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WATER-SOLUBLE POLYMERS. XXXIV. AMPHOLYTIC TERPOLYMERS OF SODIUM 3-ACRYLAMIDO-3-METHYLBUTANOATE WITH 2-ACRYLAMIDO-2-METHYLPROPANE-DIMETHYLAMMONIUM CHLORIDE AND ACRYLAMIDE: SYNTHESIS AND ABSORBENCY BEHAVIOR

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ABSTRACT

Synthesis and absorbency studies of a series of terpolymers of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB) and 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) are reported. Terpolymers were synthesized with varying molar feed ratios of the three monomers; those containing greater than 1% charged groups were not water soluble but formed hydrogels. Ampholytic terpolymers synthesized from monomer mixtures of 5% AMPDAC, 10% NaAMB, and 85% AM exhibit a 230-fold weight gain in pure water and a 30-fold gain in 0.514 *M* NaCl. Enhanced water absorbency of terpolymers with a charge imbalance is consistent with operative osmotic forces in crosslinked polyelectrolytes. The good absorbency in NaCl solutions can be attributed to hydration of paired cationic and anionic mer units in this terpolymer series.

INTRODUCTION

Inter- and intramolecular ionic interactions are known to influence the solution behavior of polyelectrolytes. Polyampholytes exhibit unusual properties relative to conventional polyelectrolytes as a result of attractive ionic forces between oppositely charged mer units. Although polyampholytes have not received the attention that conventional polyelectrolytes have, several recent studies illustrate the utility of ampholytic polymers [1–7]. Salamone et al. reported the synthesis of polyampholytes from cationic–anionic monomer pairs [1, 2, 7]. Several studies have also been conducted on aliphatic and aromatic sulfobetaine polyampholytes. Several of these inner salt polymers are reported to possess hydrogel characteristics. A recent study by Peiffer and Lundberg reveals the importance of incorporating noncharged monomers into ampholytic polymers for attainment of optimum viscosity behavior [3].

Polyampholytes of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) with sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and acrylamide (AM) have been studied previously in our laboratories [4–6]. The solution properties of these polymers are determined by charge distribution, polymer microstructure, molecular weight, hydrophobic/hydrophilic balance, pH, and ionic strength. In particular, intramolecular ionic interactions dominate solution behavior of high charge density copolymers, while intra- and intermolecular interactions control low-to-moderate charge density polyampholyte behavior.

Past studies in our laboratories have demonstrated that when carboxylated (NaAMB) and sulfonated (NaAMPS) monomers are copolymerized with acrylamide they produce chain extended, relatively electrolyte tolerant, water-soluble polymers [8–10]. The lack of phase separation and the attractive viscosity characteristics of copolymers of sodium 3-acrylamido-3-methylbutanoate (NaAMB) with acrylamide have been attributed to neighboring group and intra-unit interactions. The interactions include chain stiffening effects brought about by hydrogen bonding.

The objectives of this work were to prepare low-to-moderate charge density ampholytic terpolymers of AMPDAC with acrylamide and sodium 3-acrylamido-3-methylbutanoate (NaAMB). The strong ion binding character of the carboxylate group as compared to the previously studied sulfonate group would be expected to enhance mer binding in ampholytic terpolymers. Such polymers might be expected to exhibit polymeric associations in aqueous solutions and chain expansion in electrolytes—properties of great interest in rheology modification, drag reduction, and superabsorbency.

EXPERIMENTAL

Materials and Monomer Synthesis

2-Acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC) was synthesized as previously described [11]. AMPDAC was converted to the base, 2-acrylamido-2-methylpropanedimethylamine (AMPDA), prior to purification. The crude AMPDA was then recrystallized twice from methyl ethyl ketone prior to use (mp 61–63°C).

Analysis. Calculated 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 cm^{-1} (s), 1550 cm^{-1} (m); tertiary amine, 1160 cm^{-1}.

3-Acrylamido-3-methylbutanoic acid (AMBA) was synthesized via a Ritter reaction using acrylonitrile and 3,3-dimethylacrylic acid in the presence of water and excess sulfuric acid. The procedure of Hoke and Robbins [12] was employed for the synthesis of AMBA. Acrylonitrile from Aldrich Chemical Co. was used without further purification. 3,3-Dimethylacrylic acid was obtained from Aldrich Chemical Co. and recrystallized once from acetone prior to use. In a typical monomer synthesis, 3.0 mol acrylonitrile, 3.0 mol 3,3-dimethylacrylic acid, and 1.5 mol H_2O were placed in a 2000-mL, 3-necked flask equipped with a mechanical stirrer, ice bath, and addition funnel. Approximately 0.3 g 4,4′-methylene-bis-(2,6-di-*tert*-butylphenol) was added as a polymerization inhibitor. After cooling the mixture to 5°C, 6.2 mol concentrated H_2SO_4 was added dropwise while stirring and maintaining the temperature below 40°C. The reaction was allowed to proceed for 6–8 h following the complete addition of the sulfuric acid. The contents of the flask were then cooled to 5°C, followed by dilution with 2–3 L H_2O while holding the temperature below 40°C. 3,3-Dimethylacrylic acid formed a white precipitate and was filtered from the solution. The aqueous solution was extracted with chloroform, and the crude AMBA was isolated by rotary evaporation of the chloroform. The yield of AMBA was approximately 60%. The product was then recrystallized twice in a mixture of MEK and petroleum ether prior to use (mp 89–91°C).

Analysis. Calculated for $C_8H_{13}NO_3$: C, 56.14; H, 7.60; N, 8.19%. Found: C, 55.98; H, 7.56; N, 8.20%. IR N–H stretch, 3250 cm^{-1}; C=C–H, 3075 cm^{-1}; aliphatic C–H, 2950 cm^{-1}; amide C=O, 1660 cm^{-1} (s), 1530 cm^{-1} (m); acid C=O, 1720 cm^{-1}.

Acrylamide (AM) was obtained from Aldrich Chemical Co. and recrystallized twice from acetone followed by vacuum drying at room temperature prior to use (mp 83°C).

Polymer Synthesis

Terpolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (*A*MP*D*AC) with sodium 3-acrylamido-3-methylbutanoate (Na*A*M*B*) and acrylamide (*AM*) (1), the ADABAM series, were prepared via free radical initiation in water at 30°C employing potassium persulfate as the initiator. The monomers were then mixed to form a single solution. Following adjustment of the pH to 7, the reaction mixture was transferred to a 500-mL, 3-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. The mixture was purged with nitrogen for 20 min, then initiated with a specified quantity of potassium persulfate. The pH adjustment was performed to ensure that all of the monomers were in the ionized form. The total monomer concentration in each reaction was held constant at 0.45 *M*. An aliquot was collected at low conversion to measure possible copolymer drift. The reaction was typically terminated at <60% conversion due to the high viscosity of the reaction medium. The reaction mixture was diluted with two to four volumes of deionized water followed by precipitation in reagent grade acetone while stirring. After purification, the FTIR spectrum indicated the following for a typical terpolymer, ADABAM 15-15: amide I, 1623 cm^{-1}; amide II, 1555 cm^{-1}; C–H stretch 2963 cm^{-1}; asymmetrical $(C{=}O)_2$ stretch, 1580 cm^{-1}; symmetrical $(C{=}O)_2$ stretch, 1398 cm^{-1}; ammonium ion N–H stretch, 3062 cm^{-1}; tertiary amine salt, 2779 cm^{-1}; N–H broad, 3400 to 3300 cm^{-1}.

Polymer Purification

Following the initial precipitation of the polymers from the reaction mixture, the samples were subjected to two cycles of dissolution in pure water followed by precipitation in acetone to remove residual monomer, initiator, nonbound inorganic ions, etc. The solid polymer was then redissolved in water and lyophilized to remove residual nonsolvent acetone and all water other than bound water.

Compositional Calculations

Terpolymer compositions for the ADABAM series were determined using elemental analysis for carbon, hydrogen, and nitrogen using Eqs. (1)–(3):

$$\frac{\%\ \mathrm{C}}{12.01} = 8\mathrm{A} + 9\mathrm{B} + 3\mathrm{C} \tag{1}$$

$$\frac{\%\ \mathrm{H}}{1.01} = 12\mathrm{A} + 19\mathrm{B} + 5\mathrm{C} \tag{2}$$

$$\frac{\%\ \mathrm{N}}{14.01} = 1\mathrm{A} + 2\mathrm{B} + 1\mathrm{C} \tag{3}$$

A, B, and C represent the number of moles of NaAMB, AMPDAC, and AM, respectively, in a normalized weight of sample, e.g., 100 g. After determining A, B, and C using matrix algebra, the mole-% compositional data were calculated using Eqs. (4)–(6):

$$\text{mole-\% NaAMB} = \frac{\mathrm{A}}{\mathrm{A} + \mathrm{B} + \mathrm{C}} \times 100 \tag{4}$$

$$\text{mole-\% AMPDAC} = \frac{\mathrm{B}}{\mathrm{A} + \mathrm{B} + \mathrm{C}} \times 100 \tag{5}$$

$$\text{mole-\% AM} = \frac{C}{A + B + C} \times 100 \qquad (6)$$

Absorbency Studies

ADABAM terpolymers containing greater than 1% charged groups in the feed mixture were not water-soluble. Since characterization by viscometry was precluded, absorbency studies were conducted in pure water and 0.514 *M* NaCl.

The sample treatment involved placing approximately 0.1 g lyophilized polymer in an excess of solvent in a 100-mL beaker. After 24 h the beakers were inverted in a funnel equipped with filter paper and the samples were allowed to drain of excess water. The samples were then removed from the funnel and transferred onto dry filter paper to absorb any additional surface water before weighing. The percent weight gain and percent water content were then calculated using Eqs. (7) and (8):

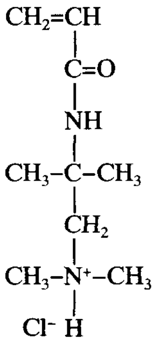
$$\text{percent weight gain} = \frac{(\text{final weight}) - (\text{initial weight})}{\text{initial weight}} \times 100 \qquad (7)$$

$$\text{percent water content} = \frac{(\text{final weight}) - (\text{initial weight})}{\text{final weight}} \times 100 \qquad (8)$$

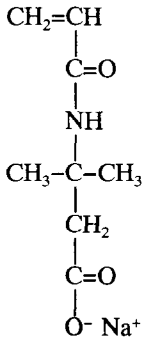
RESULTS AND DISCUSSION

The previously observed chain extending attributes of NaAMB-AM copolymers suggested property enhancement by the incorporation of NaAMB units into low-to-moderate charge density ampholytic terpolymers. We also suspected that incorporation of NaAMB in low charge density polyampholytes would allow strong binding of the carboxylate anion with cationic sites. It was anticipated that the above considerations might result in superior viscometric properties for low charge density polyampholytes in the semidilute concentration range. Polyampholytes in this concentration regime are known to possess intermolecular ionic interactions. The propensity for formation of strong intermolecular ionic bonds should be greater for ampholytic NaAMB terpolymers than for ampholytic NaAMPS terpolymers.

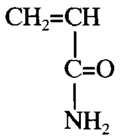
Terpolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (*A*MP*D*AC) (1) with sodium 3-acrylamido-3-methylbutanoate (Na*A*M*B*) (2) and acrylamide (*AM*) (3), the ADABAM series, were synthesized and characterized as outlined in the Experimental Section. The polymers were prepared by separately placing a specified quantity of each monomer in deionized water followed by the addition of the corresponding acid or base; the solutions were then mixed and polymerization was initiated. This procedure is similar to that used previously in our laboratories for the terpolymerization of AMPDAC with NaAMPS and AM [6].



AMPDAC (1)



NaAMB (2)



AM (3)

Compositional Studies

Terpolymer compositions were calculated using elemental analysis (Table 1) as detailed in the Experimental Section. Terpolymer reaction parameters and compositional data for the synthesis of 2-acrylamido-2-methylpropanedimethylammonium chloride (*A*MP*D*AC)/sodium 3-acrylamido-3-methylbutanoate (Na*A*M*B*)/ acrylamide (*AM*), ADABAM, polyampholytes are shown in Table 2. The terpolymer compositional data indicate that AMPDAC is preferentially incorporated relative to NaAMB. In previous work in our laboratories, reactivity

TABLE 1. ADABAM Series: Elemental Analysis Data

Sample name	% C	% H	% N
ADABAM 0.5–0.5	46.31	6.36	17.11
ADABAM 2.5–2.5L[a]	—	—	—
ADABAM 5–5L	47.50	7.08	15.87
ADABAM 10–10	48.22	7.78	14.05
ADABAM 15–15	48.94	7.87	13.87
ADABAM 5–10	47.09	7.16	14.94
ADABAM 10–5	47.04	6.97	13.78

[a] L denotes low conversion.

TABLE 2. ADABAM Series: Reaction Parameters[a] and Terpolymer Compositions

Sample name	Feed composition (AMPDAC:NaAMB:AM)	Terpolymer composition[b] (AMPDAC:NaAMB:AM)
ADABAM 0.5–0.5	0.5:0.5:99.0	0.66:1.40:97.94
ADABAM 2.5–2.5L[c]	2.5:2.5:95.0	—
ADABAM 5–5L	5:5:90	11.63:3.99:84.32
ADABAM 10–10	10:10:80	36.21:5.61:58.18
ADABAM 15–15	15:15:70	37.47:8.20:54.33
ADABAM 5–10	5:10:85	17.08:5.60:77.32
ADABAM 10–5	10:5:85	22.26:2.33:75.41

[a] pH = 7.0; T = 30°C; total monomer concentration = 0.45 M; $[K_2S_2O_8] = 4.5 \times 10^{-4} M$.
[b] Determined via elemental analysis for carbon, hydrogen, and nitrogen.
[c] L denotes low conversion.

ratios for the copolymerization of AM (M_1) with NaAMB (M_2) were reported to be $r_1 = 1.2$ and $r_2 = 0.47$, respectively [8, 9]. Reactivity ratios for the copolymerization of AM (M_1) with AMPDAC (M_2) were reported to be $r_1 = 0.96$ and $r_2 = 0.20$, respectively [8, 11].

Despite the balance of cationic and anionic monomer feed ratios for five of the seven samples, experimentally determined compositions of the copolymers are far from balanced. This was not anticipated since pairing of oppositely charged monomers during polymerization has been suggested [1, 2, 4–6] for similar systems.

Absorbency Studies

All terpolymers, with the exception of ADABAM 0.5–0.5, were water insoluble. Attempts to form aqueous solutions of these terpolymers in concentrations up to 1 M NaCl were not successful. The salt solutions did solubilize a greater percentage of some polymers than deionized water; however, aggregates of hydrogel particles remained detectable. Suspensions subjected to shear partially dissolved; when shear was removed, aggregates again became noticeable.

The presence of strong intermolecular ionic bonds between the carboxyl groups of NaAMB mers and the tertiary ammonium groups of AMPDAC mers is responsible for the insolubility of the ADABAM terpolymers. The weak basicity of the sulfonate group of NaAMPS, reported previously [6], apparently prevented the ADABAM terpolymers of AMPDAC, NaAMPS, and AM from forming similar hydrogels.

The lack of solubility of the ADABAM copolymers precluded viscosity and light-scattering studies. Therefore, absorbency studies were conducted. Percent water content and percent weight gain data for the ADABAM terpolymers are shown in Table 3. The method for determination of these values is described in detail in the Experimental Section. The absorbency tests were conducted in deionized water and 0.514 *M* NaCl. In 0.514 *M* NaCl, the hydrogels are composed of from 95.8 to 96.8% water by weight. The samples increased in weight from 2000 to 3000% relative to their initial states. ADABAM 5-10 displayed slightly superior absorbency characteristics relative to the other terpolymers in 0.514 *M* NaCl.

The ability of the ADABAM terpolymers to absorb solute is significantly greater for deionized water than for 0.514 *M* NaCl. Again, ADABAM 5-10 with a 17.1/5.6/77.3 composition of monomers is the top performer with a percent weight gain of water greater than 20 000%, and 0.514 *M* NaCl greater than 3000%. ADABAM 10-5 with a 22.3/2.3/75.4 ratio absorbed slightly less water than ADABAM 5-10, although the former sample consumed water rapidly and gelled in only a few seconds. Enhanced water absorbency of terpolymers with higher degrees of ionic character is consistent with operative osmotic forces in polyelectrolytes. The good absorbency in saline solution is likely due to hydration of paired cationic and anionic mer units in the ADABAM series.

CONCLUSIONS

Terpolymers of 2-acrylamido-2-methylpropanedimethylammonium chloride (AMPDAC), sodium-3-acrylamido-3-methylbutanoate (NaAMB), and acrylamide (AM) have been prepared and studied in terms of their absorbencies. Terpolymer compositional data indicate that AMPDAC is preferentially incorporated relative to NaAMB.

TABLE 3. ADABAM Series: Absorbency Data

	% Weight gain		% Water content	
Sample name	Pure water	0.514 *M* NaCl	Pure water	0.514 *M* NaCl
ADABAM 0.5–0.5[a]	—	—	—	—
ADABAM 2.5–2.5	3500	2780	97.2	96.5
ADABAM 5–5	2580	1980	96.3	95.2
ADABAM 10–10	6530	2470	98.5	96.1
ADABAM 15–15	7670	2310	98.7	95.8
ADABAM 5–10	23200	3020	99.6	96.8
ADABAM 10–5	18500	2540	99.5	96.2

[a] Sample is soluble in water and 0.514 *M* NaCl.

Due to the strong ion binding nature of the carboxylate group of NaAMB, these low-to-moderate charge density terpolymers were not water soluble above 1% charged groups. Ionic interactions apparently precluded dissolution of the terpolymers, even at elevated NaCl concentrations. In contrast, previously studied sulfonated ampholytic polymers [6] were water soluble. Absorbency studies were conducted on the ADABAM terpolymers in pure water and 0.257 *M* NaCl. In pure water, one of the samples absorbed up to 20 000% of its weight in water, while that value decreased to about 3000% in salt water. The enhanced water absorbency properties of these terpolymers is attributed to the residual polyelectrolyte character due to charge imbalance. Aqueous saline absorbency is likely enhanced by hydration of the ampholytic ion pairing of mer units in the copolymers. Work is currently being conducted to prepare balanced ampholytes for enhanced saline absorbency.

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