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Water-Soluble Polymers. 28. Ampholytic Copolymers of Sodium 2-Acrylamido-2-methylpropanesulfonate with (2-Acrylamido-2-methylpropyl)dimethylammonium Chloride: Synthesis and Characterization

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ABSTRACT: Copolymers of (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) and 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were prepared by free radical polymerization employing potassium persulfate as the initiator. Copolymer compositions were determined from elemental analysis and ^{13}C NMR data. Reactivity ratio studies yielded r_1 and r_2 values of 0.22 and 0.31 for the AMPDAC (M_1) and NaAMPS (M_2) monomer pair. Molecular weights, determined by using low-angle laser light scattering, were found to decrease with AMPDAC content and ranged from 1.6 to 9.5×10^6 g/mol. Copolymer microstructures were predicted by calculation of reactivity ratios. The viscosity behavior is interpreted in terms of polymer composition, molecular weight, and microstructure in the following paper in this series.

Introduction

Ampholytic copolymers represent a special class of polyelectrolytes which contain both positive and negative charges along the macromolecular backbone. Solution behavior of ampholytic copolymers is often difficult to predict since a number of parameters including charge type and distribution, polymer microstructure, molecular weight, hydrophobic/hydrophilic balance, solvent type, pH, and ionic strength are operative. In our continuing efforts to prepare electrolyte-tolerant, water-soluble copolymers[1-11] we now report the synthesis and characterization of high charge density polyampholytes.

Although extensive research has been conducted on ordinary polyelectrolytes, very few studies have been conducted on ampholytic polymers, particularly in neutral salt solutions. Peiffer and Lundberg[12] reported the synthesis and viscometric properties of high and low charge density polyampholytes. Sodium styrenesulfonate was copolymerized with (methacrylamidopropyl)trimethylammonium chloride (MAPTAC) and terpolymerized with MAPTAC and acrylamide. The viscometric properties of the high charge density polymers were found to be a function of intramolecular ionic interactions in pure water and neutral salt solutions. In contrast, the viscometric properties of low charge density terpolymers were found to be highly dependent on intermolecular interactions, particularly at polymer concentrations in the region of chain overlap (C^*).

Salamone et al.[13,14] reported the synthesis of polyampholytes derived from cationic–anionic monomer pairs. These high charge density copolymers incorporated equal amounts of the comonomers and were found to display viscosity behavior in salt solution that is quite different from that of classical polyelectrolytes. In a more recent study, Salamone et al. reported the spontaneous polymerization and aqueous solution behavior of several ion pair comonomers.[15] The viscosities of the copolymers increased with increasing potassium chloride concentration in the

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polymer solution. Several studies have also been conducted on aliphatic and aromatic sulfobetaine polyampholytes.[16,17] These polymers are composed of monomer units which incorporate positive and negative charges within the mer unit. Several of these inner salt polymers were reported to possess hydrogel characteristics. Salamone and co-workers[18] have also studied absorption characteristics of ampholytic polysaccharides prepared via ceric ion and cobalt-60 initiation using hydroxyethyl cellulose and starch as substrates. The grafted chains were synthesized from comonomer ion pairs of (3-methacrylamidopropyl)trimethylammonium 2-acrylamido-2-methylpropanesulfonate with acrylamide.

The contrasting responses of balanced polyampholytes and conventional polyelectrolytes upon addition of electrolytes (in particular NaCl and $CaCl_2$) to their respective aqueous solutions has led to this research effort. Of special interest are ampholytic polymers with excess anionic or cationic functional groups.

The goal of this work is to conduct a systematic study of the effects of changes in ampholytic polymer structure, e.g., changes in composition, charge, charge distribution, and microstructure, on the macroscopic properties of the polymers. As an initial step toward our goal, polymers were synthesized which incorporate only charged monomers. Therefore, a series of high charge density copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) with (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) were synthesized. These ampholytic copolymers are thus composed of mer units which are homologous in structure; the mer units are identical outside the region of electrolyte functionality.

Copolymers of acrylamide (AM) with NaAMPS and AMPDAC have been studied previously in our laboratories.[1,2,10,11] Data from these studies allow a number of informative comparisons to be made in terms of copolymerization and solution properties. The latter will be reported in a subsequent paper in this series.

Experimental Section

Materials. (2-Acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) was synthesized by the reaction of acryloyl chloride with dimethylamino-2-amino-2-methylpropane in THF.[10] The product was found to be prone to spontaneous polymerization if stored in the acid form. Therefore, AMPDAC was converted to the base (2-acrylamido-2-methylpropyl)dimethylamine (AMPDA) prior to purification. AMPDAC was first placed in a large excess of water followed by the addition of NaOH to attain a pH of 12. The solid AMPDA was then filtered and recrystallized twice from methyl ethyl ketone prior to use (mp 61–63 °C) Anal. Calcd for $C_9H_{18}N_2O$: C, 63.49; H, 10.65; N, 16.46. Found: C, 63.42; H, 10.27; N, 16.58. IR: N—H, 3270 cm^{-1}; C=C—H, 2980 cm^{-1}; aliphatic C—H, 2880 cm^{-1}; C=O, 1660 (s), 1550 cm^{-1} (m); tertiary amine, 1160 cm^{-1}. 2-Acrylamido-2-methylpropanesulfonic acid (AMPSA), obtained from Fluka Chemical Co., was recrystallized 3 times from a mixture of dry methanol and 2-propanol prior to use. Potassium persulfate, obtained from J.T. Baker Co., was recrystallized twice from deionized water prior to use.

Copolymer Synthesis. Copolymers of *A*MP*D*AC with Na*AMPS*, the ADAS series, as well as the two homopolymers, were prepared in aqueous solution at 30 °C by using 0.1 mol % potassium persulfate as the free-radical initiator. Each reaction was conducted in a 500-mL, three-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. A specified amount of each monomer was placed in water followed by the addition of an equimolar amount of NaOH for AMPSA and HCl for AMPDA. The separate solutions were then combined, after which the pH of the mixture was adjusted to 6.0 by dropwise addition of either 0.5 M NaOH or 0.5 M HCl. The pH adjustment was performed to ensure that all of the monomers were in the ionized form. Prior to the injection of a designated amount of potassium persulfate in water, the reaction mixture was deaerated for 20 min. The total monomer concentration in each reaction was held constant at 0.45 M. An aliquot was taken at low conversion to allow reactivity ratio studies to be performed. The reaction was typically terminated at <60% conversion due to the high viscosity of the reaction medium and as a precaution to minimize copolymer drift. Copolymer drift may occur at higher conversions particularly if the monomer feed ratios are skewed. The reaction mixture was diluted with two to four volumes of deionized water followed by addition of the solution into three volumes of reagent grade acetone while stirring. The polymers were further purified by repeated dissolution in water and precipitation into acetone, followed by lyophilization and vacuum drying for 2 days. Conversions were determined gravimetrically. IR, typical copolymer, ADAS-40: amide I, 1657 cm^{-1}; amide II, 1552 cm^{-1}; asymmetrical CH_3 bending, 1468 cm^{-1}; geminal dimethyls, 1390, 1370 cm^{-1}; S=O stretch, 1040, 1210 cm^{-1}; ammonium ion N—H stretch, 3062 cm^{-1}; tertiary amine salt, 2746 cm^{-1}; N—H br, 3400–3300 cm^{-1}.

Table I
ADAS Series Reaction Parameters[a]

sample	molar feed ratio AMPDAC: NaAMPS	reactn time, min	%[b] conv
ADAS-0	0:100	85	4.6
ADAS-10L[c]	10:90	85	7.4
ADAS-10	10:90	85	22.1
ADAS-25L	25:75	35	10.0
ADAS-25	25:75	80	23.5
ADAS-40L	40:60	27	7.2
ADAS-40	40:60	78	63.7
ADAS-50L	50:50	35	4.9
ADAS-50	50:50	108	53.5
ADAS-70L	70:30	43	6.1
ADAS-70	70:30	118	46.0
ADAS-90L	90:10	30	5.4
ADAS-90	90:10	47	16.1
ADAS-100	100:0	130	43.8

[a] pH 6.0; T = 30 °C; total monomer concentration = 0.45 M; $[K_2S_2O_8] = 4.5 \times 10^{-4}$ M. [b] Determined gravimetrically. [c] L denotes low conversion.

Compositional Calculations. Compositions were determined on all samples by elemental analysis and on selected samples by ^{13}C NMR peak integration. Copolymer compositions for the ADAS copolymers were calculated from %C and %N data by using eq 1 and 2 in which A and B represent the number of moles

$$\%C/12.01 = 7A + 9B \tag{1}$$

$$\%N/14.01 = 1A + 2B \tag{2}$$

of NaAMPS and AMPDAC, respectively, in a normalized weight of sample, e.g., 100 g. After A and B were determined for each of the copolymers by using matrix algebra, mole percent compositional data were calculated according to eq 3 and 4. Equations

$$\text{mol \% (Na)AMPS} = \frac{A}{A+B}100 \tag{3}$$

$$\text{mol \% AMPDA(C)} = \frac{B}{A+B}100 \tag{4}$$

3 and 4 represent only the relative abundance of the two basic types of repeat units. These equations do not take into account the presence or absence of inorganic counterions or water. Monomer feed and copolymer composition data as derived from elemental analysis and ^{13}C NMR spectroscopy are shown in Table II. The compositional data as determined by the two methods are in agreement.

For the high-conversion samples, elemental analysis for oxygen was also performed. Percent oxygen data allowed for the calculation of percent water in those samples. Equation 5 was solved

$$\%O/16.01 = 4A + 1B + 1C \tag{5}$$

for C by using the values for A and B as determined from eq 1 and 2. C represents the number of moles of water in a normalized weight of sample. Weight percent water was then calculated by using eq 6.

$$\text{weight percent water} = 18.02C \tag{6}$$

Table II
ADAS Series Compositional Data

	feed comp, mol %		polym comp, mol %			
sample	AMPDAC	NaAMPS	AMPDAC[a]	NaAMPS[a]	AMPDAC[b]	NaAMPS[b]
ADAS-0	0	100	0.0	100.0	0.0	100.0
ADAS-10L	10	90	25.7	74.5		
ADAS-10	10	90	25.1	74.9	24.8	75.2
ADAS-25L	25	75	40.6	59.4		
ADAS-25	25	75	38.9	61.1	37.9	62.1
ADAS-40L	40	60	46.9	53.1		
ADAS-40	40	60	45.0	55.0	45.8	54.2
ADAS-50L	50	50	47.4	52.6		
ADAS-50	50	50	46.9	53.1	46.5	53.5
ADAS-70L	70	30	62.3	37.7		
ADAS-70	70	30	63.4	36.6	61.9	38.1
ADAS-90L	90	10	78.1	21.9		
ADAS-90	90	10	77.8	22.2		
ADAS-100	100	0	100.0	0.0	100.0	0.0

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

Table III
ADAS Series Elemental Analysis and Sample Compositional Data

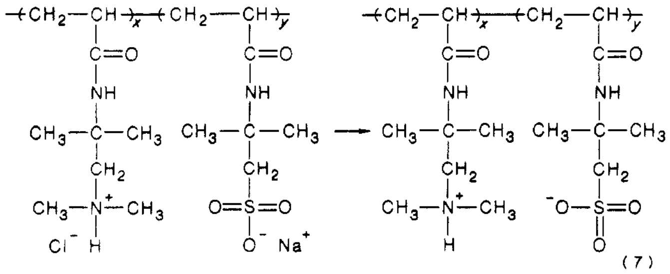
	elem anal.			polym comp, mol %			
sample	%C	%N	%O	AMPDAC	NaAMPS	% water	ICDI[a]
ADAS-0[b]	36.68	6.11	27.92	0.0	100.0	13.6	0
ADAS-10L[c]	38.47	7.50		25.5	74.5		
ADAS-10	38.55	7.50	32.59	25.1	74.9	11.7	5.9
ADAS-25L	42.21	8.86		40.6	59.4		
ADAS-25	42.67	8.89	30.27	38.9	61.1	10.8	9.0
ADAS-40L	43.13	9.31		46.9	53.1		
ADAS-40	44.04	9.43	29.96	45.0	55.0	11.6	10.8
ADAS-50L	44.83	9.70		47.4	52.6		
ADAS-50	45.95	9.92	29.19	46.9	53.1	11.2	13.2
ADAS-50*	46.12	10.09	19.84	50.0	50.0	9.4	14.0
ADAS-70L	45.77	10.51		62.3	37.7		
ADAS-70	44.81	10.33	28.19	63.4	36.6	14.7	11.7
ADAS-90L	45.78	11.11		78.1	21.9		
ADAS-90	45.81	11.01	24.80	77.8	22.2	14.7	8.2
ADAS-100	52.29	13.56	7.74	100.0	0.0	16.3	3.1

[a] Inorganic counterion deficiency index. [b] Theoretical values are given for %C, %N, and %O. [c] L denotes low conversion.

Following the calculation of compositional data using eq 1-6, the inorganic counterion deficiency index (ICDI) of each copolymer was calculated and appears in Table III. The ICDI is a measure of the quantity of inorganic counterions (grams) which has been displaced by organic counterions during mer pairing. For example, as the NaAMPS sulfonate anion pairs with the AMPDAC cation, the NaAMPS and AMPDAC mers lose or become deficient in Na$^+$ and Cl$^-$ ions, respectively, relative to their initial states. These ions are lost during purification and their mass must be accounted for; therefore we describe this in terms of the ICDI. The pairing and loss of counterions is depicted in eq 7. The ICDI is expressed mathematically in eq 8; *A*, *B*, and

$$\text{inorganic counterion deficiency index} = 100 - 229.22A - 206.71B - 18.02C \quad (8)$$

C are previously defined. Since the numerical coefficients of the factors *A* and *B* correspond to the molecular weights of the repeat units in the ionized form with inorganic counterions, the calculation of ICDI is based on the ionized form of the repeat units with inorganic counterions. The contribution from bound water is accounted for in the ICDI of the samples. The samples which contained excess NaAMPS, as determined via (1) and (2), were normalized against ADAS-0. This normalization was needed as a base-line correction factor in those samples which contained Na$^+$ ions.



(7)

Table IV
ADAS Series Inorganic Counterion Data

	ICDI			ICDI	
sample	theor[a]	exptl	sample	theor[a]	exptl
ADAS-10	6.3	5.9	ADAS-50*	14.0	14.0
ADAS-25	10.4	9.0	ADAS-70	9.7	11.7
ADAS-40	12.2	10.8	ADAS-90	5.7	8.2
ADAS-50	13.2	13.2	ADAS-100	0	3.1

[a] Assuming 100% exchange of inorganic counterions for mer counterions.

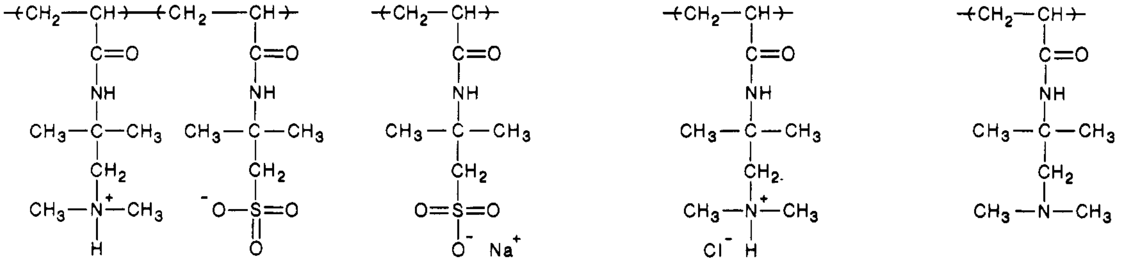
If one assumes that each repeat unit for which there is an oppositely charged mer unit exchanges its inorganic counterion for the mer counterion, a theoretical ICDI may be calculated. Theoretical and experimental ICDI values are illustrated in Table IV. In fact, the absolute difference in the experimental and theoretical values of the ICDI can be used to calculate the number of moles of uncharged AMPDAC, AMPDA, in the normalized weight of the copolymer. Equation 9 applies if there is an excess of NaAMPS in the copolymer and eq 10 applies if there is an

$$\text{mol of AMPDA} = \frac{|\text{theor ICDI} - \text{exptl ICDI}|}{\text{atomic wt of Na, } 22.99 \text{ g/mol}} \quad (9)$$

$$\text{mol of AMPDA} = \frac{|\text{theor ICDI} - \text{exptl ICDI}|}{\text{atomic wt of Cl, } 35.45 \text{ g/mol}} \quad (10)$$

excess of AMPDAC, as calculated using (1) and (2). These data are also listed in Table IV.

Table V
ADAS Series Compositions Derived from ICDI Data



sample	mol % AMPDA-AMPS	mol % NaAMPS	mol % AMPDAC	mol % AMPDA
ADAS-0	0.0	100.0	0.0	0.0
ADAS-10	42.2	53.9	0.0	4.0
ADAS-25	51.2	35.4	0.0	13.3
ADAS-40	63.8	23.1	0.0	13.1
ADAS-50	93.8	6.2	0.0	0.0
ADAS-50*	100.0	0.0	0.0	0.0
ADAS-70	73.2	0.0	14.4	12.4
ADAS-90	44.2	0.0	39.7	16.0
ADAS-100	0.0	0.0	79.3	20.7

Following the calculation of the number of moles of AMPDA, the number of moles of the other components in a normalized weight of the polymer can be calculated. These include the moles of AMPDAC complexes with NaAMPS (AMPDA-AMPS), the moles of free NaAMPS, and the moles of free AMPDAC. The number of moles of these species is calculated by using eq 11-14, where (11) and (12) apply to the polymers containing an excess of NaAMPS, while (13) and (14) apply to polymers containing an excess of AMPDAC.

$$\text{mol of AMPDA-AMPS} = 2(B - \text{mol of AMPDA}) \quad (11)$$

$$\text{mol of NaAMPS} = A - B + \text{mol of AMPDA} \quad (12)$$

$$\text{mol of AMPDA-AMPS} = 2(A - \text{mol of AMPDA}) \quad (13)$$

$$\text{mol of AMPDAC} = B - A + \text{mol of AMPDA} \quad (14)$$

The mole percent of each of the components of the ADAS polymers can then be calculated by using eq 15-18. These data are listed in Table V.

$$\text{mol \% AMPDA-AMPS} = \frac{\text{mol of AMPDA-AMPS}}{\text{total mol}} \quad (15)$$

$$\text{mol \% NaAMPS} = \frac{\text{mol NaAMPS}}{\text{total mol}} \quad (16)$$

$$\text{mol \% AMPDAC} = \frac{\text{mol of AMPDAC}}{\text{total mol}} \quad (17)$$

$$\text{mol \% AMPDA} = \frac{\text{mol of AMPDA}}{\text{total mol}} \quad (18)$$

^{13}C Nuclear Magnetic Resonance Spectroscopy. Carbon-13 NMR spectra for the ADAS copolymers and the homopolymers 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. Copolymer composition determinations were performed utilizing a 90° pulse angle, gated decoupling, and pulse repetitions $\geq 5T_1$. Well-resolved, representative peaks were chosen for each copolymer constituent and multiple integrations were performed. The procedure performed is analogous to that described for random copolymers of acrylamide with sulfonated comonomers.[19] Briefly, the amide carbonyls were used as standards, and other AMPDAC and NaAMPS peaks were integrated to give the copolymer compositions. Typically, 5000-10 000 transients were accumulated. A typical ^{13}C spectrum for the ADAS series can be seen in Figure 1.

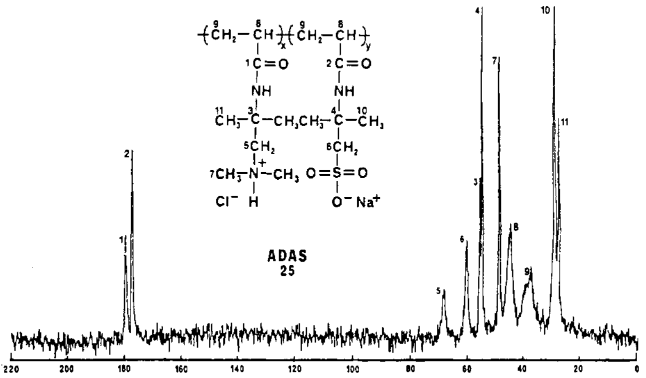


Figure 1. Typical ^{13}C NMR spectrum of a copolymer in the ADAS series: ADAS-25.

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra for all synthesized materials were obtained by using a Nicolet 5DX Fourier transform infrared spectrophotometer. The spectra were obtained by accumulating 20 scans of the sample in KBr pellets. An FT-IR spectrum representative of the ADAS series is shown in Figure 2.

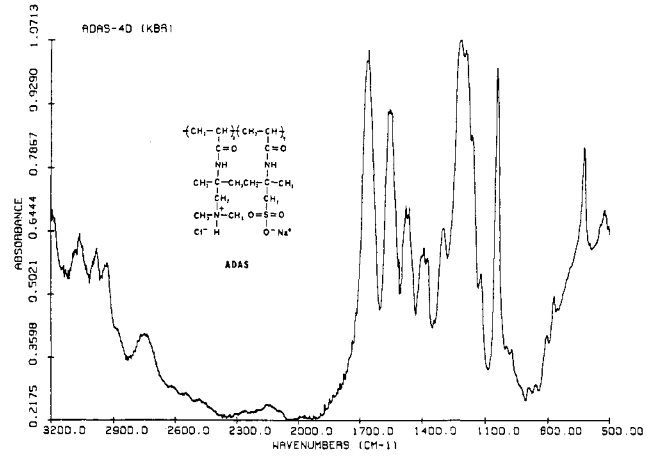
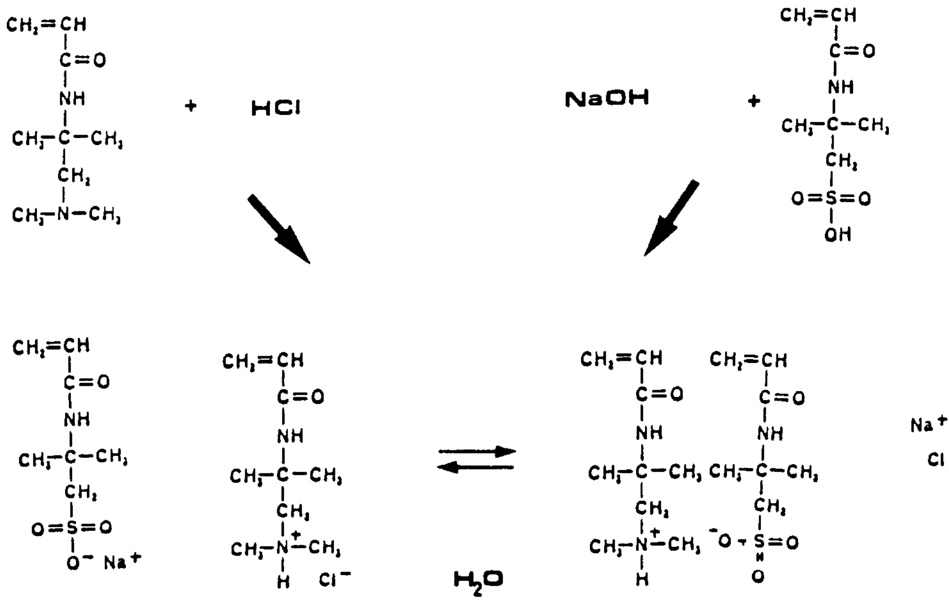


Figure 2. Typical FT-IR spectrum of a copolymer in the ADAS series: ADAS-40.

Low-Angle Laser Light Scattering (LALLS). Light scattering studies were performed on a Chromatix KMX-6 low-angle laser light scattering spectrophotometer utilizing a 2-mW He-Ne laser operating at 633 nm. All measurements were conducted at 25 °C in 1.0 M NaCl aqueous solutions at a pH of 7.0. For quasi-elastic light scattering a Langley-Ford Model LF1-64 channel digital correlator was used in conjunction with the KMX-6. Sample time was adjusted to provide the optimum single-exponential autocorrelation function as viewed in a Tektronix T922 oscilloscope. The apparatus was interfaced with a

Scheme I



Hewlett-Packard 85 computer for numerical analysis. The autocorrelation function was evaluated via the method of cumulants.[20]

Results and Discussion

Structural features of NaAMPS, a monomer known for its hydrolytic stability in copolymers, led us to synthesize the AMPDAC monomer. Not only does it possess hydrolytic stability but potential for forming molecularily balanced ampholytic structures when copolymerized with NaAMPS. Removal of charge from the immediate region of the polymer backbone has been shown to markedly enhance viscosity behavior of water-soluble polymers. The NaAMPS and AMPDAC monomers contain spacer groups which allow the charges to have greater mobility while linked to the backbone. Additionally, the acrylamido functionality on both monomers allows formation of copolymers with easily regulated structure. Copolymers with balanced charge, excess anionic charge, or excess cationic charge can be produced by simply changing the ratio of respective monomers in the feed.

Polymer Preparation. The reaction parameters for the copolymerization of AMPDAC with AMPS, as well as for the homopolymers, are shown in Table I. The polymers were prepared as described in the Experimental Section by separately placing a specified quantity of each monomer in deionized water followed by the addition of the corresponding salt. The solutions were then mixed and eventually initiated (Scheme I). This procedure is different from the methods employed by Salamone et al.[13-15] who synthesized similar copolymers by forming the ion pair of the comonomers, or the dimonomeric salt, prior to initiation. Although our procedure has great utility in tailoring copolymers with a wide range of composition, characterization methods must be utilized to account for counterion losses during monomer pairing.

Macromolecular Structure. Compositional Analysis. Compositional analysis of ampholytic copolymers is more complex than that for uncharged polymers or for ordinary polyanions or polycations. The charged units of polyampholytes may pair with inorganic counterions or with the oppositely charged mer unit. In addition, in areas of high cation concentration, the positvely charged AMPDAC mer may deprotonate leaving an uncharged unit. All of these possible states, as well as the amount of water retained by the sample, must be considered when calculating copolymer composition from elemental analysis data.

Copolymer compositions were determined as an initial step in the elucidation of polymer structure. As outlined in the experimental section, compositions were determined by elemental analysis and ^{13}C NMR. The compositional data from the two methods are in agreement. Additionally, copolymer compositions calculated for aliquots collected at low and high conversions agree favorably (Table III). Therefore, we conclude that complications arising from variations in molecular structure due to compositional drift are negligible. Percent oxygen data allow calculation of percent water in the high-conversion samples.

Compositional data must necessarily take into account loss of inorganic counterions present in the original monomers upon conversion to polymer. Therefore we have defined the inorganic counterion deficiency index (ICDI) for each copolymer. The ICDI is a measure of the quantity of inorganic counterions which have been displaced by organic counterions during mer pairing. For example, as the NaAMPS sulfonate anion pairs with the AMPDAC cation, the NaAMPS and AMPDAC mers lose or become deficient in Na^+ and Cl^- ions, respectively, relative to their initial states. The values of ICDI, calculated as described in the Experimental Section, can be used to accurately define copolymer repeating unit frequency.

The variation of ICDI with copolymer composition follows a definite pattern (Table III). The values are low with excess AMPDAC or NaAMPS in the copolymer, e.g., ADAS-10 and ADAS-90. However, as the copolymers approach equimolar incorporation of AMPDAC and NaAMPS, the values increase. In fact, the maximum value is seen for ADAS-50*.

If one assumes that each repeat unit for which there is an oppositely charged mer unit exchanges its inorganic counterion for the mer counterion, a theoretical ICDI may be calculated. Theoretical and experimental ICDI values are shown in Table IV. As the mole percent of AMPDAC in the copolymer increases, the difference between experimental and theoretical values increases. The increasing difference with larger concentration of AMPDAC can be explained in the following manner. As a means of charge stabilization, the tertiary ammonium salt deprotonates to form the tertiary amine.[7] In fact, the difference in the experimental and theoretical values of the ICDI can be used to calculate the mole percent of uncharged AMPDA in the copolymer. The experimental and theoretical ICDI values also allow calculation of the mole percent of AMPDAC counterion bound with NaAMPS as AMPDA–AMPS, "free" NaAMPS, and "free" AMPDAC (Table V). "Free" implies that the repeat unit is associated with its inorganic counterion as opposed to a mer counterion.

Polymers ADAS-0 through ADAS-50 contain an excess of (Na)AMPS units relative to AMPDA(C) units. As the amount of AMPDA–AMPS increases from ADAS-0 to ADAS-50, the amount of "free" NaAMPS decreases and the mole percent of uncharged AMPDA increases. ADAS-50 possesses the maximum mole percent of AMPDA–AMPS (93.8%) among the remainder of the samples with one exception, ADAS-50*. ADAS-50* contained the same feed composition as ADAS-50 but was synthesized by mixing stoichiometric quantities of AMPS with AMPDA. ADAS-50 contains 6.2% "free" NaAMPS while ADAS-50* is composed of 100% AMPDA–AMPS units.

Polymers ADAS-70 through ADAS-100 contain an excess of AMPDA(C) units relative to (Na)AMPS units. As the amount of AMPDA-AMPS decreases from ADAS-70 to ADAS-100, the amount of "free" AMPDAC increases from 14.4 to 79.3%. Likewise the mole percent of uncharged AMPDA increases from 12.4 to 20.7%.

The fact that ADAS-40 and ADAS-50 are almost identical in composition but display different ICDIs is an indication that the counterion exchange for ADAS-50 may occur in the monomer reaction mixture, before the polymerization is even initiated. The results imply that the polymerization conditions of the polymer may be varied such that not only is the polymer composition affected, the microstructure is also influenced. Therefore, two different reaction mixtures may produce essentially identical polymers in terms of their composition but different polymers in terms of their microstructure. This is a consequence of the reactivity ratios for the series coupled with a tendency for the ADAS-50 polymer to approach perfect alternation.

Several groups of researchers have studied polyampholytes which are similar in structure to the ADAS polymers. Peiffer and Lundberg[12] prepared two high charge density copolymers of (methacrylamidopropyl)trimethylammonium chloride (MAPTAC) with sodium styrenesulfonate (SSS) and sodium vinylsulfonate (SVS) in the presence of nonpolymerizable counterions. The copolymers of MAPTAC with SSS and SVS were synthesized from equimolar mixtures of the two monomers and were reported to not be completely self-neutralized. The polymers contained 6 and 20 mol % SSS and SVS species in the copolymer, respectively. These copolymers were insoluble, forming nonoptically clear solutions in pure water and simple electrolyte (salt) solutions. In contrast, the ADAS copolymers of this work form true, clear solutions when dissolved in deionized water or salt solutions.

High charge-density polyampholytes derived from cationic–anionic monomer pairs, studied by Salamone et al.,[13,14] displayed viscosity behavior in salt solution different from that of normal polyelectrolytes. In a more recent study, Salamone et al. reported the spontaneous polymerization and aqueous solution behavior of several ion pair comonomers which increased with potassium chloride concentration.[15]

Molecular Weight Studies. Weight-average molecular weights, second virial coefficients, degrees of polymerization ($\overline{DP}_w$), and intrinsic viscosities in 1.0 M NaCl are listed for the ADAS copolymer series in Table VI. In general, as the mole percent of AMPDAC in the copolymer increased, the molecular weight decreased from about 9.5 × 10^6 to about 2.5 × 10^6 g/mol.

Table VI
ADAS Series Low-Angle Laser Light Scattering Data[a]

sample	mol % AMPDAC copolymer	$\bar{M}_w \times 10^{-6}$, g mol^{-1}	$A_2 \times 10^4$, mL mol g^{-2}	$\overline{DP}_w \times 10^{-4}$	$[\eta]$,[b] dL g^{-1}
ADAS-0	0.0	8.47	1.38	3.70	6.73
ADAS-10	25.1	9.46	1.58	4.24	8.01
ADAS-25	38.9	7.73	1.84	3.52	10.11
ADAS-40	45.0	7.55	1.22	3.46	9.75
ADAS-50	46.9	2.66	4.47	1.22	9.26
ADAS-70	63.4	2.68	2.30	1.25	5.95
ADAS-100	100.0	1.60	2.89	0.774	1.36

[a] pH 7.0; T = 25 °C; [NaCl] = 1.0 M. [b] pH 7.0; T = 25 °C; [NaCl] = 1.0 M; via Contraves low shear LS-30 rotational rheometer.

Table VII
ADAS Series Quasi-Elastic Light Scattering Data[a]

sample	mol % AMPDAC	$\overline{DP}_w \times 10^{-4}$	$[\eta]$,[b] dL g^{-1}	$D_0 \times 10^8$, cm^2 s^{-1}	d_0, Å
ADAS-0	0.0	3.70	6.73	3.43	1300
ADAS-10	25.1	4.24	8.01	2.49	2030
ADAS-25	38.9	3.52	10.11	2.32	2400
ADAS-40	45.0	3.46	9.75	1.54	2613
ADAS-50	46.9	1.22	9.26	4.02	1056
ADAS-70	63.4	1.25	5.95	2.74	1799
ADAS-100	100.0	0.774	1.36	5.80	800

[a] pH 7.0; T = 25 °C; [NaCl] = 1.0 M. [b] pH 7.0; T = 25 °C; [NaCl] = 1.0 M; via Contraves low shear LS-30 rotational rheometer.

The molecular weights of the monomers are not greatly different, 229.22 g/mol for NaAMPS and 206.72 g/mol for AMPDAC. Slight increases in molecular weight were observed (8.47 × 10^6 to 9.46 × 10^6 g/mol) for ADAS-0 (homopoly NaAMPS) and ADAS-10, respectively. However, the molecular weight of ADAS-25 of 7.73 × 10^6 g/mol was slightly below that of ADAS-0. ADAS-100 (homopoly AMPDAC) displayed the smallest value of molecular weight for the polymers in the series with $M_w = 1.60 \times 10^6$ g/mol.

Copolymer composition, molecular weight, and intrinsic viscosity data indicate that microstructure apparently also affects the properties of the polymer. For example, those samples that displayed the largest viscosities, ADAS-25 and ADAS-40, did not possess the highest molecular weights. A compositional effect is also apparent at high mole percentages of AMPDAC in addition to obvious lowering of molecular weight.

Quasi-elastic light scattering data, which include diffusion coefficients and mean hydrodynamic diameters, are given in Table VII along with values for degrees of polymerization and intrinsic viscosities in 1.0 M NaCl. The diffusion data range from 1.54 to 5.80 × 10^{-8} cm^2 s^{-1} and again clearly indicate that the hydrodynamic volume is not dependent on molecular weight alone. Compositional considerations must also be taken into account, particularly for ADAS-0 through ADAS-40. The diffusion data suggest that although ADAS-40 and ADAS-50 are very similar in composition, their hydrodynamic volumes and likely microstructures (as implied by the ICDI) are very different. ADAS-40, ADAS-50, and ADAS-70 have diffusion coefficients of 1.54, 4.02, and 2.74 × 10^{-8} cm^2/s, respectively. The differences in degrees of polymerization and diffusion coefficients among these three samples are a clear indication that microstructural effects contribute largely to the behavior of ADAS-50 relative to a polymer of almost identical overall composition, ADAS-40. Although the DP of ADAS-50 is about the same as that for ADAS-70, the diffusion coefficient for ADAS-50 is greater than for ADAS-70.

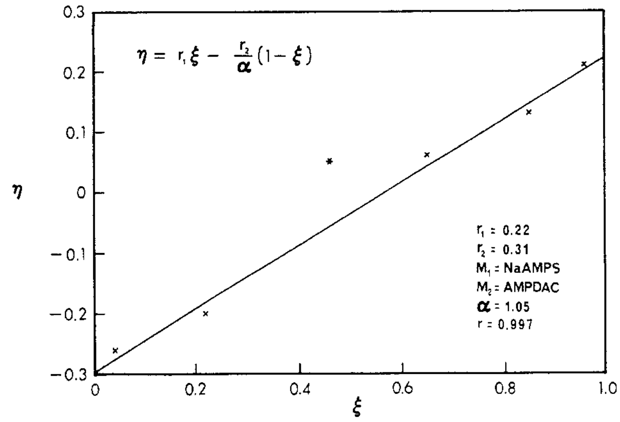


Figure 3. Kelen–Tüdos plot for the determination of reactivity ratios for the copolymerization of AMPDAC with NaAMPS.

Table VIII
ADAS Series Reactivity Ratios[a]

method	r_1	r_2	r_1r_2
Fineman-Roos	0.22	0.33	0.07
Kelen-Tüdos	0.22	0.31	0.07

[a] M_1 = NaAMPS; M_2 = AMPDAC.

Macromolecular Microstructure. Reactivity Ratio Studies. Monomer feed compositional data as well as low conversion polymer compositional data (Table III) derived from elemental analysis were used to calculate reactivity ratios for the ADAS copolymer series. The methods of Fineman–Ross[21] and Kelen–Tüdos[22] were employed for study of copolymers of NaAMPS (M_1) with AMPDAC (M_2). A plot of the data according to the Fineman–Ross method yielded reactivity ratios of $r_1 = 0.22$ and $r_2 = 0.33$. A plot of the data according to the Kelen–Tüdos method is shown in Figure 3. A graphical evaluation yields reactivity ratios of $r_1 = 0.22$ and $r_2 = 0.31$ for the monomer pair. Interestingly, the data points corresponding to ADAS-50 and ADAS-50* do not fit on the line and were excluded from the regression analysis used to determine reactivity ratios by the two methods. It is assumed that for some reason the two samples deviated from normal copolymerization behavior. This may be the result of spontaneous polymerization as noted for other equimolar cation–anion monomer pairings by Salamone and coworkers.[23] The reactivity ratios and their products as determined by the two methods are given in Table VIII. These data suggest that the ADAS copolymers are alternating in nature with essentially an equal preference for cross-propagation.

The observed linearity of the data in the Kelen–Tüdos plot indicates that the copolymerization of the ADAS series, excluding ADAS-50 and ADAS-50*, follows conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is determined only by the terminal monomer unit.[24] Using Marguot's algorithm, the penultimate copolymerization model was shown not to fit the data, confirming that the reactivity of the propagating species is dependent only on the ultimate unit. Since depropagation does not occur and high polymer is formed, the reactivity of the two monomers can be expressed in terms of two reactivity ratios via the first-order Markov or terminal model of copolymerization.

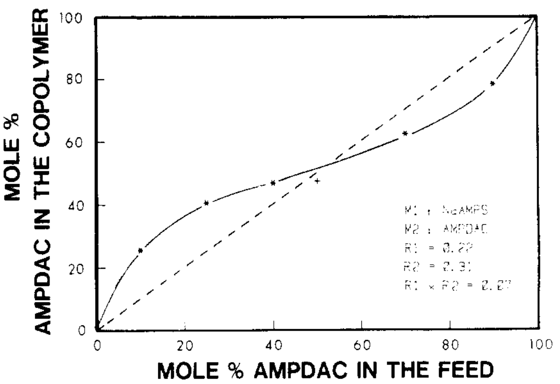


Figure 4. Copolymerization curve for the copolymerization of AMPDAC with NaAMPS.

Figure 4 shows the copolymerization curve for the ADAS series in which mole percent AMPDAC in the copolymer, as derived from elemental analysis data, has been plotted against mole percent AMPDAC in the feed. The broken line represents the ideal copolymerization where r_1 and r_2 are unity and is included for reference. The solid curve is derived from the experimentally determined reactivity ratios as established via the Kelen–Tüdos method. The copolymer data fit the calculated curve well with a crossover point, or azeotropic copolymer composition, near 50 mol %.

Statistical Microstructural Analysis. The calculation of the statistical distribution of monomer sequences, M_1–M_1, M_2–M_2, and M_1–M_2, was performed, according to Igarashi,[25] using experimental reactivity ratios. Mean sequence lengths, μ_1 and μ_2, were calculated according to the method of Pyun.[26] These statistical data are shown in Table IX. As expected, the maximum values in blockiness, M_1–M_1 and M_2–M_2, occur for ADAS-10 (49.8) and ADAS-90 (56.8), respectively. The maximum in alternation, M_1–M_2, occurs for ADAS-40 which has a high alternation number of 78.5. The mean sequence lengths average about one except for the samples with extremes in composition, ADAS-10 and ADAS-90. The small values for the mean sequence length reinforce the tendency for alternation in the copolymers.

Table X lists additional microstructural data calculated for monomer feed increments of 10 mol %. The calculation of run numbers and higher order sequence distributions, i.e., triads and pentads, were made according to the methods of Harwood and Ritchey.[27] Feed and polymer compositional data are designated as *F* and *P*, respectively, while *R* represents the run number. Although all of the

Table IX
ADAS Series Copolymer Statistics[a]

	comp		blockiness			μ[b]	
sample	M_1	M_2	M_1–M_1	M_2–M_2	alternation M_1–M_2	M_1	M_2
ADAS-10	74.5	25.5	49.8	0.8	49.4	3.1	1.0
ADAS-25	59.5	40.5	22.8	3.9	73.3	1.7	1.1
ADAS-40	53.1	46.9	13.7	7.5	78.8	1.4	1.2
ADAS-50	52.6	47.4	13.1	7.9	79.0	1.2	1.3
ADAS-70	37.7	62.3	2.9	27.6	69.5	1.1	1.7
ADAS-90	21.9	78.1	0.5	56.8	42.7	1.0	3.6

[a] M_1 = NaAMPS; M_2 = AMPDAC; $r_1 = 0.22$; $r_2 = 0.31$. [b] Mean sequence length.

Table X
ADAS Series Copolymer Statistics[a]

M_2 *F*	M_2 *P*	*R*[c]	*P*(ABA)	*N*(ABA)	*P*(BABAB)	*N*(BABAB)
5	16.4	32.2	0.97	15.9	0.04	0.6
10[b]	25.8	49.8	0.93	24.0	0.10	2.7
15	31.9	60.5	0.90	28.7	0.18	5.7
20	36.4	67.6	0.86	31.3	0.24	8.9
25[b]	39.9	72.3	0.82	32.7	0.30	11.9
30	42.8	75.5	0.78	33.3	0.34	14.5
35	45.3	77.6	0.73	33.2	0.37	16.7
40[b]	47.6	78.8	0.68	32.6	0.39	18.4
45	49.7	79.2	0.63	31.5	0.39	19.6
50[b]	51.8	78.9	0.58	30.1	0.39	20.2
55	54.0	78.0	0.52	28.2	0.38	20.3
60	56.2	76.4	0.46	26.0	0.35	19.8
65	58.6	74.1	0.40	23.4	0.32	18.7
70[b]	61.3	70.8	0.33	20.4	0.28	17.1
75	64.4	66.4	0.27	17.1	0.23	14.9
80	68.1	60.5	0.20	13.4	0.18	12.1
85	72.8	52.4	0.13	9.5	0.12	8.8
90[b]	78.9	41.3	0.07	5.4	0.07	5.2
95	87.3	25.1	0.02	1.8	0.02	1.8

[a] M_2 = B = AMPDAC; A = NaAMPS; *F* = feed composition; *P* = polymer composition; $r_1 = 0.22$; $r_2 = 0.31$; *N* = number per 100 repeat units. [b] Synthesized copolymers. [c] Run number.

possible probabilities and frequencies for AMPDAC- and NaAMPS-centered triads and pentads were calculated, only two were considered significant and included herein. *P*(ABA) and *P*(BABAB) are the probabilities of AMPDAC-centered alternating triads and pentads, respectively. NABA and NBABAB are the calculated number of AMPDAC centered triads and pentads, respectively, per 100 mer units, obtained by multiplying the respective probabilities by the corresponding polymer compositions, M_2P.

A maximum run number of approximately 79 corresponds to a polymer containing 45 mol % AMPDAC in the feed. The maximum frequency of AMPDAC-centered triads occurs at a copolymer composition of about 30 mol % AMPDAC, while the maximum frequency of AMPDAC-centered pentads occurs at a copolymer composition of approximately 55 mol % AMPDAC. Triad and pentad sequences are related to solution behavior in the subsequent paper in this series.

Conclusions

Copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) with (2-acrylamido-2-methylpropyl)dimethylammonium chloride (AMPDAC) have been prepared in aqueous solution in the presence of equimolar amounts of inorganic counterions. Elemental analysis and ^{13}C NMR were used to determine copolymer compositions. The inorganic counterion deficiency index of the copolymers indicated that the number of inorganic counterions in the samples decreased as the feed ratio approached unity. Also, the percent of uncharged AMPDAC, AMPDA, increased with incorporation of the cationic species. The composition of a polymer prepared in the absence of inorganic electrolytes, ADAS-50*, was essentially the same as that prepared in the presence of an equimolar amount of counterions, ADAS-50.

Copolymer molecular weights were in the range 1.6–9.5 × 10^6 g/mol with degrees of polymerization ranging from 0.77 to 4.24 × 10^4. The general trend for molecular weights and DPs was an initial increase with increasing mole percent of AMPDAC in the copolymer followed by a slow, then sharp decrease for the homopolymer of AMPDAC. Reactivity ratios, as determined by the low conversion methods of Fineman–Ross and Kelen–Tüdos, express the high alternating tendency of the copolymers; $r_1r_2 = 0.07$. A plot of mole percent AMPDAC in the feed versus mole percent AMPDAC in the copolymer, the copolymerization curve, revealed an azeotropic copolymer composition at about 50 mol %.

Copolymer microstructures have been calculated and indicate the high alternating tendency of the polymers. Sequence distributions for AMPDAC centered alternating triads and pentads display maximums at 30 and 55 mol % AMPDAC in the copolymer, respectively. The knowledge of copolymer composition, molecular weight, and microstructural data are essential in discerning the relationships which exist between structure and solution properties of the copolymers as discussed in the subsequent paper in this series.

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Registry No. (AMPDAC)(NaAMPS) (copolymer), 111255-99-3; AMPDAC, 74444-21-6; NaAMPS, 5165-97-9.

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