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### Water-Soluble Copolymers. XIX. Copolymers of Acrylamide with Sodium 3-(N-Propyl)acrylamido-3-Methylbutanoate: Synthesis and Characterization

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## **Water-Soluble Copolymers. XIX. Copolymers of Acrylamide with Sodium 3-(N-Propyl)acrylamido-3-Methylbutanoate: Synthesis and Characterization**

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### ABSTRACT

The copolymerization of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB) has been studied in the range from 40 to 90% AM in the feed. The copolymer compositions have been determined from elemental analysis and  $^{13}\text{C}$  NMR. Reactivity ratio studies have been performed, and the value of  $r_1 r_2$  determined to be 0.36. The molecular weights, as determined by low-angle laser light scattering of the copolymers, were found to decrease sharply with increasing NaPAMB content, and were in the range  $0.5\text{--}7.0 \times 10^6$ . The copolymer microstructures, including mean sequence length distributions, were calculated from the reactivity ratios. Knowledge of polymer composition, microstructure, and molecular weight is utilized for assessment of structure/dilute solution property relationships reported in a subsequent paper in this series.

## INTRODUCTION

Water-soluble polymers have shown many properties lending themselves to a wide variety of industrial applications [1, 2]. Copolymers of acrylamide have especially increased in importance due to their utility as water-soluble viscosifiers and displacement fluids in enhanced oil recovery [3, 4]. Furthermore, recent developments in the area of hydrophobically modified acrylamide copolymers have shown great promise as a "new breed" of water-soluble viscosifiers, suitable for enhanced oil recovery applications [5, 6].

The aim of our continuing research is to prepare model water-soluble copolymers of acrylamide with large hydrodynamic dimensions in solution by tailoring the macromolecules with selected structures. In this paper we report the synthesis, reactivity ratio studies, molecular characterization, and classical laser light-scattering studies of charged copolymers of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB). In previous papers [7-10] we reported the synthesis, characterization, and solution properties of copolymers of AM with sodium 3-acrylamido-3-methylbutanoate (NaAMB) and sodium 3-methacrylamido-3-methylbutanoate (NaMAMB). The substitution of an n-propyl group for the amide hydrogen of NaAMB to produce NaPAMB was performed to assess the effects of increased hydrophobicity on solution properties, while maintaining the polyelectrolytic character of the polymers. Furthermore, substitution of a propyl group for the amide hydrogen would eliminate the possibility of a 6-membered intraunit hydrogen-bonded ring.

## EXPERIMENTAL

Materials and Monomer Synthesis

The synthesis of 3-(N-propyl)acrylamido-3-methylbutanoic acid (PAMBA) involved three steps. In the first step, n-propylamine (Aldrich Chemical Co.) was added dropwise with stirring to an equimolar amount of 4-methyl-3-penten-2-one (mesityl oxide, Aldrich Chemical Co.). The temperature was maintained at 15-25°C and the reaction allowed to continue for 8 h. This addition product was obtained in 80-90% yield based on remaining mesityl oxide double bonds present from  $^{13}\text{C}$  NMR. The reaction product was then diluted with 4-5 volumes of tetrahydrofuran (THF), and a slight molar excess of triethylamine (TEA) was added. Acryloyl chloride (Aldrich Chemical Co.) was then added dropwise with stirring while maintaining the temperature of the reaction at 10°C with an ice bath. After approximately 6 h the TEA:HCl salt was filtered and the THF removed by distillation. A dark, viscous material was obtained; upon cooling to

-80°C in an acetone bath, a yellow solid was isolated. After recrystallization of the solid from a mixture of methyl ethyl ketone and petroleum ether, the desired intermediate product, N-propyl diacetone acrylamide (PDAAM), was obtained in a 30-40% yield (mp 50-51°C).

PDAAM analysis. Calculated for  $C_{12}H_{21}NO_2$ : C, 68.25; H, 9.95; N, 6.64%. Found: C, 68.15; H, 9.98; N, 6.73%.

In the final step of the monomer synthesis to convert the keto-methyl group to an acid group, potassium hypobromite (KOB) was used. To 2.0 mol KOH in 400 mL  $H_2O$ , 0.5 mol  $Br_2$  was added with stirring while maintaining the temperature at about 10°C in an ice bath. This KOB solution was then added dropwise with stirring to 0.1 mol PDAAM dissolved in 2000 mL p-dioxane while maintaining the temperature at 10°C. The reaction was allowed to proceed for approximately 8 h, after which the pH of the mixture was adjusted to 2-3 by addition of concentrated HCl. The acidified mixture was then extracted with chloroform. After removal of the chloroform, a viscous material was obtained which could be isolated by recrystallization from ether. The desired monomer, 3-(N-propyl)acrylamido-3-methylbutanoic acid (PAMBA), was obtained in 40-60% yield (mp 76-78°C).

PAMBA analysis. Calculated for  $C_{11}H_{19}NO_3$ : C, 61.97; H, 8.92; N, 6.57%. Found: C, 61.41; H, 8.82; N, 6.58%. IR: COOH (broad), 3 200-3 000  $cm^{-1}$ ; C=C-H, 2 980  $cm^{-1}$ ; aliphatic C-H, 2 880  $cm^{-1}$ ; amide C=O, 1 650  $cm^{-1}$ ; acid C=O, 1 730  $cm^{-1}$  (s), 1 390  $cm^{-1}$  (m)

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-(N-Propyl)Acrylamido-3-Methylbutanoate) and Poly(Acrylamide-co-Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate)

The homopolymer of sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB) and the copolymers of acrylamide (AM) with NaPAMB 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 3-necked flask equipped with a mechanical stirrer and nitrogen inlet tube. A designated amount of 3-(N-propyl)acrylamido-3-methylbutanoic acid (PAMBA) 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 PAMBA solution, and the pH of the entire mixture was adjusted to  $9.0 \pm 0.1$  by dropwise addition of 0.5 M NaOH. The pH adjustment was performed to insure that all of the

TABLE 1. Reaction Parameters for the Copolymerization of Acrylamide ( $M_1$ ) with Sodium 3-(N-Propyl)-Acrylamido-3-Methylbutanoate ( $M_2$ ) and Homopolymerization of NaPAMB

Sample	Feed ratio $M_1:M_2$	Reaction time, h	Conversion, %	Analysis, wt% C	Analysis, wt% N	$M_2$ in copolymer, mol% <sup>a</sup>	$M_2$ in copolymer, mol% <sup>b</sup>
PAMB-10-1	90:10	4	2.1	47.01	14.86	8.62 ± 0.15	-
PAMB-10-2	90:10	10	30.3	47.02	14.81	8.79 ± 0.16	8.4 ± 0.9
PAMB-25-1	75:25	8	3.4	45.82	11.75	19.36 ± 0.41	-
PAMB-25-2	75:25	14	31.5	47.85	12.03	20.49 ± 0.43	19.6 ± 2.3
PAMB-40-1	60:40	10	4.1	46.54	9.90	31.04 ± 0.76	-
PAMB-40-2	60:40	27	37.9	49.84	10.38	32.51 ± 0.76	31.7 ± 0.6
PAMB-60-1	40:60	17	5.2	47.59	8.26	46.50 ± 1.32	-
PAMB-60-2	40:60	41	43.9	48.44	7.77	53.40 ± 1.59	51.6 ± 1.2
PAMB	0:100	72	64.1	56.17 <sup>c</sup>	5.96 <sup>c</sup>	100	100
PAM-2	100:0	6.5	38.0	50.63 <sup>c</sup>	19.69 <sup>c</sup>	0	0

<sup>a</sup>From elemental analysis.

<sup>b</sup>From <sup>13</sup>C NMR.

<sup>c</sup>Theoretical value.

carboxylated monomer was in the sodium salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 min. The designated quantity (0.1 mol%) 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 desired reaction intervals, the resulting polymer was diluted with deionized water and precipitated into reagent-grade acetone. The polymers were subsequently purified by reprecipitation into acetone followed by freeze-drying and then vacuum drying for 2 days. Conversions were determined gravimetrically. Table 1 lists reaction parameters for the copolymers of AM with NaPAMB and the homopolymer of NaPAMB.

IR: PAMB homopolymer, C-H, 2 970  $\text{cm}^{-1}$ ; amide C=O, 1 660  $\text{cm}^{-1}$ ; sodium salt C=O, 1 590  $\text{cm}^{-1}$  (s), 1 420  $\text{cm}^{-1}$  (s). Typical copolymer: PAMB-40-2, N-H (broad), 3 500-3 200  $\text{cm}^{-1}$ ; C-H, 2 970  $\text{cm}^{-1}$ ; AM amide C=O, 1 680  $\text{cm}^{-1}$ ; NaPAMB amide C=O, 1 660  $\text{cm}^{-1}$ ; sodium salt C=O, 1 585  $\text{cm}^{-1}$  (s), 1 420  $\text{cm}^{-1}$  (s).

### Elemental Analysis

Elemental analyses for carbon, hydrogen, and nitrogen of the AM-NaPAMB copolymers were conducted by M-H-W Laboratories of Phoenix, Arizona (Table 1). The copolymer compositions were calculated using C/N ratios to reduce 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. The calculated copolymer compositions at high and low conversion were found to be in good agreement; thus, the effects of compositional drift can be considered to be minimal.

### $^{13}\text{C}$ Nuclear Magnetic Resonance Spectroscopy

$^{13}\text{C}$  NMR spectra for the AM-NaPAMB copolymers and NaPAMB homopolymer were obtained at 22.5 MHz on a JEOL FX-90Q spectrometer using 5-10 wt% aqueous ( $\text{D}_2\text{O}$ ) polymer solutions in 10-mm tubes. A pulse repetition of 2 s and a  $70^\circ$  flip angle with gated decoupling to remove all NOE were used for quantitative studies. Typically, a total of 40 000 transients was accumulated.

### 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 obtained with a Chromatix

TABLE 2. Molecular Weight and Second Virial Coefficient Data for the Copolymers of Acrylamide (AM) with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate (NaPAMB) and Homopolymer of NaPAMB

Sample	Composition, mol% <sup>a</sup>		$\bar{M}_w \times 10^{-6}$	$\bar{DP}_w \times 10^{-4}$	$A_2 \times 10^4$ , (mL·mol)/g <sup>2</sup>
	AM	NaPAMB			
PAM-2	100.0	0	8.9	12.5	3.5
PAMB-10-2	91.2	8.8	7.0	8.2	2.4
PAMB-25-2	79.5	20.5	3.3	3.2	2.9
PAMB-40-2	67.5	32.5	1.4	1.1	16
PAMB-60-2	46.6	53.4	0.52	0.33	8.1
PAMB	0	100.0	0.26	0.11	39

<sup>a</sup> From elemental analysis.

KMX-16 laser differential refractometer. All measurements were performed at 25°C in 0.514 M NaCl aqueous solutions at a pH of 8.0. Weight-average molecular weights and second virial coefficients are shown in Table 2 for the AM-NaPAMB polymers and, for comparative purposes, a homopolyacrylamide sample prepared under the same reaction conditions.

## RESULTS AND DISCUSSION

### Reactivity Ratio Studies

The monomer feed ratios and the resultant copolymer compositions as determined from elemental analysis (Table 1) were used to calculate reactivity ratios for the AM-NaPAMB monomer pair. The Fineman-Ross method [11] and the Kelen-Tüdös method [12] were employed to determine the reactivity ratios at low conversion. Figure 1 is the Fineman-Ross plot for acrylamide ( $M_1$ ) and sodium 3-(N-propyl)acrylamido-3-methylbutanoate ( $M_2$ ). The reactivity ratio  $r_1$  was determined to be  $1.11 \pm 0.02$  from the slope of the line and  $r_2 = 0.26 \pm 0.03$  from the intercept. A plot of the data according to the Kelen-Tüdös method is shown in Fig. 2, and graphical evaluation yields reactivity ratios of  $1.14 \pm 0.02$  and  $0.32 \pm 0.04$  for  $M_1$  and  $M_2$ , respectively. A comparison of the reactivity ratios obtained from the two low-conversion methods is given in Table 3. The observed data in the Kelen-Tüdös plot (Fig. 2) are linear, an indication that the copolymerizations of AM with NaPAMB follow conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit [13].

The copolymer composition (determined from elemental analysis) as a function of feed composition for the copolymerization of AM with NaPAMB is shown in Fig. 3. The copolymerization curve was derived from the copolymerization equation using the experimentally determined Kelen-Tüdös reactivity ratios. The experimental data are in excellent agreement with the projected copolymerization curve. From the reactivity ratios and the subsequent microstructural analyses, it can be seen that the AM-NaPAMB copolymers are gener-

TABLE 3. Reactivity Ratios for the Copolymerization of Acrylamide ( $M_1$ ) with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate ( $M_2$ )

Method	$r_1$	$r_2$	$r_1 r_2$
Fineman-Ross	$1.11 \pm 0.02$	$0.26 \pm 0.03$	0.29
Kelen-Tüdös	$1.14 \pm 0.02$	$0.32 \pm 0.04$	0.36



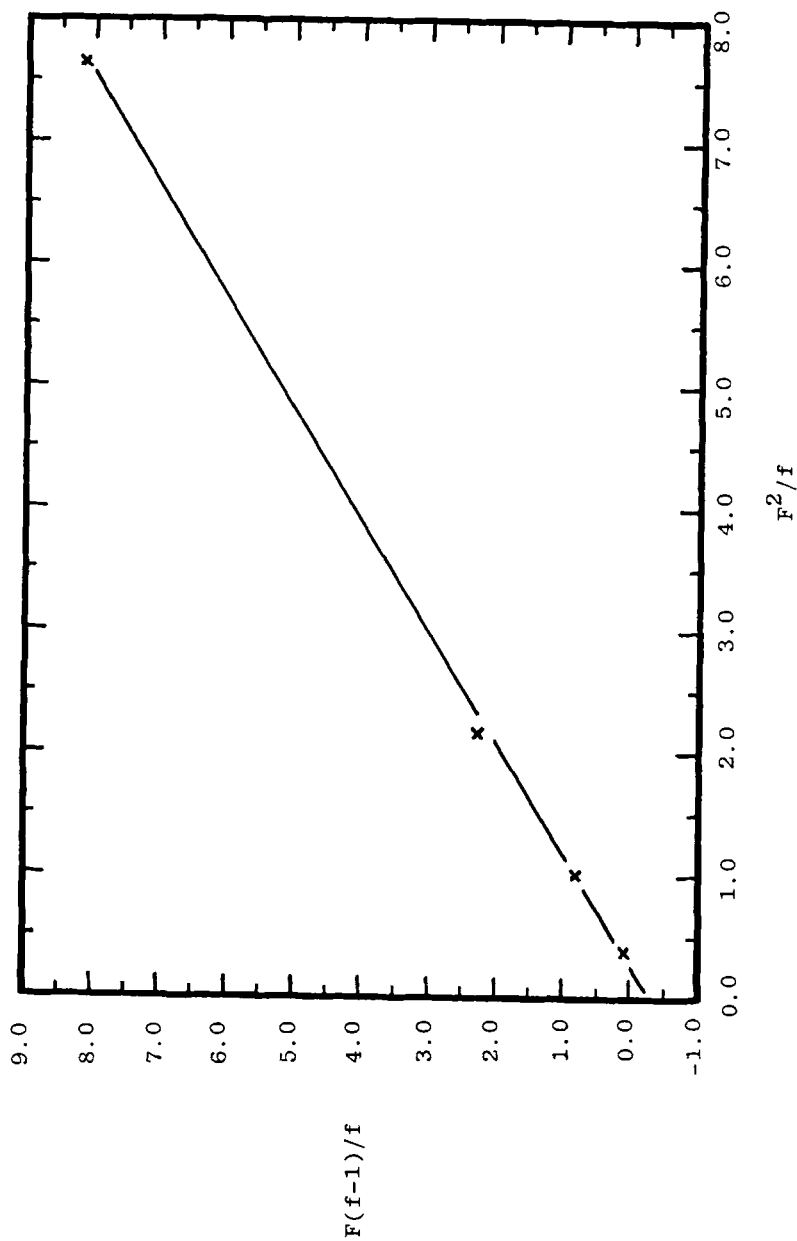


FIG. 1. Determination of reactivity ratios for the copolymerization of acrylamide ( $M_1$ ) with sodium 3-(N-propyl)-acrylamido-3-methylbutanoate ( $M_2$ ) by the Fineman-Ross method.

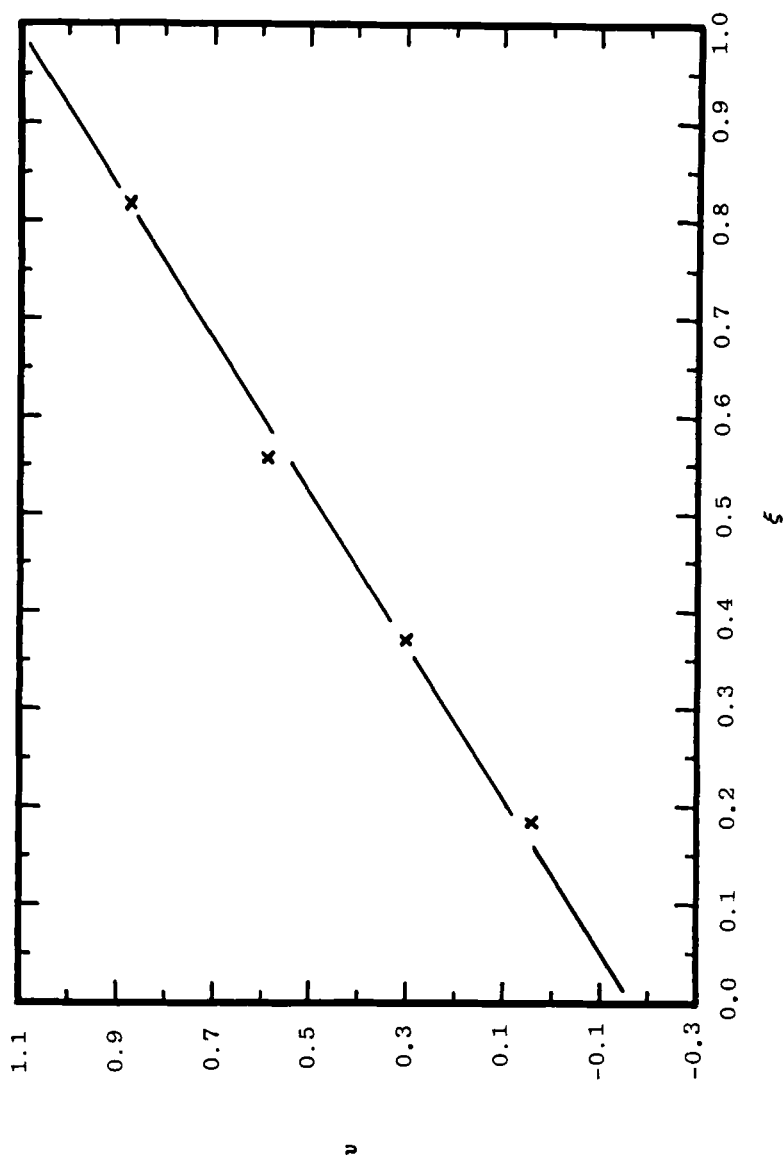


FIG. 2. Kelen-Tüdös plot for the determination of reactivity ratios for the copolymerization of acrylamide with sodium 3-(N-propyl)acrylamido-3-methylbutanoate.

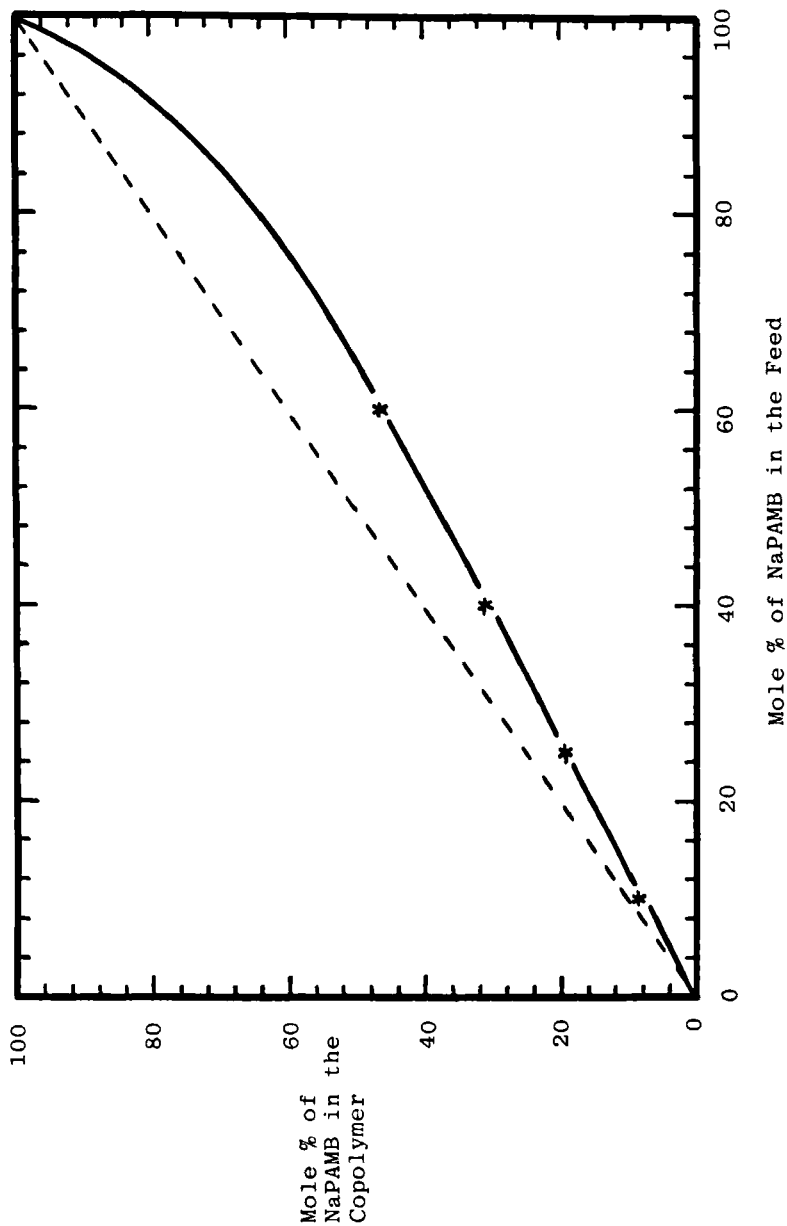


FIG. 3. Copolymer composition as a function of feed composition for the copolymerization of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB).

ally random in nature, possessing a slight alternating tendency with respect to the NaPAMB ( $M_2$ ) monomer.

### Macromolecular Structure

The structures of the AM-NaPAMB copolymers and NaPAMB homopolymer were verified by IR,  $^{13}\text{C}$  NMR, and elemental analyses. The copolymer compositions obtained from  $^{13}\text{C}$  NMR were determined using the procedure described for random copolymers of acrylamide with sulfonated comonomers [14]. Briefly, the carbonyl region at 177-181 ppm was used as a standard, and other NaPAMB peaks (Nos. 9 and 10 in Fig. 4) were integrated to give the percent of NaPAMB in the copolymer. The copolymer compositions as determined by  $^{13}\text{C}$  NMR are shown in Table 1, and agree favorably with the compositions as determined from elemental analysis. A typical  $^{13}\text{C}$  NMR spectrum of a copolymer of AM with NaPAMB (PAMB-40-2) is shown in Fig. 4, while the typical copolymer peak assignments and spin-lattice relaxation times,  $T_1$ , are given in Table 4.

As a further step in the macromolecular characterization of the AM-NaPAMB polymers, weight-average molecular weights were determined by low-angle laser light scattering and found to decrease sharply with increasing NaPAMB content. The molecular weight and second virial coefficient data are shown in Table 2.

### Effect of Feed Composition on Molecular Weight

The effect of feed composition on molecular weight is shown in Table 2 for the AM-NaPAMB polymers and, for comparative purposes, a homopolymer of acrylamide prepared under the same reaction conditions. Second virial coefficients were also obtained from the light-scattering data. The molecular weight was found to decrease sharply with increasing NaPAMB content, and ranged from  $7.0 \times 10^6$  for PAMB-10-2 (8.8 mol% NaPAMB) to  $0.52 \times 10^6$  for PAMB-60-2 (53.4 mol% NaPAMB). The homopolymer of NaPAMB had a weight-average molecular weight of only  $0.26 \times 10^6$ . A lower degree of polymerization would be expected with increasing NaPAMB content in the feed due to the presence of a large number of potentially abstractable hydrogen atoms on the NaPAMB monomer. Furthermore, the bulkiness of the pendent group of NaPAMB could adversely affect the degree of polymerization.

The second virial coefficients of the AM-NaPAMB copolymers vary widely due to large differences in molecular weights. The polymer-solvent interaction would also vary with the changing hydrophobic character as a function of NaPAMB content. The homopoly-acrylamide sample exhibited the highest molecular weight, apparently

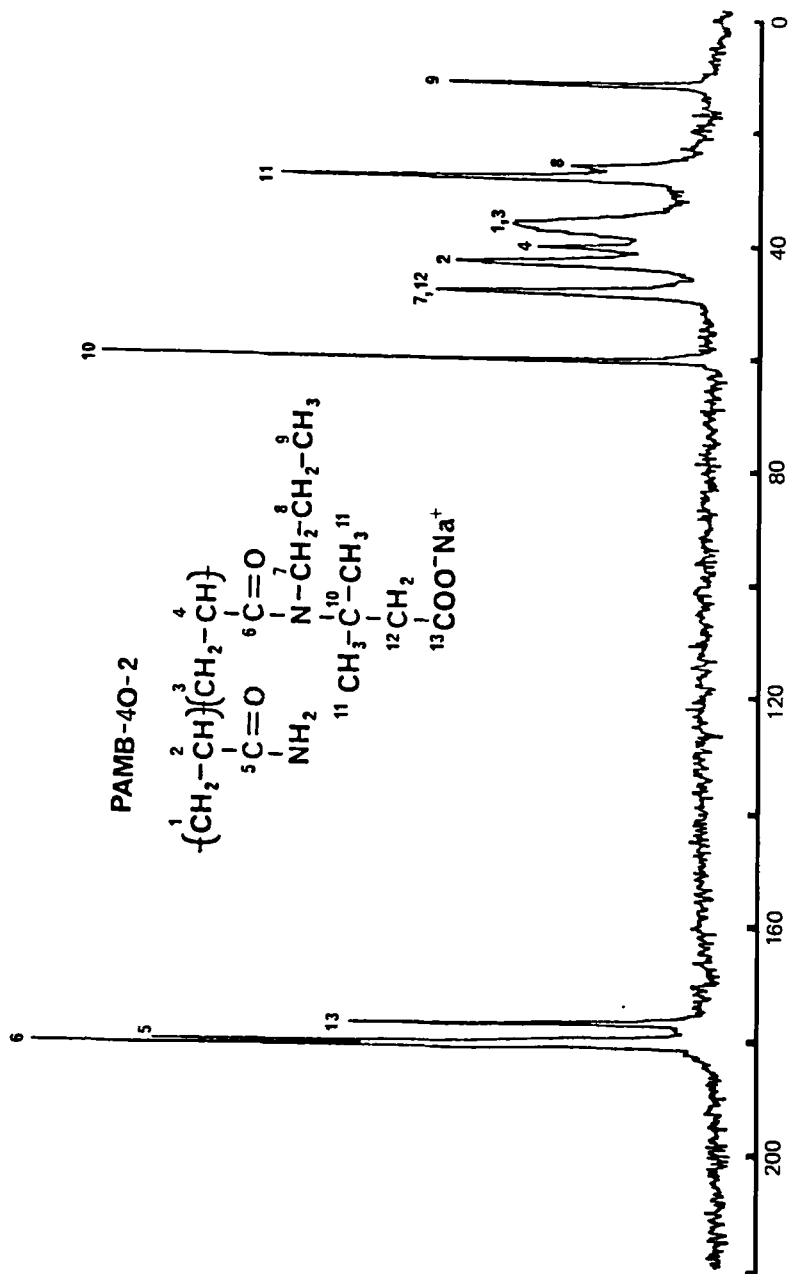


TABLE 4.  $^{13}\text{C}$  NMR Peak Assignments for Copolymers of Acrylamide with Sodium 3-(N-Propyl)-Acrylamido-3-Methylbutanoate

Peak number	Chemical shift, ppm	Spin-lattice relaxation times $T_1$ , s
1, 3	36.4	0.04
2	43.2	0.07
4	40.3	0.07
5	180.5	1.2
6	181.2	1.2
7, 12	48.1	0.04
8	27.0	0.05
9	11.5	0.3
10	60.2	0.7
11	28.2	0.07
13	177.2	1.0

due to the very slow rate of termination observed for acrylamide [15, 16].

### Copolymer Microstructure

The microstructure of the copolymers of acrylamide ( $M_1$ ) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate ( $M_2$ ) is expected to be important in determining the solution properties which the copolymers exhibit. The statistical distribution of monomer sequences  $M_1$ - $M_1$ ,  $M_2$ - $M_2$ , and  $M_1$ - $M_2$  may be calculated using the method of Igarashi [17]. Mean sequence lengths,  $\mu_1$  and  $\mu_2$ , can be calculated utilizing Eqs. (1) and (2) [18]:

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

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

TABLE 5. Structural Data for the Copolymers of Acrylamide (AM) with Sodium 3-(N-Propyl)Acrylamido-3-Methylbutanoate (NaPAMB)

Sample	Composition, mol% <sup>a</sup>			Blockiness, mol% <sup>b</sup>			Alternation, mol% <sup>b</sup> AM-NaPAMB	Mean sequence length	
	AM	NaPAMB	AM-AM	AM-AM	NaPAMB-NaPAMB	$\mu_{AM}$		$\mu_{NaPAMB}$	
PAMB-10-1	91.38	8.62	83.1	83.1	0.3	16.6	11.3	1.0	
PAMB-25-1	80.64	19.36	63.1	63.1	1.8	35.1	4.4	1.1	
PAMB-40-1	68.96	31.04	43.4	43.4	5.5	51.1	2.7	1.2	
PAMB-60-1	53.50	46.50	22.5	22.5	15.5	62.0	1.8	1.5	

<sup>a</sup> From elemental analysis.

<sup>b</sup> Statistically calculated by reactivity ratios.

where  $r_1$  and  $r_2$  are the reactivity ratios for the monomer pair. The calculated structural data for the copolymers of AM with NaPAMB are listed in Table 5. The mean sequence length of acrylamide,  $\mu_{AM}$ , varied from 11.3 at a 91.4/8.6 mole ratio of AM/NaPAMB in the copolymer to 1.8 at a 53.5/46.5 mole ratio. For those copolymer compositions, values of  $\mu_{NaPAMB}$  were 1.0 and 1.5, respectively. Table 6 lists additional structural data for the copolymers of AM with NaPAMB involving triad and pentad sequence distributions, as well as run numbers, calculated using the method of Harwood and Ritchey [19]. The relatively low (as compared to an alternating system) run numbers calculated for the AM-NaPAMB series would indicate the general randomness of addition of the two monomers. As seen from the mean sequence length data (Table 5), longer blocks of AM units would be formed due to the slight preference of addition of AM to itself.

In Table 6,  $P_{ABA}$  and  $P_{AABAA}$  are the probabilities of a NaPAMB-centered triad and pentad, respectively, while  $N_{ABA}$  and  $N_{AABAA}$  are the expected numbers of NaPAMB-centered triads and pentads per 100 monomer units. The maximum number of NaPAMB-centered triads was found to occur at a copolymer composition containing about 38 mol% NaPAMB, while the maximum number of NaPAMB-centered pentads occurred at a copolymer composition containing approximately 21 mol% NaPAMB. The maximum triad and pentad values were obtained by calculating a broad spectrum of AM-NaPAMB copolymer compositions from the copolymerization equation using the experimentally derived Kelen-Tüdös reactivity ratios of  $r_1 = 1.14$  and  $r_2 = 0.32$ .

TABLE 6. Calculated Structural Data for the AM-NaPAMB Copolymer System

Sample	Run	$P_{ABA}$	$P_{AABAA}$	$N_{ABA}$	$N_{AABAA}$
PAMB-10-1	16.3	0.93	0.77	7.9	6.5
PAMB-25-1	36.2	0.81	0.48	16.4	9.8
PAMB-40-1	51.0	0.67	0.27	21.0	8.4
PAMB-60-1	61.7	0.45	0.08	20.9	3.9



## CONCLUSIONS

Copolymers of acrylamide (AM) with sodium 3-(N-propyl)acrylamido-3-methylbutanoate (NaPAMB) were prepared in aqueous solution using potassium persulfate as the initiator. Elemental analysis and  $^{13}\text{C}$  NMR were used to determine the copolymer compositions. The reactivity ratios,  $r_1 r_2 = 0.36$ , were determined from two low conversion methods, and indicate the randomness of addition of these monomers.  $^{13}\text{C}$  NMR peak assignments have been made and spin-lattice relaxation studies performed. The copolymer microstructures were predicted utilizing statistical methods of Igarashi [17] and Harwood and Ritchey [19]. Weight-average molecular weights in the range  $0.3\text{--}7.0 \times 10^5$  were measured for the AM-NaPAMB polymers; these were found to decrease sharply with increasing NaPAMB content. The molecular weight, copolymer composition, and microstructural data of the AM-NaPAMB copolymers are used for the assessment of structure/dilute solution property relationships in a subsequent paper.

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