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Water-Soluble Copolymers. XLI. Copolymers of Acrylamide and Sodium 3-Acrylamido-3-methylbutanoate

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WATER-SOLUBLE COPOLYMERS. XLI. COPOLYMERS OF ACRYLAMIDE AND SODIUM 3-ACRYLAMIDO-3-METHYLBUTANOATE

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ABSTRACT

Copolymers of acrylamide (AM, M_1) with sodium 3-acrylamido-3-methylbutanoate (NaAMB, M_2) synthesized in 1 *M* NaCl (the ABAM2 series) are compared to those synthesized in deionized water (the ABAM1 series). At fixed feed ratios, higher incorporation rates were found for NaAMB with increasing ionic strength of the polymerization solvent. Reactivity ratios calculated by the methods of Kelen-Tüdös changed from $r_1 = 1.23$ and $r_2 = 0.50$ in deionized water to $r_1 = 1.00$ and $r_2 = 0.64$ in 1 *M* NaCl. This change is in accord with a decrease in electrostatic repulsion between the macroradical and unreacted NaAMB. Dilute solution properties, examined as a function of composition and added electrolytes, indicate differences in microstructure for the ABAM1 and ABAM2 copolymers.

INTRODUCTION

Water-soluble polymers that maintain high solution viscosities in the presence of added electrolytes have been the subject of our continuing research [1–3]. We have previously studied the copolymers of sodium 3-acrylamido-3-methylbutanoate (NaAMB, M_2) with acrylamide (AM, M_1) synthesized in deionized water [4, 5]. NaAMB (Fig. 1) is the carboxylated version of the pH stable monomer sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS). These monomers feature two geminal methyl groups that protect the amide functionality from hydrolysis. The

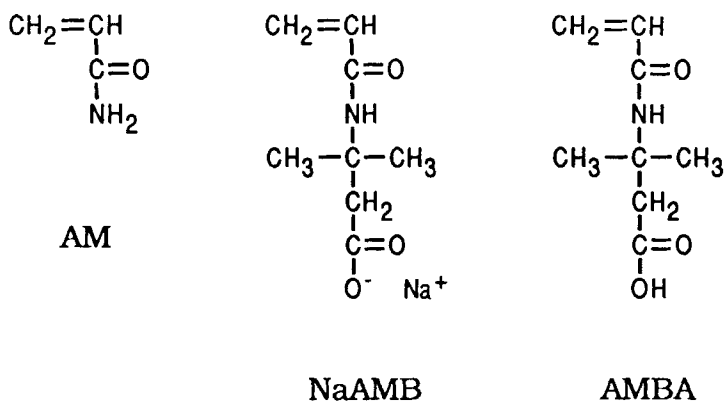


FIG. 1. Structures of comonomers: acrylamide (AM); sodium 3-acrylamido-3-methylbutanoate (NaAMB); and 3-acrylamido-3-methylbutanoic acid (AMBA).

acrylamido functionality allows polymerization to high molecular weights due to a high value of k_p^2/k_t .

Homopolymers of NaAMB and copolymers with AM are chain-extended, water-soluble polymers known for their phase stability in the presence of Na^+ and Ca^{2+} and in high-temperature environments [4, 5]. Their attractive viscosity characteristics and electrolyte tolerance have been attributed to neighboring group and intraunit interactions.

In this study, we examine the effects of changing the ionic strength of the polymerization solvent (water) on polymer microstructure and on solution properties. By synthesizing the homopolymer of NaAMB, and the copolymers with AM, in the presence of electrolytes, we anticipate changes in microstructure and thus in solution behavior [6].

EXPERIMENTAL

Materials and Monomer Synthesis

3-Acrylamido-3-methylbutanoic acid (AMBA) monomer was synthesized via a Ritter reaction of equimolar amounts of 3,3-dimethylacrylic acid with acrylonitrile as reported by Hoke and Robins [7] and modified by McCormick and Blackmon [4]. AM from Aldrich was recrystallized twice from acetone prior to use. Potassium persulfate from Aldrich was recrystallized twice from water prior to use. Reagent-grade sodium chloride from Fisher Scientific was used without further purification.

Synthesis of Copolymers of Sodium 3-Acrylamido-3-Methylbutanoate and Acrylamide in the Presence of NaCl

The ABAM2 series of copolymers was synthesized by free radical polymerization of NaAMB with AM in 1 M NaCl solution. These copolymers were compared with the copolymers of the analogous ABAM1 series previously synthesized in deionized water by McCormick and Blackmon [4]. In both cases potassium persulfate

was used as the initiator; the reactions were conducted at 30°C and pH 9 with a 0.46 *M* monomer concentration. For each series the amount of acrylamide in the feed varied from 25 to 90 mol%.

A typical synthesis involved the dissolution of specified quantities of the monomers in separate solutions. The sodium salt NaAMB was obtained by the addition of NaOH to AMBA. The monomers were then mixed to form a single solution. Following adjustment of the pH to 9, the reaction mixture was transferred to a 500-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and gas bubbler. The mixture was sparged with nitrogen for 20 min and then initiated with 0.1 mol% potassium persulfate. Samples were taken at low and moderate conversions to study copolymer drift. The polymers were precipitated in acetone, redissolved in deionized water, and then dialyzed using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12,000–14,000 Daltons. After isolation by lyophilization, the copolymers were stored in desiccators. IR: ABAM2-100 homopolymer, N—H (broad), 3400–3300 cm^{-1} ; C—H, 2955 cm^{-1} ; amide C=O, 1655 cm^{-1} ; sodium salt C=O, 1580 cm^{-1} . Typical copolymer: ABAM2-40, N—H (broad), 3450–3300 cm^{-1} ; AM amide C=O, 1665 cm^{-1} ; NaAMB amide C=O, 1655 cm^{-1} (s), 1520 cm^{-1} (m); sodium salt C=O, 1580 cm^{-1} . ^{13}C NMR: ABAM2-40, Acrylamido C=O, 182.3 ppm; NaAMB C=O, 178.1 ppm; chain CH_2 , 38.0 ppm; chain CH, 44.6 ppm; gem CH_3 , 29.0 ppm; NaAMB C, 55.4 ppm; NaAMB CH_2 , 50.8 ppm.

Copolymer Characterization

Elemental analyses for carbon, hydrogen, and nitrogen were conducted by M-H-W Laboratories (Phoenix, AZ) on both the low- and high-conversion copolymer samples. ^{13}C NMR spectra were obtained using 10 wt% aqueous (D_2O) polymer solutions. The procedure for quantitatively determining copolymer compositions from ^{13}C NMR has been discussed in detail elsewhere [8]. FT-IR spectra for all materials synthesized were obtained using a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Light-scattering studies were performed on a Chromatix KMX-6 low-angle laser light-scattering spectrophotometer, and refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. All measurements were conducted at 25°C in 0.512 *M* NaCl at a pH of 7.0 ± 0.1 .

Viscosity Measurements

Stock solutions of sodium chloride (0.042, 0.086, 0.257, and 0.514 *M* NaCl) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. Polymer solutions were then made by dissolution and dilution to appropriate concentrations. After 2–3 weeks of aging, the solutions were analyzed with a Contraves LS-30 rheometer.

RESULTS AND DISCUSSION

Copolymers of NaAMB and AM synthesized in deionized water (the ABAM1 series) are expected to be different from those synthesized in a 1 *M* NaCl aqueous solution (the ABAM2 series). At pH 9, well above the pKa of the carboxylic acid

group, AMBA exists in its charged form, NaAMB (Fig. 1). During polymerization the presence of NaCl should shield electrostatic interactions between charged groups, minimizing charge-charge repulsion between the NaAMB units on the growing macromolecular chain and the unreacted NaAMB.

Effects of NaCl on Composition

Varying comonomer feed compositions were used to synthesize the ABAM2 copolymer series with aqueous 1 M NaCl as the polymerization solvent (Table 1). The low conversion aliquots were taken when the reaction mixture first showed signs of increased viscosity. The polymerizations were then allowed to proceed to high conversion for optimum polymer yield. The compositions in Table 1 show a small amount of compositional drift as a result of the increased conversion. For example, the copolymerization conducted at a 60:40 ratio of AM:NaAMB showed a 1.2% increase in M2 composition at 24% conversion over that observed at 4.1% conversion. The copolymers synthesized in deionized water did not exhibit copolymer drift with increased conversion.

Elemental analysis was used to determine the copolymer compositions. The weight percentages of carbon and nitrogen obtained from elemental analysis can be represented by Eqs. (1) and (2).

$$\% C/12.01 = 3A + 8B \quad (1)$$

$$\% N/14.01 = A + B \quad (2)$$

TABLE 1. Reaction Parameters for the Copolymerization of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in 1 M NaCl

Sample number	Feed ratio (AM:NaAMB)	Reaction time (h)	Conversion (%)	Weight (% C)	Weight (% N)	NaAMB in copolymer (mol%) ^a
ABAM2-10-1	90:10	2.25	8.6	46.47	15.42	9.6 ± 0.2
ABAM2-10-2	90:10	4.42	20.1	45.66	15.08	10.6 ± 0.2
ABAM2-25-1	75:25	1.33	3.8	46.64	12.98	23.8 ± 0.5
ABAM2-25-2	75:25	10.25	14.1	—	—	24.8 ± 1.2 ^b
ABAM2-40-1	60:40	1.5	4.1	47.21	11.44	36.3 ± 0.9
ABAM2-40-2	60:40	8.0	24.0	46.46	11.12	37.5 ± 0.9
ABAM2-60-1	40:60	1.5	11.4	47.62	9.83	53.0 ± 1.4
ABAM2-60-2	40:60	4.0	17.8	46.63	9.15	56.4 ± 1.5
ABAM2-75-1	25:75	1.5	8.6	46.87	8.57	67.6 ± 1.9
ABAM2-75-2	25:75	3.0	30.6	45.49	8.15	70.2 ± 1.9
ABAM2-100	0:100	5.42	5.5	44.76	6.27	100 ^c
ABAM2-0	100:0	6.5	50.3	—	—	0 ^c

^aDetermined from elemental analysis.

^bDetermined from ¹³C NMR.

^cTheoretical value.

TABLE 2. Reaction Parameters for the Copolymerization of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in Solvents of Varying Ionic Strengths at a Fixed Feed Ratio

Sample number	Feed ratio (AM:NaAMB)	Ionic strength (mol/L)	Reaction time (h)	Conversion (%)	Weight (% C)	Weight (%N)	NaAMB in copolymer (mol%) ^a
ABAM2-75(D.I.)	25:75	0.00	2.66	4.0	44.36	8.53	61.3 ± 1.6
ABAM2-75(0.15)	25:75	0.15	2.66	7.1	44.39	8.60	60.4 ± 1.7
ABAM2-75(0.20)	25:75	0.20	4.00	3.5	46.34	8.76	63.4 ± 1.7
ABAM2-75(0.30)	25:75	0.30	3.75	23.6	46.88	8.58	67.5 ± 1.8
ABAM2-75(0.45)	25:75	0.45	2.33	7.0	45.86	8.23	70.0 ± 1.9
ABAM2-75(1.00)	23:75	1.00	1.50	8.6	45.49	8.15	67.6 ± 1.2

^aDetermined by elemental analysis.

The coefficients *A* and *B* are the number of moles of AM and NaAMB, respectively, in a normalized amount of copolymer, e.g., 1 g. The mole percent of each monomer in the copolymer may then be determined using Eqs. (3) and (4).

$$\text{mol\% AM} = A/(A + B) \times 100\% \quad (3)$$

$$\text{mol\% NaAMB} = B/(A + B) \times 100\% \quad (4)$$

A second set of copolymers was synthesized in which the ionic strength of the polymerization solvent was varied while the copolymer composition was maintained at 25:75 AM:NaAMB (Table 2). As illustrated in Fig. 2, increasing the ionic strength

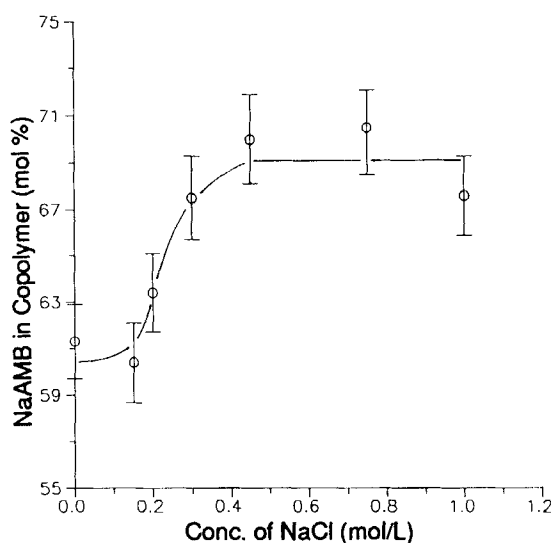


FIG. 2. Mole percent NaAMB incorporated into a copolymer as a function of salt concentration when the feed ratio is kept constant at 25/75 mol% AM/NaAMB.

of the polymerization solvent allows more NaAMB to be incorporated into the copolymers up to a limiting composition. These results are similar to those of Breslow and Kutner [9], who prepared polymers of sodium ethylenesulfonate. They found an increase in the rate of polymerization and molecular weight upon the addition of sodium acetate. This was attributed to the reduction of an electrostatic effect which repels the ionic monomer from the negative charges on the growing chain. The compositions of the copolymers in Table 2 indicate that a similar reduction in electrostatic repulsion has occurred in the presence of NaCl. However, the relative hydrophobic character of NaAMB may also enhance its reactivity with the terminal NaAMB mer on the propagating chain.

Effects of NaCl on Reactivity Ratios

The compositions of the low-conversion copolymers of the ABAM1 and ABAM2 series are compared in Table 3. For every feed composition, the copolymers synthesized in the presence of NaCl had greater amounts of NaAMB incorporated. This information is presented graphically in Fig. 3. The data for the ABAM2 copolymers lie closer to the dashed line, which represents completely random copolymerization. The reactivity ratios (Table 4) derived by the methods of Fineman-Ross [10] and Kelen-Tüdös [11] are closer to "ideal" ($r_1 = r_2 = 1$) with added NaCl; r_1, r_2 values are 1.2, 0.5 in water and 1.0, 0.6 in NaCl solution, respectively. It is interesting that the product $r_1 r_2$ does not change significantly for the copolymers made in the absence or presence of salt (Table 4).

TABLE 3. Compositions of Copolymers of Acrylamide (AM) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB) Synthesized in Deionized Water (the ABAM1 series) and in 1 M NaCl (the ABAM2 Series)

Sample number	Feed composition (mol%)		Polymer composition ^a (mol%)	
	AM	NaAMB	AM	NaAMB
ABAM1-10-1	90	10	92.0	8.0
ABAM1-25-1	75	25	79.7	20.3
ABAM1-40-1	60	40	68.6	31.2
ABAM1-60-1	40	60	51.6	48.4
ABAM1-75-1	25	75	37.9	63.1
ABAM2-10-1	90	10	90.4	9.6
ABAM2-25-1	75	25	76.2	23.8
ABAM2-40-1	60	40	63.7	36.3
ABAM2-60-1	40	60	47.0	53.0
ABAM2-75-1	25	75	32.4	67.6

^aDetermined from elemental analysis.

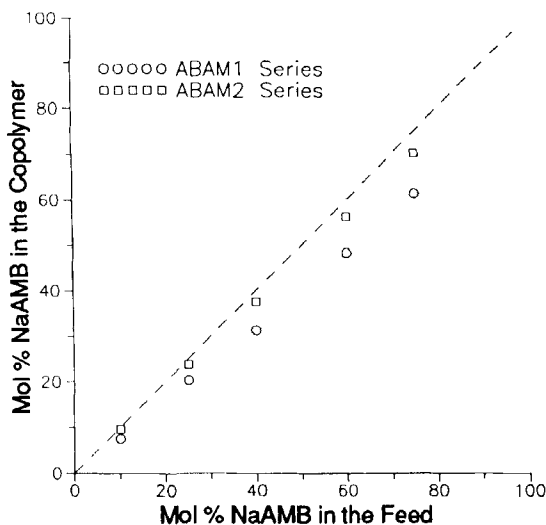


FIG. 3. Mole percent NaAMB incorporated into the copolymers as a function of comonomer feed ratio for the copolymers synthesized in deionized water (ABAM1 series) and in 1 *M* NaCl (ABAM2 series). The dashed line represents $r_1 = r_2 = 1.0$.

Changes in Copolymer Microstructure

Statistical microstructural information can be obtained using the equations of Igarashi [12] and Pyun [13]. These methods allow calculation of the fractions of M_1 - M_1 , M_2 - M_2 , and M_1 - M_2 units in the copolymers from experimentally determined reactivity ratios and copolymer composition.

The results obtained for the copolymers (Table 5) support the premise that changing the ionic strength of the polymerization solvent should lead to different copolymer microstructures. However, when the number of NaAMB-centered triads is plotted as a function of copolymer composition (Fig. 4), the ABAM1 and ABAM2 series data fall on the same curve. The dashed line represents the triad distribution for an $r_1 r_2$ value of 0.64. Igarashi's equations depend on the inverse of $r_1 r_2$, and as long as this product remains the same, the outcome of the equations will be the same.

Harwood, Park, and Santee discussed the inadequacies of reactivity ratios by examining the microstructure of acrylamide copolymers using a catalyzed intra-

TABLE 4. Reactivity Ratios for the ABAM1 and ABAM2 Copolymer Series Determined Using the Methods of Kelen-Tüdös and Fineman-Ross

Method	ABAM1			ABAM2		
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
Kelen-Tüdös	1.23 ± 0.02	0.50 ± 0.04	0.62	1.00 ± 0.03	0.64 ± 0.05	0.64
Fineman-Ross	1.20 ± 0.02	0.47 ± 0.05	0.56	0.98 ± 0.03	0.59 ± 0.05	0.58

TABLE 5. Structural Data for the Copolymers of Acrylamide (AM, M_1) with Sodium 3-Acrylamido-3-Methylbutanoate (NaAMB, M_2) Synthesized in Deionized Water and 1 M NaCl

Sample number	NaAMB in copolymer (mol%)	Blockiness (mol%)		Alternation (mol%) (M_1-M_2)	Mean sequence length	
		M_1-M_1	M_2-M_2		M_1	M_2
ABAM1-10-1	8.0	84.3	0.4	15.3	11.8	1.1
ABAM1-25-1	20.3	62.2	2.8	35.0	4.6	1.2
ABAM1-40-1	31.2	44.8	7.2	48.0	2.8	1.3
ABAM1-60-1	48.4	21.3	19.9	57.0	1.8	1.7
ABAM1-75-1	63.1	10.6	36.8	52.6	1.4	2.4
ABAM2-10-1	9.6	81.4	0.6	18.1	9.8	1.1
ABAM2-25-1	23.8	56.4	4.0	39.6	3.9	1.2
ABAM2-40-1	36.3	37.8	10.4	51.9	2.5	1.4
ABAM2-60-1	53.0	18.7	24.8	56.5	1.7	1.9
ABAM2-75-1	67.6	8.0	43.2	48.8	1.3	2.8

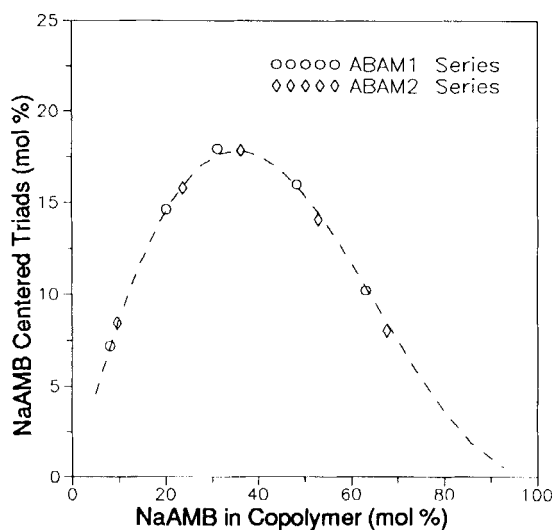


FIG. 4. Number of NaAMB monomer unit centered triads as a function of polymer composition for ABAM1 and ABAM2 copolymers. The dashed line represents the triad distribution for any polymer with $r_1 r_2 = 0.64$ regardless of the values of r_1 and r_2 .

sequence cyclization technique [14]. They found that synthesizing copolymers of acrylamide with styrene in a variety of solvents led to copolymers with the same microstructure despite extreme differences in reactivity ratios.

Viscometric Studies

Effects of Copolymer Composition

The viscosity data obtained in this work indicate a change in the microstructure of the copolymers after change of the ionic strength of the polymerization solvents. The intrinsic viscosities, obtained from Huggins plots, for the ABAM1 and ABAM2 series copolymers are shown in Fig. 5. For both series, the highest intrinsic viscosities were obtained from the copolymers containing less than 40 mol% of NaAMB. Counterion condensation likely occurs at compositions with more NaAMB. Additionally, decreasing molecular weight occurs with increasing NaAMB incorporation yielding lower viscosities.

The differences in location of the viscosity maxima may be due to neighboring group effects. At certain compositions, the monomer units along the backbone can interact via hydrogen bonding to form chain-stiffening structures [2]. The frequency of these interactions will depend on the polymer microstructure. From Fig. 6 it appears that the highest viscosities in deionized water are produced when the composition of NaAMB lies between 10 and 25 mol% for the ABAM1 series and between 20 and 40 mol% for the ABAM2 series. The lack of smoothness of the viscosity copolymer composition curve from the ABAM1 series has been reported previously and may be due to conformational restrictions due to nearest-neighbor interactions [5].

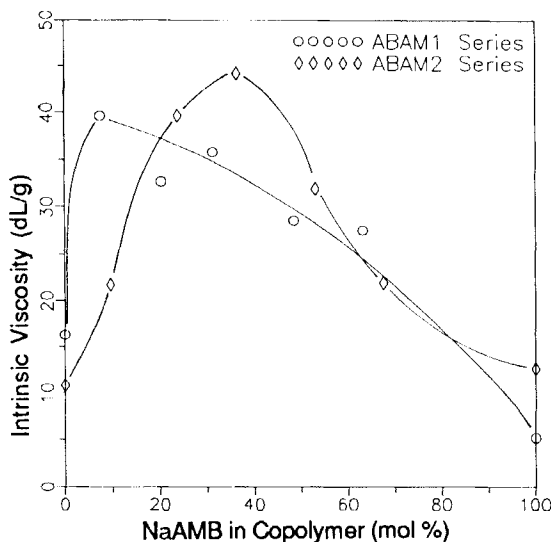


FIG. 5. Compositional effect on intrinsic viscosity for the ABAM1 and ABAM2 copolymer series in 0.514 *M* NaCl determined with a shear rate of 1.75 s⁻¹ at 30°C.

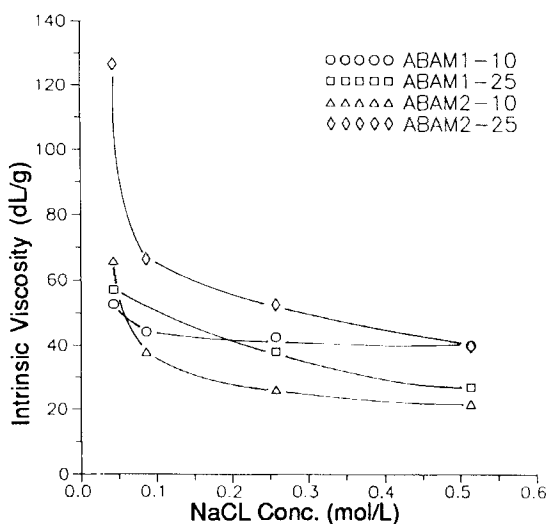


FIG. 6. Effect of sodium chloride concentration on the intrinsic viscosities of ABAM1 and ABAM2 copolymers determined at 30°C with a shear rate of 1.25 s⁻¹

Effects of Molecular Weight

Molecular weight affects the dilute solution behavior of copolymers. Table 6 compares the molecular weights of the copolymers made in deionized and salt water. Samples ABAM1-10-2 and ABAM2-25-2 have molecular weights of 15.6×10^6 and 16.0×10^6 g/mol, respectively. These two copolymers also have similar zero-shear intrinsic viscosities. Second-virial coefficients indicate that even though ABAM1-10-2 has less charge than ABAM2-25-2, it is better solvated.

Samples ABAM1-25-2 and ABAM2-40-2 also have similar molecular weights, but their viscosities are markedly different. The dissimilar second-virial coefficients indicate the importance of polymer solvation on hydrodynamic volumes in solution.

TABLE 6. Molecular Weight and Second-Virial-Coefficient Data for the ABAM1 and ABAM2 Copolymer Series

Sample number	Composition		MW ($\times 10^{-6}$ g/mol)	A_2 ($\times 10^4$ mL \cdot mol/g ²)
	AM	NaAMB		
ABAM1-10-2	91.6	8.4	15.6	4.28
ABAM1-25-2	79.9	20.1	12.9	1.52
ABAM1-60-2	50.2	49.8	14.0	3.49
ABAM2-10-2	90.4	9.6	6.8	4.39
ABAM2-25-2	76.2	23.8	16.0	3.60
ABAM2-40-2	63.7	36.3	11.9	4.02

The small A_2 values for both ABAM1-25-2 and ABAM2-25-2 suggest the existence of microstructural interactions like those discussed above.

Effects of Added Electrolytes

The relationship of zero-shear intrinsic viscosity to ionic strength for a number of ABAM1 and ABAM2 copolymers as a function of ionic strength is illustrated in Fig. 6. Typical polyelectrolyte behavior is observed. The polymer chains collapse as the ionic strength of the solvent increases. The change of intrinsic viscosity with ionic strength has been used as a qualitative measure of chain flexibility. Smidsrod and Haug [15] obtained what they called a "stiffness parameter," B , utilizing Eq. (5) in which S is the slope of the plot of $[\eta]$ as a function of the inverse square root of the ionic strength and $[\eta]_M$ is the intrinsic viscosity at a given salt concentration. The exponent r is assumed invariant to polymer type and has an approximate value of 1.3

$$S = B \cdot ([\eta]_M)^r \quad (5)$$

Values of B are generally low for polymers that retain their viscosity (remain extended) with increasing electrolyte concentration. Higher B values are reported for flexible polymers. It should be noted that B is inversely related to measures of stiffness such as persistence length on the steric factor [15]. In general, B values (Table 7) for the copolymers in this work are higher for the ABAM2 series than for the ABAM1 series for similar overall compositions up to 65 mol%. Differences in the aqueous solution viscosities for very similar molecular weights can only be attributed to microstructural differences.

Interestingly, ABAM1-10-2 with 8.4 mol% NaAMB in the copolymer exhibits the best electrolyte tolerance over a wide range of NaCl concentrations consistent

TABLE 7. Comparison of the ABAM1 and ABAM2 Copolymer Series Based on the Smidsrod and Haug Stiffness Parameter

Sample number	NaAMB in copolymer (mol%)	B ($[\eta]_{0.514M}$)
ABAM1-10-2	8.4	0.03
ABAM1-25-2	20.1	0.07
ABAM1-40-2	31.4	0.12
ABAM1-60-2	49.8	0.12
ABAM1-75-2	63.6	0.11
ABAM2-10-2	10.6	0.06
ABAM2-25-2	24.8	0.15
ABAM2-40-2	37.5	0.20
ABAM2-60-2	56.4	0.16
ABAM2-75-2	70.2	0.11

with our previous observations [2, 4, 5]. Neighboring-group interactions between isolated NaAMB units and acrylamide are suggested to be responsible for chain stiffening. More random placement of NaAMB units, as experimentally observed in synthesis from NaCl solutions, leads to higher B values and less stiffening. Finally, above 65 mol% few isolated NaAMB units are available for placement between neighboring acrylamide units and smaller differences in stiffness are observed in the two series of copolymers.

CONCLUSIONS

The addition of NaCl to the aqueous reaction medium results in more random copolymerization of acrylamide with NaAMB. Reactivity ratios determined experimentally at pH 9 changed from $r_1 = 1.23$ and $r_2 = 0.50$ for AM, NaAMB (M_1 , M_2) in deionized water to $r_1 = 1.00$ and $r_2 = 0.64$ in NaCl. The change is in accord with screening of electrostatic repulsion between the growing chain and the charged monomer [16, 17]. As a result, 7.1% more NaAMB is incorporated at a 25:75 AM:NaAMB feed ratio.

It was anticipated that reactivity ratio changes might lead to significantly different distributions of monomer sequences and persistence of length changes. Calculations using Igarashi's method show nearly identical NaAMB-centered triad distributions for copolymerizations in deionized or 1 M NaCl solutions. Unfortunately, the calculated distributions only reflect that the mathematical product $r_1 \cdot r_2$ is approximately 0.6 in both cases. This has no apparent physical significance.

Dilute solution behavior of the respective ABAM1 and ABAM2 series as a function of electrolyte concentration reveals significant microstructural differences. Qualitative comparisons of chain stiffness using the Smidsrod-Haug treatment [15] indicate microstructural effects—probably hydrogen-bonding interactions of NaAMB with adjacent AM units—are more effective in maintaining chain dimensions. Such interactions are more effectively attained in synthesis at pH 9 from deionized water than from 1 M NaCl.

Technologically the NaAMB/AM copolymers continue to be of great interest owing to their unusually high viscosity maintenance and phase stability in high-electrolyte and high-temperature environments.

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REFERENCES

- [1] G. S. Chen, PhD dissertation, University of Southern Mississippi, Hattiesburg, 1982.
- [2] K. P. Blackmon, PhD dissertation, University of Southern Mississippi, Hattiesburg, 1986.

- [3] L. C. Salazar, PhD dissertation, University of Southern Mississippi, Hattiesburg, 1991.
- [4] C. L. McCormick and K. P. Blackmon, *J. Poly. Sci., Polym. Chem.*, **24**, 2635 (1986).
- [5] C. L. McCormick, K. P. Blackmon, and D. L. Elliot, *Ibid.*, **24**, 2619 (1986).
- [6] C. L. McCormick and L. C. Salazar, *Polym. Mat. Sci. Eng.*, **57**, 859 (1987).
- [7] D. Hoke and R. Robins, *J. Polym. Sci.*, **10**, 3311 (1971).
- [8] C. L. McCormick and B. H. Hutchinson, *Polymer*, **27**(4), 623 (1988).
- [9] D. S. Breslow and A. Kutner, *J. Polym. Sci.*, **27**, 295 (1958).
- [10] M. Fineman and S. Ross, *Ibid.*, **5**(2), 259 (1950).
- [11] T. Kelen and F. Tüdös, *J. Macromol. Sci. – Chem.*, **A9**, 1, (1975).
- [12] S. Igarashi, *J. Polym. Sci. Polym. – Lett. Ed.*, **1**, 359 (1963).
- [13] C. W. Pyun, *J. Polym. Sci.*, **A2**(8), 1111 (1970).
- [14] H. J. Harwood, K. Y. Park, and E. R. Santee, *Polym. Preprints*, **27**(2), 81 (1986).
- [15] O. Smidsrod and A. Haug, *Biopolymers*, **10**, 1213 (1971).
- [16] V. A. Kabonov, D. A. Topchiev, and T. M. Karaputadze, *J. Polym. Sci.*, ACS Symp. **42**, 173 (1973).
- [17] D. A. Kangas and R. R. Pelletier, *J. Polymer Sci., Part A-1*, **8**, 3543 (1970).

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