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Water-Soluble Copolymers. 67. Polyelectrolytes of *N*-Vinylformamide with Sodium 3-Acrylamido-3-methylbutanoate, Sodium 2-Acrylamido-2-methylpropanesulfonate, and Sodium Acrylate: Synthesis and Characterization

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ABSTRACT: Copolymers of *N*-vinylformamide (NVF) with sodium 3-acrylamido-3-methylbutanoate (NaAMBA), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and sodium acrylate (NaA) were prepared by free-radical polymerization in aqueous solution using 2,2′-azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride as the water-soluble azo initiator. Copolymer compositions were determined utilizing ^{13}C NMR by integration of the carbonyl resonances. Reactivity ratios were determined for NVF (M_1)/NaAMBA (M_2) (the BAVF series) and NVF (M_1)/NaAMPS (M_2) (the PSVF series). Both series, with r_1 and r_2 <1 and $r_1r_2 < 0.075$, are representative of copolymers that display alternating tendencies. Microstructural data calculated statistically by the methods of Igarashi support these findings. Weight-average molecular weights range from 0.9×10^6 to 7.5×10^6 and were determined by low-angle laser light scattering in 1 M NaCl solution. The findings are compared to previous results obtained for the copolymerization of acrylamide with the various anionic comonomers.

Introduction

Water-soluble and water-dispersible copolymers represent one of the fastest growing classes of industrial products. The growth has been stimulated by the demand for environmentally compliant systems prepared in and processed from water. Applications include water treatment, remediation, coatings and personal care formulations, viscosity modification, and frictional drag reduction.[1−8]

Although a large number of monomers are capable of polymerization into polymers with water solubility, only a few have sufficient water solubility and reactivity with appropriate comonomers to yield commercially viable systems. *N*-Vinylformamide (NVF), an isomer of acrylamide (AM), has recently received renewed attention since purification procedures have been refined and high molecular weights are easily attainable.[9−18] In addition, the pendant formamide moiety of poly(NVF) is readily hydrolyzed to the corresponding amine. Both NVF and AM yield water-soluble homopolymers by free-radical polymerization; however, the structural differences of the monomers significantly alter copolymerization tendencies with various comonomers and microstructural attributes. Knowledge of reactivity ratios of NVF and AM with specific comonomers, therefore, is an important factor in tailoring microstructure for desired rheological characteristics.

Previous studies in our laboratories confirmed that NVF copolymerizes with electron-deficient monomers such as acrylamide and maleic anhydride to form copolymers with strongly alternating tendencies.[19,20] In this paper, we report the synthesis and molecular characterization of copolymers of NVF with sodium 3-acrylamido-3-methylbutanoate (NaAMBA), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and sodium acrylate (NaA). The reactivity ratios for the copolymers with NaAMBA and NaAMPS were determined by several methods and then used to statistically predict the microstructures of the resulting copolymers. Additionally, the molecular weight values were also determined by low-angle laser light scattering. These studies complement previous research in our laboratories on copolymers of acrylamide with the same comonomer systems.[21−29]

Experimental Section

Materials. *N*-Vinylformamide (NVF) from Air Products and Chemicals Inc. was vacuum distilled prior to use (72 °C at 5 Torr). Acrylic acid from Aldrich Chemical Co. was vacuum distilled prior to use. 3-Acrylamido-3-methylbutanoic acid was synthesized via a Ritter reaction of equimolar amounts of 3,3-dimethylacrylic acid with acrylonitrile as reported by Hoke and Robins[30] and as modified by McCormick and Blackmon.[21,24] 2-Acrylamido-2-methylpropanesulfonic acid from Aldrich Chemical Co. was recrystallized from methanol and vacuum dried at room temperature. 2,2′-Azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride (VA-044) from Wako Chemicals USA, Inc., was used as received.

Poly(*N*-vinylformamide-*co*-sodium 3-acrylamido-3-methylbutanoate) and Poly(*N*-vinylformamide-*co*-sodium 2-acrylamido-2-methylpropane sulfonate). The copolymers of *N*-vinylformamide (NVF) and sodium 3-acrylamido-3-methylbutanoate (NaAMBA), the BAVF series, and copolymers of *N*-vinylformamide (NVF) and sodium 3-acrylamido-3-methylbutanoate (NaAMPS), the PSVF series, were prepared in an aqueous solution at 45 °C using 0.1 mol % of VA-044 as the initiator. Each reaction was conducted in a 500 mL, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube. A designated amount of either 3-acrylamido-3-methylbutanoic acid or 2-acrylamido-2-methylpropanesulfonic acid was added to a specific volume of deionized water. To this was added an equimolar amount of sodium hydroxide, and the pH of this mixture was adjusted to pH = 8.5. Once the materials were completely dissolved, the appropriate amount of NVF was added and the mixture was then deaerated with oxygen-free nitrogen for 30 min and placed in a water bath at 45 °C. After the reaction mixture had equilibrated, VA-044 dissolved in 5 mL of deionized water was injected into the stirring solution. The total monomer concentration was held constant at 0.5 M in each reaction. A low-

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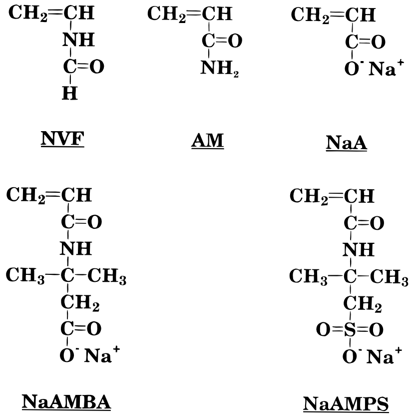

Figure 1. Structures for the monomers *N*-vinylformamide (NVF), acrylamide (AM), sodium acrylate (NaA), sodium-3-acrylamido-3-methylbutanoate (NaAMBA), and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS).

conversion aliquot was taken for the determination of reactivity ratios. High conversion was terminated at less than 40% due to the high viscosity of the polymerization medium and as a precaution against copolymer drift. Polymerizations were terminated by precipitation into reagent grade acetone. The low-conversion samples were further purified by reprecipitation into acetone followed by vacuum drying for 2 days. High-conversion samples were purified by dialysis (using Spectra/Por 4 dialysis bags with molecular weight cutoffs of 12 000−14 000) against deionized water adjusted to pH = 8 for 10 days. After dialysis, the polymer solutions were frozen and isolated by lyophilization. Conversions were determined gravimetrically from the purified samples.

Poly(*N*-vinylformamide-*co*-sodium acrylate). The copolymers of *N*-vinylformamide (NVF) and sodium acrylate (NaA) were prepared in an aqueous solution as reported previously except for AAVF-100, in which the monomer concentration was 1.0 M.[15] Polymer purification was performed in the same manner as discussed above.

Copolymer Characterization. ^{13}C NMR spectra of the copolymers were obtained at 50.3 MHz on a Bruker AC200 spectrometer using 15−20 wt % aqueous (D_2O) polymer solutions with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) as a reference. A recycle delay of 8 s, 90° pulse length, and gated decoupling to remove all NOE were used for quantitative spectral analysis with an accuracy of ±6%. Molecular weight studies were performed on a Chromatix KMX-6 low-angle laser light scattering instrument at 25 °C in 1 M NaCl at pH = 8.5 and are accurate to within ±5−10%. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer.

Results and Discussion

Compositional Studies. Copolymers of *N*-vinylformamide with sodium 3-acrylamido-3-methylbutanoate (BAVF series), sodium 2-acrylamido-2-methylpropanesulfonate (PSVF series), and sodium acrylate (AAVF series) were prepared at designated feed compositions described in the Experimental Section. The structures of the various monomers utilized in the syntheses are shown in Figure 1. Tables 1−3 compare initial feed ratios, which were varied over the entire compositional range, to resultant copolymer composition. The latter were determined by integration of appropriate carbonyl resonances obtained by ^{13}C NMR spectroscopy. Tables 1 and 2 are for the BAVF and PSVF copolymer series, respectively, and represent low-conversion samples (4−17%). Table 3 is for the AAVF copolymer series and is representative of high-conversion samples (24−38%). The mol % NVF found in the AAVF copolymers from the high-conversion samples agrees favorably with past results reported from our laboratories for low-conversion samples.[20] This finding suggests that there is no significant drift in the compositions of the copolymers at these conversions.

Table 1. Reaction Parameters for the Copolymerization of *N*-Vinylformamide (M_1) and Sodium 3-Acrylamido-3-methylbutanoate (M_2)

sample	feed ratio (mol %) (NVF:NaAMBA)	rxn time (min)	% conv	NVF found^a (mol %)
BAVF 23	90.0:10.0	55	4.0	77.0 ± 4.6
BAVF 38	75.0:25.0	65	12.0	62.0 ± 3.7
BAVF 47	60.0:40.0	40	4.5	53.0 ± 3.2
BAVF 56	40.0:60.0	30	15	44.0 ± 2.6
BAVF 65	25.0:75.0	30	5.0	35.0 ± 2.1
BAVF 75	10.0:90.0	18	17	25.0 ± 1.5
BAVF 100	0.0:100.0			0.0^b

^{a} Determined from ^{13}C NMR. ^{b} Theoretical value.

Table 2. Reaction Parameters for the Copolymerization of *N*-Vinylformamide (M_1) and Sodium 2-Acrylamido-2-methylpropanesulfonate (M_2)

sample	feed ratio (mol %) (NVF:NaAMPS)	rxn time (min)	% conv	NVF found^a (mol %)
PSVF 21	90.0:10.0	45	15	79.0 ± 4.7
PSVF 40	75.0:25.0	40	12	60.0 ± 3.6
PSVF 45	60.0:40.0	50	12	55.0 ± 3.3
PSVF 56	40.0:60.0	20	12	44.0 ± 2.6
PSVF 64	25.0:75.0	25	11	36.0 ± 2.2
PSVF 70	10.0:90.0	20	15	30.0 ± 1.8
PSVF 100	0.0:100.0			0.0^b

^{a} Determined from ^{13}C NMR. ^{b} Theoretical value.

Table 3. Reaction Parameters for the Copolymerization of *N*-Vinylformamide (M_1) and Sodium Acrylate (M_2)

sample	feed ratio (mol %) (NVF:NaA)	rxn time (min)	% conv	NVF found^a (mol %)
AAVF 22	88.0:12.0	60	25	78.0 ± 4.5
AAVF 49	60.0:40.0	35	27	51.0 ± 3.0
AAVF 62	40.0:60.0	30	24	37.5 ± 2.2
AAVF 82	12.0:88.0	30	38	17.5 ± 1.0
AAVF 100	0.0:100.0			0.0^b

^{a} Determined from ^{13}C NMR. ^{b} Theoretical value.

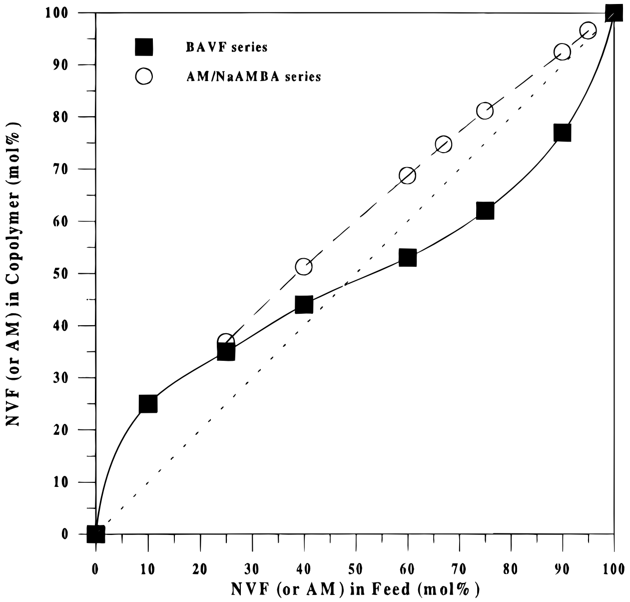

Figure 2. Mole percent NVF (■) or AM (○) incorporated into copolymers with NaAMBA as a function of comonomer feed ratio. The short dashed line represents ideal random incorporation.

In Figures 2−4, copolymer composition plots of the mol % NVF in the copolymer versus the mol % NVF in

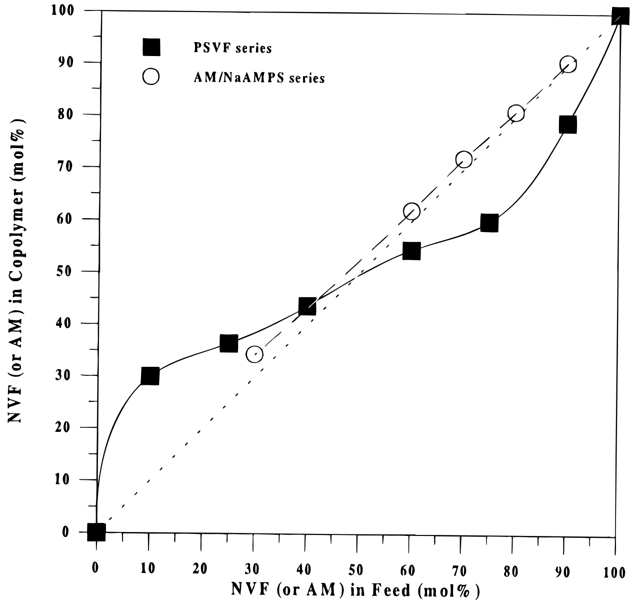

Figure 3. Mole percent NVF (■) or AM (○) incorporated into copolymers with NaAMPS as a function of comonomer feed ratio. The short dashed line represents ideal random incorporation.

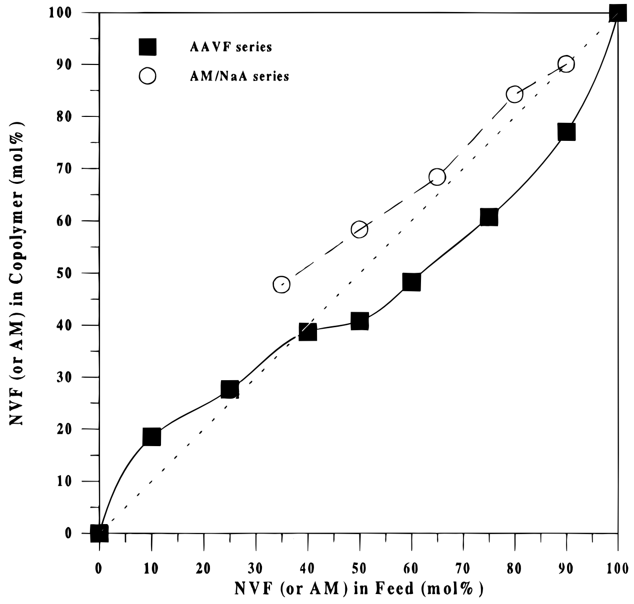

Figure 4. Mole percent NVF (■) or AM (○) incorporated into copolymers with NaA as a function of comonomer feed ratio. The short dashed line represents ideal random incorporation.

the feed for the BAVF, PSVF, and AAVF series, respectively, are shown. In addition, these figures also contain previous results from our laboratories for copolymers of AM with NaAMBA,[21] NaAMPS,[25,27] and NaA.[28] The short dashed lines which pass through the origin represent ideal incorporation while the curves through the data points were obtained by a spline smoothing fit. Copolymers of NVF exhibit a significant deviation from the dashed line. The azeotropic point is approximately 50 mol % for the BAVF and PSVF series and 40 mol % for the AAVF series. Below this point, more NVF is incorporated into the copolymers than is present in the feed while above this point, less NVF is incorporated. This behavior is typical of copolymerizations which exhibit an alternating tendency. The copolymers with acrylamide do not exhibit this preference of cross addition. In fact, acrylamide is preferentially added at all compositions, this behavior being more prevalent for the carboxylate-containing comonomers, and may be suggestive of some type of hydrogen-bonding interaction with acrylamide. The dissimilarity in the reactivity between NVF and AM can tentatively be ascribed to the electronic differences in the vinyl bond and will be addressed later.

Reactivity Ratio Studies. To further investigate the alternating behavior of the copolymers, reactivity ratios were determined. Fineman−Ross,[31] Kelen−Tudos (K−T),[32] and nonlinear least-squares (NLS)[33] methods were employed to calculate the r_1 and r_2 values, and the results obtained are listed in Table 4. In each study r_1 and r_2 were determined, designating NVF as M_1 and the anionic comonomer as M_2. Comparing values obtained by the NLS method, both the BAVF, $r_1 = 0.26$ and $r_2 = 0.28$, and PSVF series, $r_1 = 0.25$ and $r_2 = 0.22$, have nearly identical values for r_1 and r_2. Furthermore, copolymers of AM with NaAMBA and NaAMPS (Table 4) also yield similar r_1 and r_2 values. These results are not unexpected and likely due to the structural similarity of the anionic comonomers. The BAVF and PSVF series, however, have much lower r_1r_2 values than those calculated for the AM copolymers (0.075 vs 0.5−0.6). Again, this implies a greater tendency for the NVF copolymers to polymerize in an alternating fashion. The AAVF copolymers also tend to alternate as previously reported, this response being more prevalent when greater than 50 mol % NVF is present in the feed.[20] Compared to the AM copolymers, the AAVF series yields an r_1/r_2 ratio (K−T values) approximately 8 times less than obtained for the AM/NaA series. This observation may be attributable, in part, to the higher stability of the AM versus NVF radical on a propagating chain end. The ability of AM to polymerize to high molecular weight is well known and is a result of the high ratio of propagation to termination rate constants (k_p/k_t).

Statistical Microstructure Studies. The statistical distribution of monomer sequences for the BAVF and PSVF series were determined by the methods of Igarashi.[34] The reactivity ratios determined by the K−T method were used to calculate the mol % blockiness (M_1−M_1 and M_2−M_2), mol % alternation (M_1−M_2), and the mean sequence lengths of M_1 and M_2. The results are shown in Tables 5 and 6. Values obtained for the AAVF series have been previously reported.

As suggested earlier, both the BAVF and PSVF copolymer series tend to form alternating copolymers. This observation is further supported by the values presented in Tables 5 and 6. Both the BAVF and PSVF series have significantly high values for M_1−M_2, the mol % alternation. These values are graphically compared to the values obtained for the AM copolymers in Figure 5. All copolymers of NVF yield higher values than AM when the mol % incorporation of NVF and AM is approximately the same. The copolymers of NVF attain a maximum value of approximately 80 mol % alternation while those of acrylamide approach 60 mol %. In addition, the majority of the copolymers for the BAVF, PSVF, and AAVF series exhibit values of less than 2 for the mean sequence lengths. These low mean values imply the absence of any long runs of either comonomer, further substantiating the alternating tendency.

Comparable behavior has been observed for copolymers of NVF and AM. The propensity for cross addition suggests the presence of some type of donor−acceptor characteristics between NVF and acrylamido-based

Table 4. Reactivity Ratios for *N*-Vinylformamide (M_1) and Acrylamide (M_1) with Various Anionic Comonomers (M_2)

comonomer pair	Fineman−Ross	Kelen−Tüdös	NLS
N-vinylformamide and sodium 3-acrylamido-3-methylbutanoate	$r_1 = 0.27 \pm 0.02$ $r_2 = 0.33 \pm 0.02$	$r_1 = 0.25 \pm 0.02$ $r_2 = 0.29 \pm 0.02$	$r_1 = 0.26 \pm 0.02$ $r_2 = 0.28 \pm 0.02$
N-vinylformamide and sodium 2-acrylamido-2-methylpropanesulfonate	$r_1 = 0.32 \pm 0.02$ $r_2 = 0.39 \pm 0.02$	$r_1 = 0.25 \pm 0.02$ $r_2 = 0.24 \pm 0.02$	$r_1 = 0.25 \pm 0.02$ $r_2 = 0.22 \pm 0.02$
N-vinylformamide and sodium acrylate	$r_1 = 0.29 \pm 0.11$ $r_2 = 0.65 \pm 0.03$	$r_1 = 0.22 \pm 0.09$ $r_2 = 0.52 \pm 0.05$	$r_1 = 0.20 \pm 0.04$ $r_2 = 0.50 \pm 0.05$
acrylamide and sodium 3-acrylamido-3-methylbutanoate	$r_1 = 1.23 \pm 0.02$ $r_2 = 0.50 \pm 0.04$	$r_1 = 1.20 \pm 0.02$ $r_2 = 0.47 \pm 0.05$	
acrylamide and sodium 2-acrylamido-2-methylpropanesulfonate	$r_1 = 0.98 \pm 0.09$ $r_2 = 0.49 \pm 0.02$	$r_1 = 1.00 \pm 0.08$ $r_2 = 0.52 \pm 0.07$	
acrylamide and sodium acrylate	$r_1 = 1.05 \pm 0.08$ $r_2 = 0.19 \pm 0.04$	$r_1 = 1.11 \pm 0.10$ $r_2 = 0.32 \pm 0.09$	

Table 5. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium 3-Acrylamido-3-methylbutanoate (M_2)

sample	M_1 in copolymer (mol %)	blockiness (mol %) M_1-M_1	blockiness (mol %) M_2-M_2	alternation (mol %) M_1-M_2	mean seq length M_1	mean seq length M_2
BAVF 23	77.0	54.66	0.66	44.67	3.27	1.03
BAVF 38	62.0	27.23	3.23	69.55	1.76	1.10
BAVF 47	53.0	13.94	7.94	78.11	1.38	1.19
BAVF 56	44.0	5.89	17.89	76.21	1.17	1.43
BAVF 65	35.0	2.39	32.39	65.23	1.08	1.86
BAVF 75	25.0	0.83	50.83	48.33	1.03	3.59

Table 6. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium 2-Acrylamido-2-methylpropanesulfonate (M_2)

sample	M1 in copolymer (mol %)	blockiness mole % M_1-M_1	blockiness mole % M_2-M_2	alternation (mol %) M_1-M_2	mean seq length M_1	mean seq length M_2
PSVF 21	79.0	58.42	0.42	41.16	3.22	1.03
PSVF 40	60.0	23.32	3.32	73.35	1.74	1.08
PSVF 45	54.5	15.00	6.00	79.00	1.37	1.16
PSVF 56	43.7	4.94	17.54	77.52	1.16	1.35
PSVF 64	36.4	2.28	29.48	68.25	1.08	1.70
PSVF 70	30.0	1.16	41.16	57.67	1.03	3.11

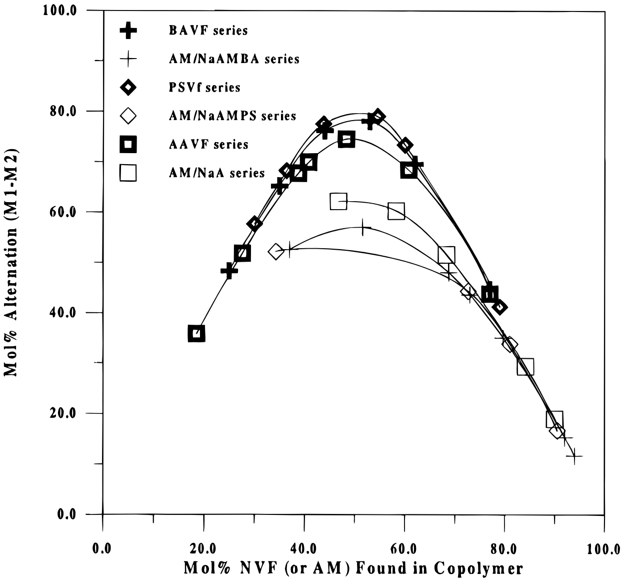

Figure 5. Mol % alternation (M1−M2) versus mol % NVF or AM incorporated into copolymers.

Table 7. Molecular Weight and Second Virial Coefficient Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium 3-Acrylamido-3-methylbutanoate (M_2)

sample	NVF found[a] (mol %)	$M_w \times 10^{-6}$	$A_2 \times 10^4$ (mL·mol/g2)	DP × 10^{-4}
BAVF 23	77.0	1.2	12.5	1.3
BAVF 38	62.0	2.4	4.0	2.0
BAVF 47	53.0	4.6	4.6	3.6
BAVF 56	44.0	6.8	2.8	4.9
BAVF 65	35.0	5.4	4.7	3.6
BAVF 75	25.0	5.7	5.3	3.5
BAVF 100	0.0[b]	1.3	8.6	0.7

[a] Determined from ^{13}C NMR. [b] Theoretical value.

monomers. The latter are expected to be an electron−accepting type monomer due to the strong electron withdrawing nature of the amide group. On the other hand, NVF is expected to be a an electron-donating type monomer because of the lone pair of electrons on the nitrogen atom adjacent to the vinyl group. These electron poor/electron rich characteristics may favor a cross addition polymerization mechanism comparable to, but to a lesser extent than, that frequently observed for maleic anhydride copolymerizations. Similar behavior has been observed by Schulz et al. for copolymers of *N*-vinylpyrrolidone (NVP) with various monomers possessing an acrylamide functionality.[35] The vinyl bonds of NVF and NVP should possess similar electronic characteristics since both are covalently bonded to the nitrogen atom of an amide functionality. In addition to these electronic effects, other structural features of both NaAMBA and NaAMPS may induce alternating tendencies. Both NaAMBA and NaAMPS are inherently bulky; therefore steric repulsions may favor cross additions with NVF. Another factor to be considered is that both NaAMBA and NaAMPS are anionically charged and Coulombic repulsions required by homoaddition are less favored than addition of NVF. This effect is likely a major factor in the AAVF series as the vinyl bond of NaA is electronically rich, therefore precluding any type of donor−acceptor interactions. Evidence for Coulombic repulsions influencing polymer composition has been reported by Salazar and McCormick for copolymers of NaAMBA with acrylamide.[24] In that study, addition of NaCl to the polymerization medium led to a more ideal incorporation of NaAMBA into the copolymer, a result of the shielding effect between NaAMBA comonomers by the addition of NaCl.

Light Scattering Studies. Molecular weights and second virial coefficients (A_2) were determined for all of the copolymers in this study at 25 °C in 1.0 M NaCl at pH = 8.5. The values obtained are displayed in Tables 7−9. For the BAVF series, the molecular weights ranged from 1.2×10^6 to 6.8×10^6 and the A_2 values ranged from 12.5×10^{-4} to 2.8×10^{-4} mL·mol/g^2. These molecular weights are considerably lower than those of the AM/NaAMBA copolymers, which ranged from 12.9×10^6 to 15.6×10^6. For the PSVF series, the molecular weights ranged from 0.9×10^6 to 7.5×10^6 and the A_2 values ranged from 44.3×10^{-4} to 1.0×10^{-4} mL·mol/g^2. The trend for these two series is that the molecular weight reaches a maximum value when there are approximately 44 mol % of NVF units

Table 8. Molecular Weight and Second Virial Coefficient Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium 2-Acrylamido-2-methylpropanesulfonate (M_2)

sample	NVF found[a] (mol %)	$M_w \times 10^{-6}$	$A_2 \times 10^4$ (mL·mol/g^2)	DP $\times 10^{-4}$
PSVF 21	79.0	0.9	44.3	0.9
PSVF 40	60.0	2.6	12.0	1.9
PSVF 45	54.5	2.3	11.1	1.6
PSVF 56	43.7	7.5	1.0	4.7
PSVF 64	36.4	6.9	1.6	4.0
PSVF 70	30.0	4.5	2.8	2.5
PSVF 100	0.0[b]	1.7	8.0	0.7

[a] Determined from ^{13}C NMR. [b] Theoretical value.

Table 9. Molecular Weight and Second Virial Coefficient Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium Acrylate (M_2)

sample	NVF found[a] (mol %)	$M_w \times 10^{-6}$	$A_2 \times 10^4$ (mL·mol/g^2)	DP $\times 10^{-4}$
AAVF 22	78.0	0.9	14.8	1.2
AAVF 49	51.0	2.9	7.8	3.5
AAVF 62	37.5	3.9	5.1	4.6
AAVF 82	17.5	6.6	3.2	7.3
AAVF 100	0.0[b]	12.0	2.8	12.7

[a] Determined from ^{13}C NMR. [b] Theoretical value.

incorporated into the copolymers. This may be a result of a faster rate of alternating propagation when nearly equimolar amounts of comonomers are incorporated into the copolymer. Interestingly, A_2 reaches a minimum value at the same copolymer composition, which may be a result of the higher molecular weights. For the AAVF series, the molecular weights ranged from 0.9×10^6 to 12.0×10^6 and the A_2 values ranged from 14.8×10^{-4} to 2.8×10^{-4} mL·mol/g^2. The trend for this series is that the molecular weights increase as the mol % of NVF incorporated into the copolymers decreases. The A_2 values exhibit the opposite trend, decreasing in value as less NVF is incorporated into the copolymers.

Conclusions

Copolymers of *N*-vinylformamide with sodium 3-acrylamido-3-methylbutanoate, sodium 2-acrylamido-2-methylpropanesulfonate, and sodium acrylate were prepared by free-radical polymerization in aqueous solution. ^{13}C NMR was used to determine the copolymer compositions by integration of the carbonyl peaks. The reactivity ratios were determined by three methods and indicate random copolymerization with a strong alternating tendency. This alternating tendency was further confirmed by calculating the copolymer microstructures by the method of Igarashi. Molecular weights were determined and found to be dependent on the amount of NVF incorporated into the copolymers for the BAVF and PSVF series, reaching a maximum around 40 mol % NVF. This dependency was not found for the AAVF series, which exhibited higher molecular weights as the mol % NVF incorporated into the copolymers decreased.

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