Water-Soluble Copolymers. 48. Reactivity Ratios of *N*-Vinylformamide with Acrylamide, Sodium Acrylate, and *n*-Butyl Acrylate

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ABSTRACT: Copolymers of *N*-vinylformamide (NVF) with acrylamide (AM), sodium acrylate (NA), and *n*-butyl acrylate (BA) have been prepared by free-radical polymerization in homogeneous solutions. Copolymer compositions were obtained by ^{13}C NMR. Reactivity ratios and microstructures of the resulting copolymers were determined. The reactivity ratios calculated by the method of Kelen–Tudos for NVF (M_1)/AM (M_2) were $r_1 = 0.046$ and $r_2 = 0.51$; for NVF (M_1)/Na (M_2), $r_1 = 0.22$ and $r_2 = 0.52$; and for NVF (M_1)/BA (M_2), $r_1 = 0.071$ and $r_2 = 0.55$. Microstructural data calculated by the method of Igarashi indicated that all three copolymer series exhibit high degrees of alternation.

Introduction

Water-soluble polymers have become increasingly important in industrial applications over the past several decades. In particular, cationic polyelectrolytes are commonly utilized in commercial processes as flocculating agents in water treatment and additives in papermaking.[1] Poly(vinylamine), one of the more simple polybases, has recieved little attention in the literature mainly because of the difficulty involved in preparing the polymer.[2] Recently, however, a considerable patent literature has appeared on the purification and polymerization of *N*-vinylformamide.[3–6] *N*-Vinylformamide, once sufficiently purified, may be readily polymerized and subsequently hydrolyzed to attain high molecular weight poly(vinylamine).[7]

N-Vinylformamide may also be copolymerized with various acrylic monomers. In tailoring copolymers for specific applications, it is useful to know the reactivity ratios of comonomer pairs. Once the reactivity ratios are calculated, a copolymer of known composition may be synthesized by simply adjusting the feed ratio of each monomer before polymerization.

Copolymers of *N*-vinylformamide with acrylamide, sodium acrylate, and *n*-butylacrylate were synthesized with a variety of compositions. The reactivity ratios were determined and then used to statistically predict the microstructures of the resulting copolymers. The synthesis and characterization of these copolymer series are discussed in this paper.

Experimental Section

Materials. *N*-Vinylformamide (NVF) from Air Products and Chemicals Inc. was vacuum distilled prior to use [72 °C (5 Torr)]. Acrylamide (AM) from Aldrich Chemical Co. was recrystallized three times from acetone and vacuum-dried at room temperature prior to use (mp 83–84 °C). Acrylic acid and *n*-butyl acrylate from Aldrich Chemical Co. were vacuum distilled prior to use. 2,2′-Azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride (VA-044) from Wako Chemicals USA, Inc., and 2,2′-azobis(isobutyronitrile) were employed as the initiators. THF was UV grade and was used as received.

Poly(*N*-vinylformamide-*co*-acrylamide). The copolymers of *N*-vinylformamide and acrylamide were prepared in an aqueous solution at 50 °C using 0.1 mol % VA-044 as the initiator. Each reaction was conducted in a 250-mL, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube. Designated amounts of NVF and AM were dissolved in 145 mL of deionized water. The reaction mixture was then deaerated with oxygen-free nitrogen for 30 min and placed in a water bath at 50 °C. After the reaction mixture had equilibrated, 0.0485 g of VA-044 dissolved in 5 mL of deionized water was injected into the stirring solution. The total monomer concentration was held constant at 1.0 M in each reaction. After a designated time (15–40 min), the resulting polymer solution was precipitated into 1 L of reagent-grade acetone. The polymers were further purified by reprecipitation into acetone followed by vacuum drying for 2 days. Conversions were determined gravimetrically. Table II lists reaction parameters for the copolymerization of NVF with AM.

Poly(*N*-vinylformamide-*co*-sodium acrylate). The copolymers of *N*-vinylformamide (NVF) and sodium acrylate (NA) were prepared in an aqueous solution at 45 °C using 0.075 mol % VA-044 as the initiator. Each reaction was conducted in a 250-mL, three-necked flask equipped with a mechanical stirrer and a nitrogen inlet tube. A designated amount of acrylic acid was dissolved in deionized water. To this solution was added an equimolar concentration of sodium hydroxide, and the pH was adjusted to 8.5. 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, 0.0485 g of VA-044 dissolved in 5 mL of deionized water was injected into the stirring solution. The total monomer concentration was held constant at 2.5 M in each reaction. After a designated time, the resulting polymer solution was precipitated into 1 L of reagent-grade acetone. The polymers were further purified by reprecipitation into acetone followed by vacuum drying for 2 days. Conversions were determined gravimetrically. Table IV lists reaction parameters for the copolymerization of NVF with NA.

Poly(*N*-vinylformamide-*co*-*n*-butyl acrylate). The copolymers of *N*-vinylformamide (NVF) and *n*-butyl acrylate (BA) were copolymerized by free-radical polymerization in THF under nitrogen at 65–67 °C using 0.1 mol % AIBN as the initiator. The feed ratio of NVF/BA was varied from 10/90 to 90/10. Each reaction was conducted in a 250-mL, three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a condenser. Designated amounts of NVF and BA were dissolved in THF, and the resulting mixture was deaerated with oxygen-free nitrogen for 30 min and placed in an oil bath at 65–67 °C. After the reaction had equilibrated, 0.013 g of AIBN dissolved in 7 mL of THF was injected into the stirring solution. The total monomer concentration was held constant at 1.0 M in each reaction. After a designated amount of time (30–60 min), the resulting polymer was precipitated into petroleum ether/ethyl ether (4/1, v/v). The polymers were further purified by dissolution in acetone followed by precipitation into petroleum ether. After vacuum drying, conversions were determined gravimetrically. Table VI lists

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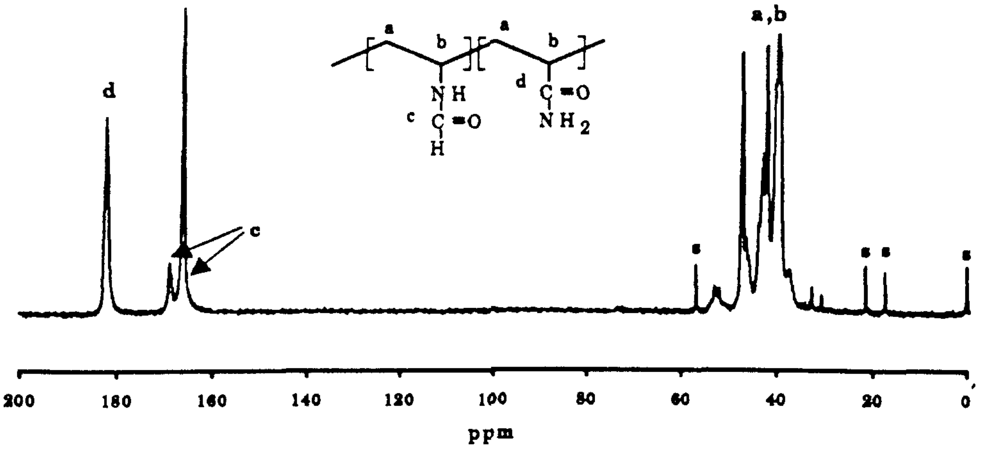

Figure 1. Typical ^{13}C NMR spectrum of *N*-vinylformamide with acrylamide.

Table I. Reactivity Ratios for *N*-Vinylformamide with Various Comonomers

comonomer pair	Fineman–Ross	Kelen–Tudos
N-vinylformamide (M_1) and acrylamide (M_2)	$r_1 = 0.053 \pm 0.023$ $r_2 = 0.534 \pm 0.111$	$r_1 = 0.046 \pm 0.035$ $r_2 = 0.517 \pm 0.065$
N-vinylformamide (M_1) and sodium acrylate (M_2)	$r_1 = 0.29 \pm 0.11$ $r_2 = 0.65 \pm 0.03$	$r_1 = 0.22 \pm 0.09$ $r_2 = 0.52 \pm 0.05$
N-vinylformamide (M_1) and *n*-butyl acrylate (M_2)	$r_1 = 0.061 \pm 0.02$ $r_2 = 0.54 \pm 0.09$	$r_1 = 0.071 \pm 0.03$ $r_2 = 0.55 \pm 0.06$

Table II. Reaction Parameters for the Copolymerization of *N*-Vinylformamide (M_1) with Acrylamide (M_2)

sample no.	feed	% convn	M_1 in copolymer[a]
NVF/AM1	9.40:90.60	16.0	14.1 ± 0.9
NVF/AM2	23.60:76.40	18.4	25.0 ± 1.5
NVF/AM3	38.40:61.60	9.6	41.0 ± 2.5
NVF/AM4	58.30:41.70	8.3	41.1 ± 2.5
NVF/AM5	74.10:25.90	9.4	49.7 ± 3.0
NVF/AM6	89.40:10.60	13.5	57.6 ± 3.5

[a] Determined by ^{13}C NMR.

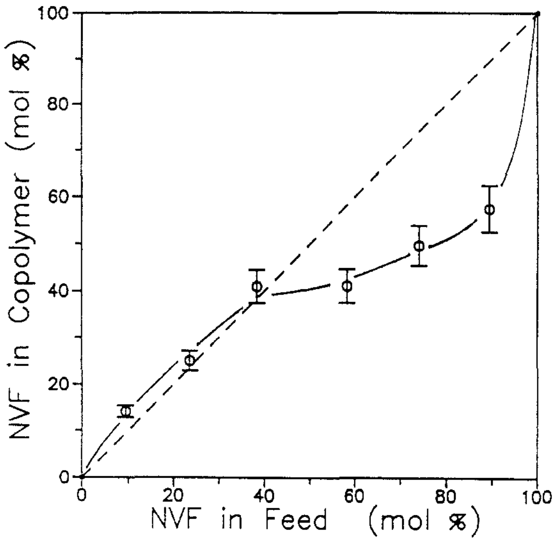

Figure 2. Mole percent NVF incorporated into the NVF/AM copolymers as a function of the comonomer feed ratio. The dashed line represents ideal random incorporation.

Table III. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with Acrylamide (M_2)

sample no.	M_1 in copolymer (mol %)	blockiness (mol %)		alteration (mol %):	mean seq length	
		M_1–M_1	M_2–M_2	M_1–M_2	M_1	M_2
NVF/AM1	14.10	0.07	71.87	28.07	1.00	5.99
NVF/AM2	25.00	0.29	50.29	49.42	1.01	2.67
NVF/AM3	41.00	1.83	19.83	78.33	1.03	1.83
NVF/AM4	41.10	1.86	19.66	78.48	1.06	1.37
NVF/AM5	49.70	6.38	6.98	86.64	1.13	1.18
NVF/AM6	57.60	17.40	2.20	80.39	1.39	1.06

reaction parameters for the copolymerization of NVF with BA.

^{13}C Nuclear Magnetic Resonance Spectroscopy. ^{13}C NMR spectra of the NVF/AM, NVF/NA, and NVF/BA were obtained at 50.3 MHz on a Bruker AC 200 spectrometer using 10–15 wt % polymer solutions in 5-mm tubes. A recycle delay of 5 s, a 90° pulse length, and gated decoupling to remove all NOE were used for quantitative spectral analysis.

Results and Discussion

Reactivity Ratio Studies. Poly(*N*-vinylformamide-*co*-acrylamide). The feed ratios of monomers and the resultant copolymer compositions as determined from ^{13}C NMR (Table II) were used to calculate the reactivity ratios for the NVF (M_1)/AM (M_2) copolymer series. Figure 1 shows a typical ^{13}C NMR spectrum of a copolymer of NVF and AM (NVF/AM6). The Fineman–Ross[8] method and the Kelen–Tudos[9] method were employed to determine the monomer reactivity ratios at low conversion. The Fineman–Ross method yielded values of $r_1 = 0.053 \pm 0.023$ and $r_2 = 0.534 \pm 0.111$ while the Kelen–Tudos method generated values of $r_1 = 0.046 \pm 0.035$ and $r_2 = 0.517 \pm 0.065$. A comparison of the reactivity ratios obtained by the two methods is given in Table I. In Figure 2, a copolymer composition plot of mol % NVF found in the copolymer versus mol % NVF in the feed is shown. The NVF/AM comonomers, with r_1 and r_2 both less than 1 and $r_1r_2 < 0.03$, possess a strong inherent tendency to form alternating copolymers. The calculation of the statistical distribution of monomer sequences M_1–M_1, M_2–M_2, and M_1–M_2 was performed for the NVF/AM copolymers by the method of Igarashi.[10] Table III lists the structural data for the copolymers. The calculated mol % of M_1–M_2 linkages is very high, again indicating a definite alternating tendency. Also, the relatively low mean sequence length values are a further indication of the alternating tendency in the NVF/AM copolymers.

The alternating tendency of the copolymers suggests that there is some donor–acceptor character between *N*-vinylformamide and acrylamide. NVF is expected to be a mildly electron-donating monomer while acrylamide, due to the strong electron-withdrawing amide group, is a mildly electron-accepting monomer. Similar behavior has been observed by Schulz et al.[11] for copolymers of *N*-vinylpyrrolidone with various monomers possessing an acrylamido functionality. Comparable behavior has been found with the NVF/AM copolymers and would be anticipated due to the similar electronic nature of the formamide and *N*-pyrrolidone groups.

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

Sample no.	feed	% convn	M_1 in copolymer[a]
NVF/NA1	90.0:10.0	13.0	77.1 ± 4.6
NVF/NA2	75.0:25.0	4.7	60.7 ± 3.6
NVF/NA3	60.0:40.0	13.0	48.3 ± 2.9
NVF/NA4	50.0:40.0	8.8	40.8 ± 2.5
NVF/NA5	40.0:60.0	10.7	38.7 ± 2.3
NVF/NA6	25.0:75.0	14.6	27.6 ± 1.7
NVF/NA7	10.0:90.0	18.0	18.5 ± 1.1

[a] Determined by ^{13}C NMR.

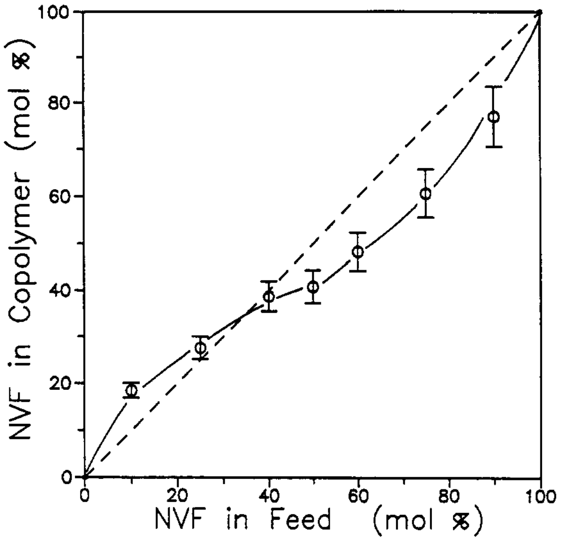

Figure 3. Mole percent NVF incorporated into the NVF/NA copolymers as a function of the comonomer feed ratio. The dashed line represents ideal random incorporation.

Table V. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with Sodium Acrylate (M_2)

sample no.	M_1 in copolymer (mol %)	blockiness (mol %)		alteration (mol %):	mean seq length	
		M_1–M_1	M_2–M_2	M_1–M_2	M_1	M_2
NVF/NA1	77.10	55.20	1.00	43.80	3.00	1.06
NVF/NA2	60.70	26.49	5.09	68.43	1.67	1.17
NVF/NA3	48.30	11.05	14.45	74.53	1.33	1.35
NVF/NA4	40.80	5.82	24.22	69.96	1.22	1.52
NVF/NA5	38.70	4.82	27.42	67.76	1.15	1.78
NVF/NA6	27.60	1.67	46.47	51.87	1.07	2.56
NVF/NA7	18.50	0.58	63.58	35.84	1.02	5.67

Poly(*N*-vinylformamide-*co*-sodium acrylate). The feed ratios of monomers and the resultant copolymer compositions as determined from ^{13}C NMR (Table IV) were used to calculate the reactivity ratios for the NVF (M_1)/NA (M_2) copolymer series. The Fineman–Ross[8] method and the Kelen–Tudos[9] method were employed to determine the monomer reactivity ratios at low conversion. The Fineman–Ross method yielded values of $r_1 = 0.29 \pm 0.11$ and $r_2 = 0.65 \pm 0.03$ while the Kelen–Tudos method generated values of $r_1 = 0.22 \pm 0.09$ and $r_2 = 0.52 \pm 0.05$. A comparison of the reactivity ratios obtained by the two methods is given in Table I. In Figure 3, a copolymer composition plot of mol % NVF found in the copolymer versus mol % NVF in the feed is shown. The calculation of the statistical distribution of monomer sequences M_1–M_1, M_2–M_2, and M_1–M_2 was performed for the NVF/NA copolymers by the method of Igarashi.[10] Table V lists the structural data for the copolymers.

The copolymers of NVF and NA also display an alternating tendency; however, the cause for alternation is likely due to electrostatic repulsions between the sodium acrylate units. Unlike acrylamide, sodium acrylate possesses a carboxylate functionality which actually donates electron density into the vinyl bond. Thus, NVF and NA both bearing a partial negative charge in the vinyl bonds should repel each other to some extent. However, the repulsion between sodium acrylate units is greater since these monomer units carry a full negative charge. If sodium acrylate is the pendant unit on the growing chain, the activation energy to add a NVF monomer will be slightly lower than the addition of a sodium acrylate due to the absence of electrostatic repulsion. Once NVF is the pendant group, the addition of sodium acrylate will be favored since the NA radical is more stable than the NVF radical. This same alternating tendency has been observed in sodium acrylate/acrylamide copolymers; however, a decrease in alternation is observed if the polymerization is carried out in 1 M NaCl.[12] This behavior is expected since, in the presence of added electrolytes, electrostatic repulsions are screened. Therefore, the structural composition of these copolymers is significantly affected by the polymerization medium which in turn will affect the physical behavior of the resulting copolymers.

Table VI. Reaction Parameters for the Copolymerization of *N*-Vinylformamide (M_1) with *n*-Butyl Acrylate (M_2)

sample no.	feed	% convn	M_1 in copolymer[a]
NVF/BA1	90.0:10.0	9.5	59.5 ± 3.6
NVF/BA2	75.0:25.0	11.2	48.2 ± 2.9 49.2[b]
NVF/BA3	60.0:40.0	12.0	47.5 ± 2.8
NVF/BA4	50.0:50.0	13.5	42.2 ± 2.5 41.6[b]
NVF/BA5	40.0:60.0	9.9	38.2 ± 2.3
NVF/BA6	25.0:75.0	10.1	24.5 ± 1.5
NVF/BA7	10.0:90.0	8.0	14.9 ± 0.9

[a] Determined by ^{13}C NMR. [b] Determined by elemental analysis.

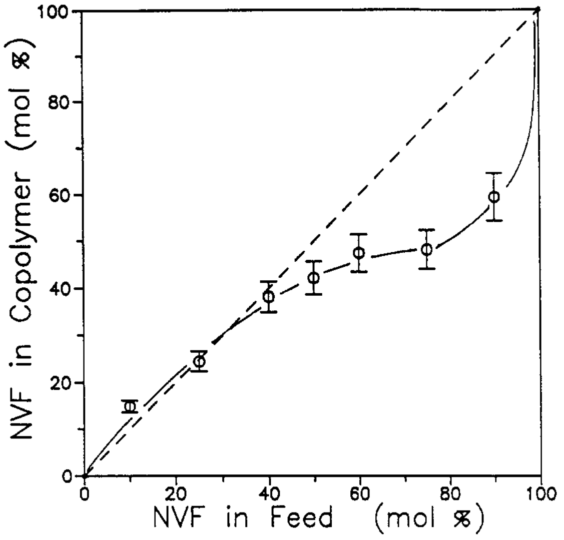

Figure 4. Mole percent NVF incorporated into the NVF/BA copolymers as a function of the comonomer feed ratio. The dashed line represents ideal random incorporation.

Poly(*N*-vinylformamide-*co*-*n*-butyl acrylate). The feed ratios of monomers and the resultant copolymer compositions as determined from ^{13}C NMR (Table VI) were used to calculate the reactivity ratios for the NVF (M_1)/BA (M_2) copolymer series. Elemental analyses were also performed on two copolymers, NVF/BA2 and NVF/BA4, and agreed favorably with the information obtained by ^{13}C NMR. The Fineman–Ross[8] method and the Kelen–Tudos[9] method were employed to determine the monomer reactivity ratios at low conversion. The Fineman–Ross method yielded values of $r_1 = 0.061 \pm 0.02$ and $r_2 = 0.54 \pm 0.09$ while the Kelen–Tudos method generated values of $r_1 = 0.071 \pm 0.03$ and $r_2 = 0.55 \pm 0.06$. A comparison

Table VII. Structural Data for the Copolymers of *N*-Vinylformamide (M_1) with *n*-Butyl Acrylate (M_2)

sample no.	M_1 in copolymer (mol %)	blockiness (mol %)		alternation (mol %):	mean seq length	
		M_1–M_1	M_2–M_2	M_1–M_2	M_1	M_2
NVF/BA1	59.50	21.60	2.60	75.80	1.64	1.06
NVF/BA2	48.20	6.62	10.22	83.15	1.21	1.18
NVF/BA3	47.50	6.07	11.07	82.85	1.11	1.36
NVF/BA4	42.40	3.25	18.45	78.29	1.07	1.55
NVF/BA5	38.20	2.00	25.60	72.39	1.05	1.82
NVF/BA6	24.50	0.44	51.44	48.12	1.02	2.64
NVF/BA7	14.90	0.12	70.32	29.56	1.01	5.92

of the reactivity ratios obtained by the two methods is given in Table I. In Figure 4, a copolymer composition plot of mol % NVF found in the copolymer versus mol % NVF in the feed is shown. The NVF/BA comonomers, with r_1 and r_2 both less than 1 and $r_1r_2 < 0.04$, also possess a strong inherent tendency to form alternating copolymers. The calculation of the statistical distribution of monomer sequences M_1–M_1, M_2–M_2, and M_1–M_2 was performed for the NVF/BA copolymers by the method of Igarashi.[10] Table VII lists the structural data for the copolymers. The calculated mol % of M_1–M_2 linkages is very high, again indicating a definite alternating tendency. Also, the relatively low mean sequence length values are a further indication of the alternating tendency in the NVF/BA copolymers.

Conclusions

Copolymers of *N*-vinylformamide with acrylamide, sodium acrylate, and *n*-butyl acrylate were prepared by free-radical polymerization. ^{13}C NMR was used to determine the copolymer compositions by integration of the carbonyl peaks. The reactivity ratios were determined by two methods and indicate a strong alternating tendency in all copolymerizations. This alternating tendency was further confirmed by determining the copolymer microstructures by the method of Igarashi.

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