mL of freshly drawn bovine blood, and the cells were tilted until clotting occurred. Measured clotting times in parentheses in minutes were **5** (>45), **6** (<5), **7** (<5), **11** (40), **12** (40), **13** (>45), **14** (<5), **15** (40), and **16** (30). Thus, the hydrophobic fluoroalkoxy side group appears to play the major role in raising blood compatibility of these polymers.

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(21) The use of a slight excess of alkoxide relative to P–Cl bonds leads to complete chlorine replacement by the shorter alkoxy chains (n = 1 or 2). However, larger excesses of alkoxide are needed for the longer glyme units (up to four equivalents per P–Cl unit). We have also found that the addition of 1–2 g of $(n\text{-Bu})_4NBr$, as a "phase-transfer catalyst" to these types of reactions, is an aid to obtaining complete substitution.

(22) This method of isolation is possible because the trifluoroethoxy groups generate an insolubility in aqueous media.

Water-Soluble Copolymers. 17. Copolymers of Acrylamide with Sodium 3-Methacrylamido-3-methylbutanoate: Synthesis and Characterization

C. L. McCormick* and K. P. Blackmon

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406. *Received November 19, 1985*

ABSTRACT: The copolymerization of acrylamide (AM) with sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) has been studied in the range from 25 to 90% AM in the feed. The value of r_1r_2 has been determined to be 0.24 for the AM–NaMAMB pair. The copolymer compositions have been determined from elemental analysis and ^{13}C NMR. The molecular weights as measured by low-angle laser light scattering of the copolymers were found to decrease with increasing NaMAMB content and ranged from 2×10^6 to 7×10^6. Second virial coefficients were also obtained from the light scattering data and ranged from 3.1×10^{-4} to 3.5×10^{-4} mL·mol/g^2. The copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. These model structures are utilized for assessment of structure/dilute solution property relationships reported in a subsequent paper in this series.

Introduction

An increasingly large number of water-soluble polymers are being studied for a wide range of potential applications.[1-4] Of growing importance are copolymers of acrylamide for use as water-soluble viscosifiers and displacement fluids in enhanced oil recovery.[5-10] However, a serious limitation of many polyelectrolytes, including those derived from hydrolyzing polyacrylamide, is the severe loss of viscosity in the presence of mono- and multivalent electrolytes. Even more catastrophic is the exhibition of phase separation in the presence of multivalent electrolytes ($CaCl_2$) as is common with many such polyelectrolytes.

The aim of our continuing research[11-16] is to prepare model water-soluble polymers with large hydrodynamic dimensions in electrolyte solutions that are stable against phase separation in the presence of divalent ions, e.g., $CaCl_2$. In two previous papers[15,16] we reported the synthesis, characterization, and solution properties of copolymers of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB). In this paper we report the synthesis, structural characterization, and molecular weight studies of charged copolymers of acrylamide (AM) with sodium-3-methacrylamido-3-methylbutanoate (NaMAMB). The introduction of a methyl group on the α-carbon of this monomer promised stiffening of the resulting polymer backbone with marked inhibition of rotation about the C–C bonds.[17] Furthermore, a more rigid molecule could increase hydrodynamic volume in solution.

Experimental Section

Materials. Sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) was prepared by neutralization of 3-methacrylamido-3-methylbutanoic acid (MAMBA). MAMBA was synthesized via a Ritter reaction involving equimolar amounts of methacrylonitrile and 3,3-dimethylacrylic acid in the presence of water and a large excess of concentrated sulfuric acid. The synthesis of MAMBA followed the procedure set forth by Hoke and Robins.[18] The crude MAMBA was recrystallized twice from a mixture of methyl ethyl ketone and petroleum ether prior to use (mp 69–70 °C). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.38; H, 8.11; N, 7.57. Found: C, 57.99; H, 8.41; N, 7.46. IR N–H stretch, 3350; $CH_2{=}C$, 2980; aliphatic C–H, 2930; amide C=O, 1690 (s), 1530 (m); acid C=O, 1710 cm^{-1}. Acrylamide (AM) from Aldrich Chemical Co. was recrystallized twice from acetone and vacuum-dried at room temperature prior to use (mp 83–84 °C). Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water prior to use.

Poly(sodium 3-methacrylamido-3-methylbutanoate) and Poly(acrylamide-*co*-sodium 3-methacrylamido-3-methylbutanoate). The homopolymer of sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) and the copolymers of acrylamide (AM) with NaMAMB were prepared in aqueous solution at 30 °C using 0.1 mol % potassium persulfate as the initiator. Each reaction was conducted in a 1000-mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet tube. A designated amount of MAMBA was partially dissolved in deionized water followed by the addition of an equimolar amount of NaOH. A designated amount of acrylamide dissolved in deionized water was then added to the neutralized MAMBA solution, and the pH of the entire mixture was adjusted to 9.0 ± 0.1 by dropwise addition of 0.5 M NaOH. The pH adjustment was performed to ensure that all of the carboxylated monomer was in the sodium salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 min. The designated quantity of potassium persulfate initiator, dissolved in deionized water, was injected into the reaction vessel. The total monomer concentration in each reaction was held constant at 0.456 M. After designated reaction intervals, the resulting polymer was diluted with deionized water and precipitated into reagent-grade acetone. The polymers were further purified by reprecipitation into acetone followed by freeze-drying and then vacuum-drying for 2 days. Conversions were determined gravimetrically. Table I lists reaction parameters for the copolymerization of AM with NaMAMB and the homopolymerization of NaMAMB. IR: MAMB homopolymer, N–H stretch (br), 3400; C–H, 2970; amide C=O, 1650; sodium salt

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Table I
Reaction Parameters for the Copolymerization of Acrylamide (M_1) with Sodium 3-Methacrylamido-3-methylbutanoate (M_2) and Homopolymerization of NaMAMB

sample	feed ratio M_1:M_2	reactn time, h	conversn, %	wt % C	wt % N	M_2 in copolymer,[a] mol %	M_2 in copolymer,[b] mol %
MAMB-10-1	90:10	1.25	2.1	45.74	13.52	15.8 ± 0.3	15.7 ± 0.8
MAMB-10-3	90:10	19	29.0	47.88	14.99	12.1 ± 0.2	
MAMB-25-1	75:25	2	1.8	46.09	10.94	31.9 ± 0.7	31.2 ± 1.6
MAMB-25-3	75:25	19	27.2	48.09	11.75	29.6 ± 0.6	
MAMB-40-1	60:40	2.75	4.0	46.82	9.75	43.4 ± 1.1	43.5 ± 2.2
MAMB-40-3	60:40	19	33.8	46.28	9.79	41.9 ± 1.0	
MAMB-60-1	40:60	4	3.1	46.12	8.50	55.5 ± 1.6	51.3 ± 2.6
MAMB-60-2	40:60	24	34.7	46.54	8.43	57.3 ± 1.6	
MAMB-75-1	25:75	7	1.4	46.27	7.61	68.2 ± 2.1	
MAMB-75-2	25:75	30	32.5	46.08	7.57	68.3 ± 2.1	
MAMB	0:100	48	34.1	52.17[c]	6.76[c]	100	100
PAM-1	100:0	6.5	38.0	50.63[c]	19.69[c]	0	0

[a] From elemental analysis. [b] From C-13 NMR. [c] Theoretical value.

Table II
Molecular Weight and Second Virial Coefficient Data for the Copolymers of Acrylamide (AM) with Sodium 3-Methacrylamido-3-methylbutanoate (NaMAMB) and Homopolymer of NaMAMB

sample	compn,[a] mol % AM	compn,[a] mol % NaMAMB	$\bar{M}_w \times 10^{-6}$	$\overline{DP}_w \times 10^{-4}$	$A_2 \times 10^4$, mL·mol/g^2
PAM-1	100	0	8.9	12.5	3.5
MAMB-10-3	87.9	12.1	7.2	8.2	3.2
MAMB-25-3	70.4	29.6	6.9	6.2	3.1
MAMB-40-3	58.1	41.9	6.6	5.2	3.5
MAMB-60-2	42.7	57.3	4.2	2.8	3.3
MAMB-75-2	31.7	68.3	2.0	1.2	3.2
MAMB	0	100	2.6	1.2	3.5

[a] From elemental analysis.

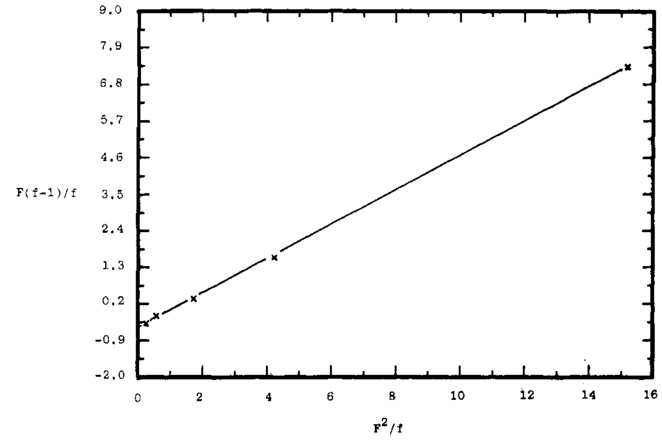

Figure 1. Determination of reactivity ratios for the copolymerization of acrylamide (M_1) with sodium 3-methacrylamido-3-methylbutanoate (M_2) by the Fineman-Ross method.

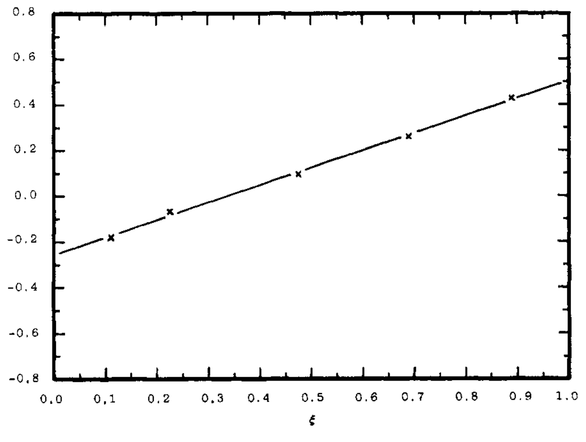

Figure 2. Kelen-Tüdös plot for the determination of reactivity ratios for the copolymerization of acrylamide with sodium 3-methacrylamido-3-methylbutanoate.

Table III
Reactivity Ratios for the Copolymerization of Acrylamide (M_1) with Sodium 3-Methacrylamido-3-methylbutanoate (M_2)

method	r_1	r_2	r_1r_2
Fineman-Ross	0.51 ± 0.01	0.51 ± 0.07	0.26
Kelen-Tüdös	0.50 ± 0.01	0.48 ± 0.06	0.24

C=O, 1590 cm^{-1}. Typical copolymer: MAMB-40-3, N-H stretch (br), 3400; C-H, 2970; AM amide C=O, 1670 (s), 1580 (m); NaMAMB amide C=O, 1660 (s); sodium salt C=O, 1585 cm^{-1}.

Elemental Analysis. Elemental analyses for carbon, hydrogen, and nitrogen of the AM-NaMAMB copolymers were conducted by M-H-W Laboratories of Phoenix, AZ (Table I). The copolymer compositions were calculated using C/N ratios because of the variability of absolute values due to the hygroscopic nature of the polymers. Elemental analyses were conducted at low and high polymer conversions to assess the effects of compositional drift and were found to be in good agreement. Thus it can be concluded that the effects of compositional drift are minimal.

^{13}C Nuclear Magnetic Resonance Spectroscopy. ^{13}C NMR spectra of the AM-NaMAMB copolymers and NaMAMB homopolymer were obtained at 22.5 MHz on a JEOL FX-90Q Spectrometer using 5-10 wt % aqueous (D_2O) polymer solutions in 10-mm tubes. A pulse repetition of 7-8 s with gated decoupling to remove all NOE was used for quantitative spectral analysis.

Low-Angle Laser Light Scattering. Low-angle laser light scattering measurements to determine molecular weights were performed with a Chromatix KMX-6 photometer. Refractive index increments were determined with a Chromatix KMX-16 laser differential refractometer. All measurements were performed at 25 °C in 1.0 M NaCl aqueous solutions at a pH of 8.0. Weight-average molecular weights and second virial coefficients derived from these data are shown in Table II for the AM-NaMAMB copolymers and NaMAMB homopolymer.

Results and Discussion

Reactivity Ratio Studies. The feed ratios of monomers and the resultant copolymer compositions as determined from elemental analyses (Table I) were used to calculate reactivity ratios for the AM-NaMAMB pair. The Fineman-Ross method[19] and the Kelen-Tüdös method[20] were employed to determine the monomer reactivity ratios at low conversion. Figure 1 is the Fineman-Ross plot for acrylamide (M_1) and sodium 3-methacrylamido-3-methylbutanoate (M_2). The reactivity ratio r_1 was determined to be 0.51 ± 0.01 from the slope and r_2 = 0.51 ± 0.07 from the intercept. A plot of the data according to the Kelen-Tüdös method is shown in Figure 2.

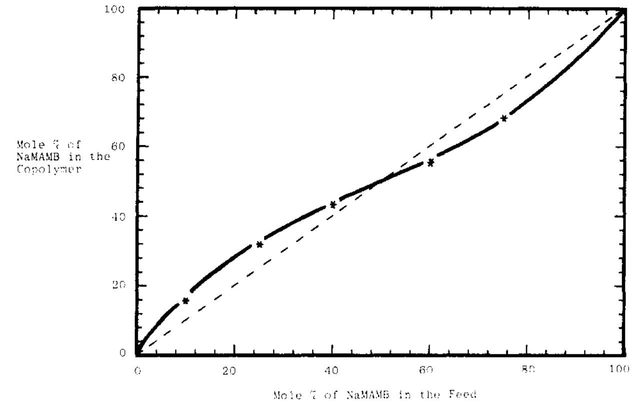

Figure 3. Copolymer composition as a function of feed composition for the copolymerization of acrylamide (AM) with sodium 3-methacrylamido-3-methylbutanoate (NaMAMB).

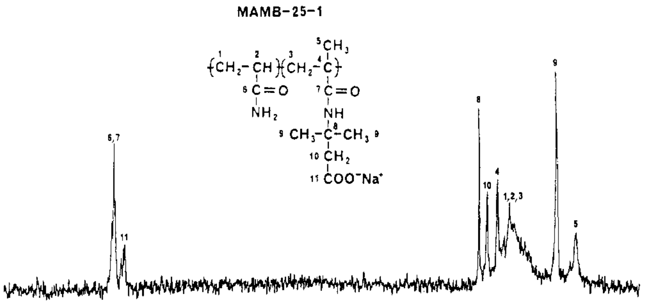

Figure 4. Typical ^{13}C NMR spectrum of a copolymer of acrylamide with sodium 3-methacrylamido-3-methylbutanoate.

Graphical evaluation of Figure 2 yields reactivity ratios for the AM–NaMAMB monomer pair of $r_1 = 0.50 \pm 0.01$ and $r_2 = 0.48 \pm 0.06$, respectively. A comparison of the reactivity ratios obtained by the two low conversion methods is given in Table III. The observed data in the Kelen–Tüdös plot (Figure 2) are linear, and indication that the copolymerizations of AM with NaMAMB follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit.[21] Figure 3 shows the copolymer composition as determined from elemental analysis as a function of feed composition for the copolymerization of AM with NaMAMB. The copolymerization curve is based on the experimentally determined reactivity ratios. The AM–NaMAMB comonomers (r_1 and r_2 both less than 1 and $r_1r_2 = 0.24$) possess a definite alternating tendency in copolymerization. It can be seen from the copolymer composition plot (Figure 3) that the azeotropic copolymerization point occurs when there is approximately 50 mol % of each monomer in the feed. At this point, the copolymer has the same composition as the monomer feed mixture, and a polymeric product of constant composition is formed throughout the copolymerization reaction.

Macromolecular Structure. The structures of the AM–NaMAMB copolymers and NaMAMB homopolymer were verified by IR, ^{13}C NMR, and elemental analysis. The procedure for determining copolymer compositions using ^{13}C NMR will be discussed in detail in a subsequent paper in this series. Briefly, the carbonyl peaks were used as a standard, and other NaMAMB peaks (no. 5, 8, and 9 in Figure 4) were integrated to give the mole percent of NaMAMB in the copolymer. The copolymer compositions as determined by ^{13}C NMR are shown in Table I and agree favorably with the compositions as determined from elemental analysis. A typical ^{13}C NMR spectrum of a copolymer of AM with NaMAMB is shown in Figure 4. The observed splitting of the carbonyl peaks (no. 6, 7, and 11 in Figure 4) can be correlated to copolymer sequence distributions. Typical copolymer peak assignments and spin–lattice relaxation times, T_1, are shown in Table IV.

Table IV
^{13}C NMR Peak Assignments for Copolymers of Acrylamide with Sodium 3-Methacrylamido-3-methylbutanoate

peak	chem shift, ppm	spin–lattice relax. times T_1, s
1, 2, 3	41–47	0.05
4	50.0	0.4
5	21.4	0.03
6, 7	182–184	0.9
8	56.3	0.9
9	28.6	0.2
10	53.4	0.05
11	178–181	1.1

As a further step in the characterization of the macromolecular structure of the AM–NaMAMB polymers, weight-average molecular weights were determined by low-angle laser light scattering. The molecular weight and second virial coefficient data are shown in Table II.

Effect of Feed Composition. The effect of feed composition on molecular weight is shown in Table II for the AM–NaMAMB polymers and, for comparative purposes, a homopolymer of AM prepared under the same reaction conditions. Second virial coefficients were also obtained from the light scattering measurements. The molecular weight was found to decrease with increasing NaMAMB content and ranged from 7.2×10^6 for MAMB-10-3 (12.1 mol % NaMAMB) to 2.0×10^6 for MAMB-75-2 (68.3 mol % NaMAMB). The second viral coefficients were relatively unaffected by copolymer composition. A lower degree of polymerization was expected with increasing NaMAMB in the feed due to enhanced chain transfer to monomer by hydrogen abstraction from the α-methyl group of NaMAMB.[2] The homopolyacrylamide sample achieved the highest molecular weight (8.9×10^6) due to the very slow rate of termination observed for acrylamide.[22,23]

Copolymer Microstructure. The microstructure of the AM–NaMAMB copolymers is expected to be important in determining the solution properties that the copolymers exhibit. The calculation of the statistical distribution of monomer sequences, M_1–M_1, M_2–M_2, and M_1–M_2 may be performed utilizing the method of Igarashi.[24] Monomer mean sequence lengths, μ_1 and μ_2, can be calculated utilizing eq 1 and 2,[25] where r_1 and r_2 are the

$$\mu_1 = 1 + r_1[M_1]/[M_2] \qquad (1)$$

$$\mu_2 = 1 + r_2[M_2]/[M_1] \qquad (2)$$

reactivity ratios for the monomer pair. Table V lists the structural data for the copolymers of AM with NaMAMB.

The calculated mole percent of AM–NaMAMB linkages in each copolymer was relatively high, indicating a definite alternating tendency. The mean sequence length of acrylamide, μ_{AM}, varied from 5.5 at an 84.2/15.8 mole ratio of AM/NaMAMB in the copolymer to 1.2 at a 31.8/68.2 mole ratio. For those copolymer compositions, values of μ_{NaMAMB} were 1.1 and 2.4, respectively. The relatively low mean sequence length values obtained are a further indication of the alternating tendency in the AM–NaMAMB copolymers.

Table VI lists additional structural data for the copolymers of AM with NaMAMB involving higher order sequence distributions, i.e., triads and pentads, calculated with the method of Harwood and Ritchey.[26] The relatively

Table V
Structural Data for the Copolymers of Acrylamide (AM) with Sodium 3-Methacrylamido-3-methylbutanoate (NaMAMB)

	compn,[a] mol %		blockiness,[b] mol %		AM–NaMAMB alternation,[b] mol %	mean sequence length	
sample	AM	NaMAMB	AM–AM	NaMAMB–NaMAMB		μ_{AM}	μ_{NaMAMB}
MAMB-10-1	84.2	15.8	69.2	0.8	30.0	5.5	1.1
MAMB-25-1	68.1	31.9	40.6	4.4	55.0	2.5	1.2
MAMB-40-1	56.6	43.4	24.0	10.7	65.3	1.8	1.3
MAMB-60-1	44.5	55.5	11.6	22.5	65.9	1.3	1.7
MAMB-75-1	31.8	68.2	4.4	40.8	54.8	1.2	2.4

[a] From elemental analysis. [b] Statistically calculated with reactivity ratios.

Table VI
Calculated Structural Data for the AM–NaMAMB Copolymer System

	compn,[a] mol %						
sample	AM	NaMAMB	run no.	P_{AMA}	P_{AAMAA}	N_{AMA}	N_{AAMAA}
MAMB-10-1	84.2	15.8	30.5	0.90	0.60	14.5	9.7
MAMB-25-1	68.1	31.9	54.6	0.74	0.27	23.6	8.5
MAMB-40-1	56.6	43.4	65.2	0.57	0.11	24.7	4.5
MAMB-60-1	44.5	55.5	65.5	0.34	0.02	19.0	1.2
MAMB-75-1	31.8	68.2	55.5	0.17	0.003	11.4	0.2

[a] From elemental analysis.

high run numbers calculated for the copolymer series indicate that few long blocks of AM or NaMAMB units were produced due to their alternating tendency. P_{AMA} and P_{AAMAA} are the probabilities of a NaMAMB-centered triad and pentad, respectively, while N_{AMA} and N_{AAMAA} are the expected numbers of NaMAMB-centered triads and pentads per 100 monomer units. The maximum frequency of NaMAMB-centered triads was found to occur at a copolymer composition containing about 40 mol % NaMAMB, while the maximum frequency of NaMAMB-centered pentads occurred at a copolymer composition containing approximately 21 mol % NaMAMB. The maximum triad and pentad values were obtained by calculating a broad spectrum of AM–NaMAMB copolymer compositions from the copolymerization equation using the experimentally derived Kelen–Tüdős reactivity ratios.

Conclusions

Copolymers of acrylamide with sodium 3-methacrylamido-3-methylbutanoate were prepared in aqueous solution using potassium persulfate as the initiator. Elemental analysis and ^{13}C NMR were used to determine the copolymer compositions. The reactivity ratios, $r_1r_2 = 0.24$, were determined from two low-conversion methods and indicate the tendency of these monomers toward alternation. ^{13}C NMR spectra were obtained on all samples; spin–lattice relaxation times were determined. The copolymer microstructures were calculated by utilizing the methods of Igarashi[24] and Harwood and Ritchey.[26] The maximum number of NaMAMB-centered triads was found to occur at a copolymer composition containing about 40 mol % NaMAMB, while the maximum number of NaMAMB-centered pentads occurred at a copolymer composition of approximately 21 mol % NaMAMB. Weight-average molecular weights in the range of 2×10^6 to 7×10^6 have been determined for the AM–NaMAMB polymers and were found to decrease with increasing NaMAMB content. This decrease in molecular weight with increasing NaMAMB content may be attributed to enhanced chain transfer to monomer due to the stability of the allylic radical formed by hydrogen abstraction from NaMAMB. The experimentally determined molecular weights, copolymer compositions, and calculated microstructures of these AM–NaMAMB polymers are used for the development of structure/dilute solution property relationships in a subsequent paper in this series.

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Registry No. NaMAMB, 101672-01-9; MAMBA, 92989-14-5; PNaMAMB, 101672-03-1; (AM)·(NaMAMB) (copolymer), 101672-02-0; $H_2C{=}C(CH_3)CN$, 126-98-7; $(CH_3)_2C{=}CHCO_2H$, 541-47-9; $H_2C{=}CHCONH_2$, 79-06-1.

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