI water. Polymer concentration = 0.025 g/dL.

With respect to the pH dependency of the HCB25 association mechanisms, the responsive solution viscosity may now be considered in terms of polymer solution concentration. At low concentrations (e.g., 0.025 g/dL; Fig. 10), HCB25 exhibits decreased solution viscosity from pH 2 through pH 7; in this regime, intramolecular hydrophobic associations coupled with intramolecular hydrogen bonding reduces the compact hydrodynamic volume of the polymer chains. As the solution pH was increased to pH 7.5, intramolecular hydrogen bonding was lessened, leading to increases in hydrodynamic volume and the local maximum in solution viscosity. Above pH 7.5, the ionized carboxybetaine moieties underwent intramolecular associations that led to chain collapse that was further promoted by the intramolecular association of the hydrophobic BPAM moieties.

At higher solution concentrations (e.g., 0.1 g/dL; Fig. 9), the maxima in HCB25 solution viscosity profiles were more pronounced because the polymers approach the semidilute regime and can undergo intermolecular associations with appropriate stimuli. For example, at pH 3 the extended polycationic chains are capable of undergoing intermolecular hydrophobic and hydrogen-bonding associations. Therefore, it appears that the solution behavior of HCB25 is the result of a complex combination of electrostatic, hydrogen-bonding, and hydrophobic effects that are readily influenced by changes in polymer concentration, solution pH, and salt concentration.

## CONCLUSIONS

A series of novel HM polysulfobetaine and polycarboxybetaine terpolymers were synthesized by micellar

copolymerization along with corresponding control (co)polymers. The solution properties of the polymers were investigated as functions polymer concentration, solution pH, and NaCl concentration. Results from rheological analysis indicated that low incorporations of sulfobetaine comonomer may promote intermolecular association above  $c^*$ , yet intramolecular associations prevailed at high sulfobetaine comonomer incorporation. In addition to being non-pH-responsive, solutions of polysulfobetaines were relatively unaffected by the addition of NaCl. Carboxybetaine-containing polymers were more responsive, attributed in part to the favored cationic charge imbalance at ambient pH (as shown by potentiometric titration) and to the antipolyelectrolyte effect. Polycarboxybetaines can exhibit varying degrees of PE or PZ behavior depending on solution pH. The HM polycarboxybetaine containing a high betaine comonomer incorporation (HCB25) exhibited solution behavior that is quite different from that of the other polymers in this study, including extreme sensitivity to the solution pH and dissolved NaCl. This behavior was attributed to a complex interplay of hydrophobic interactions, hydrogen-bonding, and electrostatic interactions that may lead to reversible network formation in solution.

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