

Poly(sodium Acrylamidoalkanoate)s: Syntheses and Solution Properties in Relation to Flocculation Study in Water Treatment

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SYNOPSIS

The micelle-forming monomers of sodium 6-acrylamidocaproate (Na 6-AAC), sodium 11-acrylamidoundecanoate (Na 11-AAU), sodium 11-(*N*-methylacrylamido)undecanoate (Na 11-MAAU), and sodium 11-(*N*-ethylacrylamido)undecanoate (Na 11-EAAU) have been synthesized and polymerized. Except poly (Na 6-AAC), the molecular weights of the other three poly (sodium acrylamidoalkanoate)s were over 10^6 . They behave as strong anionic polyelectrolytes in aqueous solutions. Their solution properties, such as viscosity, charge density, and radius of gyration, were investigated. The performance of these anionic polyelectrolytes as coagulant aids in water treatment were assessed by jar test. Poly (Na 6-AAC) and poly (Na 11-AAU) were superior to poly (Na 11-MAAU) and poly (Na 11-EAAU) in terms of flocs settling. All these four anionic polyelectrolytes tested in water treatment are as effective as a commercially available cationic polyamine organic coagulant (Hyperfloc CP 753).

INTRODUCTION

The application of synthetic polyelectrolytes in water and wastewater treatments has increased significantly in recent years. A large number of synthetic polyelectrolytes are available commercially.¹ They are characterized by the nature of their charges, e.g., anionic, cationic, or nonionic. In water treatment, cationic polyelectrolytes are used as primary coagulant or coagulant aids, whereas the anionic ones are used only as coagulant aids in conjunction with a metallic coagulant such as alum. This is primarily because the majority of colloidal matter found in nature bears negative charges.

Coagulation or flocculation is an essential stage in water and wastewater treatments. The aggregation of the colloidal particles into larger flocs is necessary for successful separation by sedimentation. This involves destabilization of the colloidal parti-

cles by addition of inorganic electrolytes and polyelectrolytes. The aggregation process is commonly known either as coagulation or flocculation. However, coagulation implies aggregation caused by compression of the electrical double layers surrounding colloidal particles² whereas flocculation arises mainly from bridging colloidal particles by long chain polymer molecules.³⁻⁵ The polyelectrolyte molecules may first serve as a coagulant to reduce the opposite charges of colloidal particles, and then as a flocculant to bridge adjacent particles via extended segments of adsorbed polymer molecules.

The majority of the synthetic anionic polyelectrolytes based on polyacrylamide and its copolymers with acrylic acid.^{1,6} The polysoaps of *n*-dodecyl bromide addition compound of poly(2-vinyl pyridine)⁷ and poly(styrene-styrylundecanoate)⁸ have also long been reported.

Recently, we have synthesized a series of surface-active monomers of sodium acrylamidoalkanoates.⁹⁻¹¹ These monomers form micelles in aqueous solutions. They can easily be polymerized by free radical to high molecular weight polymers which behave as strong anionic polyelectrolytes in water.

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These monomers can be synthesized from the unsaturated fatty acids by modifying them to different sodium acrylamidoalkanoates. The monomers are thus free of allylic hydrogens and are very reactive in polymerization to produce polymers having molecular weights of around 10^6 . In contrast, the soaps of the unsaturated fatty acids with allylic hydrogens,^{12,13} such as sodium 10-undecenoate,¹⁴⁻¹⁶ have not been successfully polymerized to high molecular weight polysoaps. In this paper, we briefly describe the polymerization of four sodium acrylamidoalkanoates, the solution behaviors of these anionic polyelectrolytes, and their uses as coagulant aids in water treatment.

EXPERIMENTAL

Materials

Acryloyl chloride, 6-aminocaproic acid, 11-aminoundecanoic acid, toluidine blue O, poly(vinyl sulfonic acid, potassium salt), and cetylpyridinium chloride monohydrate from Aldrich were all used as received. Methylamine (40% aqueous solution) and ethylamine (70% aqueous solution) were from TCI (Japan). Potassium persulfate (Reachim) was recrystallized from water. Poly(diallyl dimethyl ammonium chloride) was from Polysciences.

Synthesis of Surface-Active Monomers: Sodium Acrylamidoalkanoates

Sodium 11-acrylamidoundecanoate (Na 11-AAU) was prepared by direct reacting 11-aminoundecanoic acid and acryloyl chloride as we have described it elsewhere.⁹ Similarly, sodium 6-acrylamidocaproate (Na 6-AAC) was prepared from 6-aminocaproic acid and acryloyl chloride. The method for synthesizing sodium 11-(*N*-methylacrylamido)undecanoate (Na 11-MAAU) and sodium 11-(*N*-ethylacrylamido)undecanoate (Na 11-EAAU) have also been reported¹¹ by us recently. It involves reactions of 11-bromoundecanoic acid with methylamine or ethylamine solution followed by the addition of acryloyl chloride.

Polymerization of Sodium Acrylamidoalkanoates

An aqueous solution of either Na 6-AAC, Na 11-AAU, Na 11-MAAU, or Na 11-EAAU in a reaction flask was purged by nitrogen before it was polymerized at 50°C using potassium persulfate as an initiator. At the end of each polymerization, the polymer was precipitated in an excess of acetone. After

washing the polymer several times with methanol, it was dried in a vacuum oven at room temperature.

Molecular Weight Determination by GPC and Light Scattering

Due to the interactions of the polymers with the chromatography column, the molecular weights of the sodium salts of polyacrylamidoalkanoic acids were not determined directly by gel permeation chromatography (GPC). Instead, the acid form of the polymers which were soluble in dimethylformamide (DMF) were used for GPC measurements. They were performed on a Varian Vista 5500 liquid-chromatography system equipped with a RI-3 detector and a PL-gel 5 μ m mixed column (Polymer Laboratories). Polystyrene standards (Polysciences) dissolved in DMF were used to establish the calibration curve.

Light scattering measurements were performed on Malvern Instruments System 4700C submicron particle analyser. The intensities of the scattered light of the solutions of each poly(sodium acrylamidoalkanoate) at different concentrations of NaCl were measured over angles ranging from 10 to 150° using vertically polarized light of wavelength 633 nm and at $21 \pm 0.1^\circ\text{C}$. The experimental data were analyzed by the Zimm plot method.¹⁷

Viscosity Measurement

The reduced viscosities of the solutions of the poly(Na-acrylamidoalkanoates) were measured with an Ubbelohde dilution capillary viscometer (Kapenekas Laboratory Services, Akron, OH). The viscometer was thermostated in a water bath at $28 \pm 0.1^\circ\text{C}$.

Charge Density of Polyelectrolyte

The charge densities of the anionic poly(Na-acrylamidoalkanoate)s were determined by first complexing them with poly(diallyl dimethyl ammonium chloride) (PDADMAC), and they were backtitrated with poly(potassium vinyl sulfate) (PVSK) using toluidine blue O as an indicator. The charge density (I), expressed as milliequivalents per gram of the anionic polyelectrolytes, is calculated from the following equation:

$$I = (V_2 - V_1)N/M$$

where V_1 = mL of PVSK required to titrate the sample solution with PDADMAC, V_2 = mL of

PVSK required to titrate the PDADMAC solution, N = normality of PVSK, and M = gram of polymer used.

Flocculation Study by Jar Test

The jar test apparatus (PCI, Waterwise) was used to study flocculation in water treatment. The water sample was buffered by lime. After addition of alum and the poly(Na-acrylamidoalkanoate) to the water sample, it was mixed at 100 rpm for 1 min. Stirring was continued for 4 min at 50 rpm, followed by 15 min at 10 rpm. The floc sizes and the settling rate were recorded. After 30 min of sedimentation, a water sample was withdrawn from the middepth of the beaker with a large bore pipette for residual analysis¹⁸ of turbidity, aluminium, sulfate, and total organic compounds (TOC).

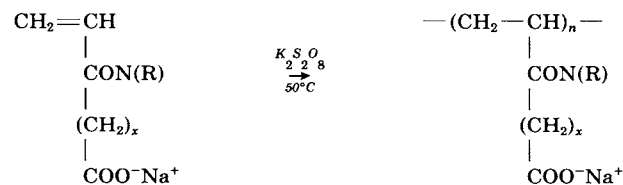
Zeta Potential, Turbidity, and Conductivity Measurements

The zeta potentials for the water samples were measured by a Zetameter 3.0 (Microscope Module) from Zetameter Inc. The zetameter was connected to a GT-2 electrophoresis cell with molybdenum anode and platinum cathode. Each raw water sample was treated with alum and the polyelectrolyte and stirred at 100 rpm for 1 min, followed by 60 rpm for another 3 min. The zeta potential, turbidity, and conductivity measurements were then carried out using a ratio turbidimeter (Hach Company, Model 18900) and a conductivity meter (Kyoto Electronics, Model GM-15).

RESULTS AND DISCUSSION

Poly(sodium Acrylamidoalkanoate)s

These strong anionic polyelectrolytes were obtained by polymerizing the sodium acrylamidoalkanoates in aqueous solutions using potassium persulfate as initiator. Their chemical compositions and the abbreviated names are shown below:



where $R = \text{H}$, $x = 5$, poly(Na 6-AAC), $R = \text{H}$, $x = 10$, poly(Na 11-AAU), $R = \text{CH}_3$, $x = 10$, poly(Na

11-MAAU), and $R = \text{C}_2\text{H}_5$, $x = 10$, poly(Na 11-EAAU).

Table I shows the weight average molecular weights (\bar{M}_w), the polydispersity index (\bar{M}_w/\bar{M}_n), and weight average degree of polymerization (\bar{P}_w) of these polyelectrolytes obtained at three polymerization temperatures. With the exception of poly(Na 6-AAC), \bar{M}_w for other three polyelectrolytes were slightly over 10^6 and their molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.32\text{--}1.46$) were rather narrow when they were obtained from polymerization at 50°C . These polyelectrolytes consisted of about 4000 carboxylate groups per polymer chain. In contrast, \bar{M}_w for poly(Na 6-AAC) was only about one-third of a million, and each polymer chain comprised of only about 2000 monomer units. As the polymerization temperature was raised from 50 to 55 or 60°C , \bar{M}_w decreased and \bar{M}_w/\bar{M}_n broadened for all four polyelectrolytes as expected.

Solution Properties

Viscosity

The reduced viscosities (η_{sp}/c) of aqueous solutions of poly(Na-acrylamidoalkanoate)s underwent a marked increase with dilutions as shown in Figure 1. Poly(Na 6-AAC) exhibited the lowest reduced viscosity, which could be due to its low molecular weight. When $(\eta_{sp}/c)^{-1}$ is plotted against $c^{1/2}$, a nearly straight line is obtained for each of the polymer solutions at low concentration (Fig. 2) as observed for the common polyelectrolytes.¹⁹ The in-

Table I Molecular Weights^a of Poly(sodium Acrylamidoalkanoate)s Obtained at Different Polymerization Temperatures

Polyelectrolyte	\bar{M}_w (10^6)	\bar{M}_w/\bar{M}_n	\bar{P}_w (10^3)
Poly(Na 6-AAC)			
50°C	0.37	1.52	1.79
60°C	0.36	2.10	1.74
Poly(Na 11-AAU)			
50°C	1.13	1.43	4.07
60°C	0.81	1.82	2.92
Poly(Na 11-MAAU)			
50°C	1.05	1.46	3.61
55°C	0.95	1.75	3.29
Poly(Na 11-EAAU)			
50°C	1.15	1.32	3.77
55°C	0.73	2.00	2.41

^a MW from GPC of acid form of polymer.

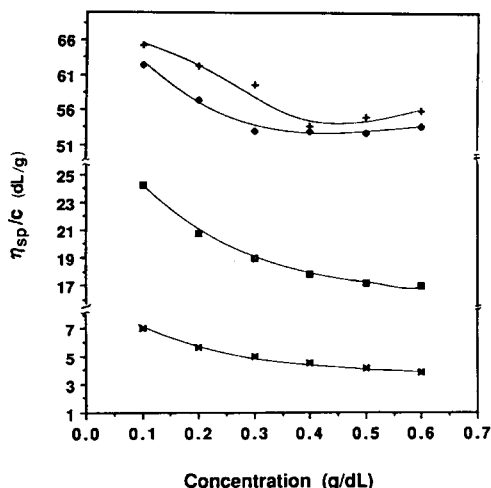


Figure 1 Dependence of reduced viscosity on concentration of poly(sodium acrylamidoalkanoate)s in water at 23°C: (+) Poly(Na 11-AAU); (◆) Poly(Na 11-MAAU); (□) Poly(Na 11-EAAU); (*) Poly(Na 6-AAC).

intrinsic viscosities $[\eta]_0$ of these polyelectrolytes were determined according to Huggins and Kraemer's methods.^{20,21} Figure 3 shows the effect of NaCl concentration on $[\eta]_0$ for poly(Na 6-AAC), poly(Na 11-MAAU), and poly(Na 11-EAAU). At low NaCl concentration, the polyelectrolyte molecules might be highly ionized resulting in the expansion of the polymer chains. The dimensions of these expanded polymer chains reduced markedly as the concentration of NaCl was increased. For a given concentra-

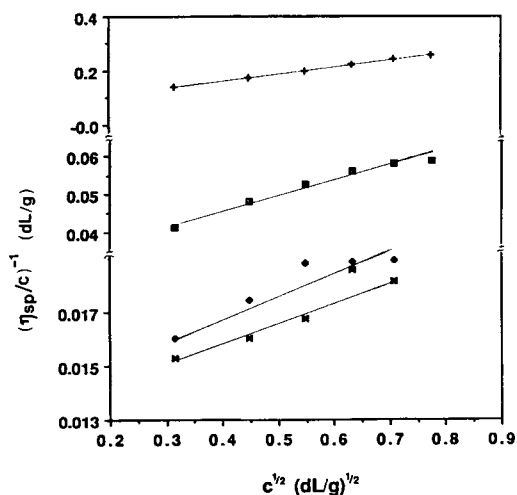


Figure 2 Dependence of reciprocal of reduced viscosity on square root of concentration of poly(sodium acrylamidoalkanoate)s at 23°C: (*) Poly(Na 11-AAU); (◆) Poly(Na 11-MAAU); (□) Poly(Na 11-EAAU); (+) Poly(Na 6-AAC).

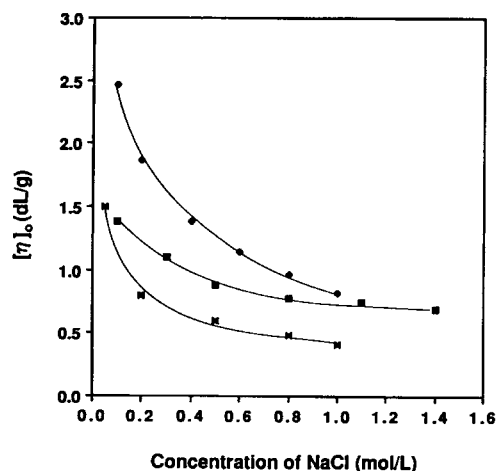


Figure 3 Effect of NaCl concentration on the intrinsic viscosities of the polyelectrolytes at 23°C: (◆) Poly(Na 11-MAAU); (*) Poly(Na 11-EAAU); (□) Poly(Na 6-AAC).

tion of NaCl, $[\eta]_0$ of poly(Na 6-AAC) was smaller than that of poly(Na 11-MAAU), but it was larger than that of poly(Na 11-EAAU). It implies that the polymer chains of low molecular weight poly(Na 6-AAC) were more extended than that of high molecular weight poly(Na 11-EAAU). This is supported by the results of radius of gyration of these polyelectrolytes to be discussed later (Table II).

Many polyelectrolyte solutions²²⁻²⁵ show a gradual decrease in viscosity with storage time. Figure

Table II Charge Densities and Radii of Gyration of Poly(sodium Acrylamidoalkanoate)s^a

Polyelectrolyte	Charge Density (meq/g)	$\langle s^2 \rangle^{1/2}$ (nm)
Poly(Na 6-AAC)	2.19	—
		79.6 (0.05 M NaCl)
		53.1 (0.20 M NaCl)
Poly(Na 11-AAU)	1.98	—
		48.2 (0.70 M NaCl)
		43.8 (0.30 M NaCl)
Poly(Na 11-MAAU)	1.80	—
		83.8 (0.10 M NaCl)
		58.2 (0.30 M NaCl)
Poly(Na 11-EAAU)	1.52	—
		36.4 (0.50 M NaCl)
		42.5 (0.20 M NaCl)
		38.8 (0.40 M NaCl)
		34.3 (0.70 M NaCl)

^a Polymers prepared at 50°C.

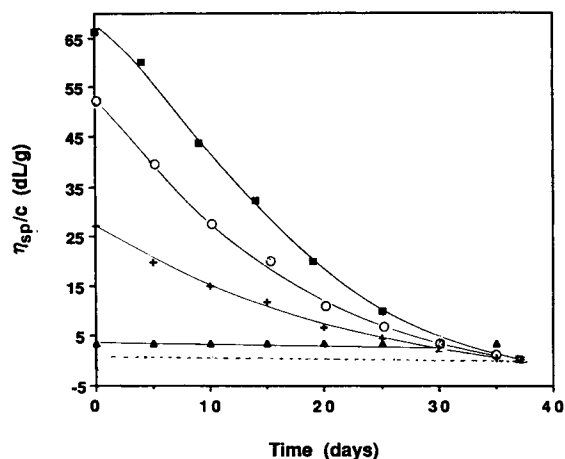


Figure 4 Aging of the aqueous solutions (0.3 g/dL) of poly(sodium acrylamidoalkanoate)s at 23°C: (□) Poly(Na 11-AAU); (○) Poly(Na 11-MAAU); (+) Poly(Na 11-EAAU); (▲) Poly(Na 6-AAC); (---) poly-electrolytes in 0.3 mol/L aqueous NaCl solution.

4 shows the aging effect on the dilute solutions (0.3 g/dL) of poly(Na-acrylamidoalkanoate)s at 23°C. Their reduced viscosities, except poly(Na 6-AAC), sharply decreased during the first 3 weeks of aging and then converged to an almost constant low value in 40 days. This low value was comparable to those poly(Na-acrylamidoalkanoate)s dissolved in 0.3 mol/L NaCl aqueous solutions. The reduced viscosities of the latter system remained almost unchanged throughout the same period of aging. The aging effect is attributed to the conformational changes for high molecular weight polyelectrolytes resulting in a diminished hydrodynamic volume as a function of time, rather than due to biodegradation of the polymers.

Charge Density and Radius of Gyration

The charge densities and radii of gyration ($\langle s^2 \rangle^{1/2}$) of poly(Na-acrylamidoalkanoate)s at different NaCl concentrations are listed in Table II. Poly(Na 6-AAC) had the highest charge density which was followed by poly(Na 11-AAU), poly(Na 11-MAAU), and poly(Na 11-EAAU). The conductivities of these polyelectrolytes also revealed the similar trend as shown in Figure 5. This is understandable because the molecular weights of the monomers of the same carboxylate group increased from Na 6-AAC to Na 11-EAAU. In a dilute NaCl solution, both poly(Na 6-AAC) and poly(Na 11-MAAU) exhibited a large $\langle s^2 \rangle^{1/2}$ of about 80 nm. This indicates that their long side chains with the negatively charged car-

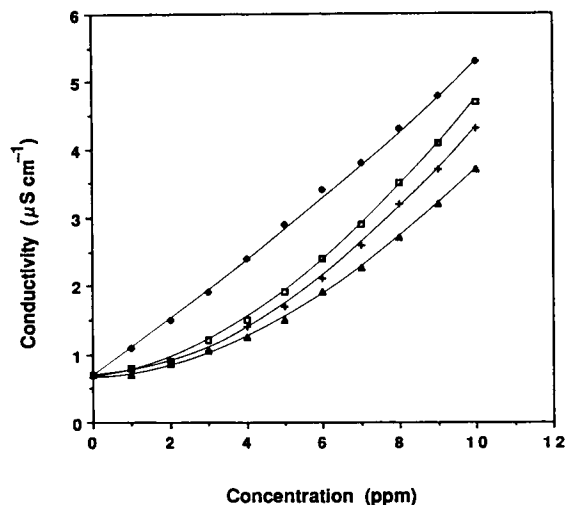


Figure 5 Conductivities of different poly(sodium acrylamidoalkanoate)s: (◆) Poly(Na 6-AAC); (□) Poly(Na 11-AAU); (+) Poly(Na 11-MAAU); (▲) Poly(Na 11-EAAU).

boxylate groups were well expanded due to charge repulsion. But the radii of gyration of all these polyelectrolytes having the comblike or octopus-type structures were substantially reduced in high ionic strength media. It is due to compression of the electrical double layers of the ionic groups by electrolyte effect. The expanded structures of these poly(Na-

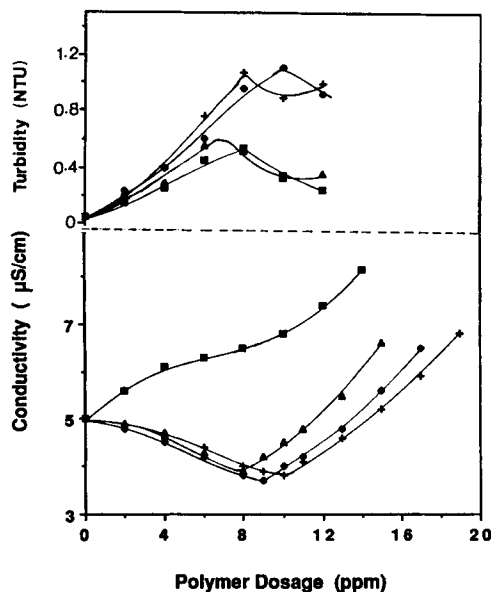


Figure 6 Variation of conductivity and turbidity of 2.5 ppm Alum in distilled water by the effect of polyelectrolytes: (▲) Poly(Na 11-AAU); (◆) Poly(Na 11-MAAU); (+) Poly(Na 11-EAAU); (□) Poly(Na 6-AAC).

Table III Conductivity and Zeta Potential of Raw and Treated Water

Sample No.	Lime (ppm)	Alum (ppm)	Polymer (ppm)	Conductivity ($\mu\text{S cm}^{-1}$)	Zeta Potential (mV)
Raw H ₂ O	—	—	—	43.0	-20.1 ± 2.3
1	—	5	—	47.0	-12.3 ± 3.0
2	—	10	—	47.5	-8.1 ± 2.5
3	1	15	—	48.5	-6.0 ± 1.0
4	1	20	—	51.5	$+7.6 \pm 2.8$
5	1	15	0.5 ^a	51.5	-12.3 ± 2.8
6	1	15	0.5 ^b	51.0	-10.1 ± 1.7

^a Poly(Na 11-AAU).^b Poly(Na 6-AAC)

acrylamidoalkanoate)s in low ionic strength media may provide enormous sites for bridging the suspended colloidal particles in water treatment.

Flocculation Study in Water Treatment Using Poly(Na-acrylamidoalkanoate)s

The effectiveness of poly(Na-acrylamidoalkanoate)s as coagulant aids in water treatment was first investigated in conjunction with alum added to distilled water. The change of conductivity of distilled water in the presence of 2.5 ppm alum was monitored after each addition of the polyelectrolyte. With the exception of poly(Na 6-AAC), the conductivity of

each solution first decreased to a minimum after adding 8–10 ppm of each polyelectrolyte. On further addition of the polyelectrolyte, the conductivity increased as shown in Figure 6. Though the conductivity of poly(Na 6-AAC) solution did not show the initial decrease, there was a change of slope at about 10 ppm. The absence of the initial decrease in conductivity could be due to its much higher conductivity in aqueous solution than its homologs as revealed in Figure 5. The decreased conductivity was due to partial neutralization of positively charged alum particles by anionic poly(Na-acrylamidoalkanoate)s. This resulted in coagulation of some alum particles. Thus the turbidity for each solution

Table IV The Settled Water Quality Treated by Different Polyelectrolytes

	Raw Water	Polyelectrolyte ^a				
		A	B	C	D	E
Alum (ppm)	—	15.0	15.0	15.0	15.0	15.0
Lime (ppm)	—	1.0	1.0	1.0	1.0	1.0
Polymer (ppm)	—	0.3	0.3	0.3	0.3	0.3
pH	6.9	6.5	6.5	6.5	6.5	6.4
Color (Hazen unit)	35	< 5	< 5	< 5	< 5	< 5
Turbidity (NTU)	8.3	0.7	0.6	0.6	0.6	0.6
Conductivity ($\mu\text{S cm}^{-1}$)	52	62	60	60	60	61
Alkalinity (ppm as CaCO ₃)	16	10	10	9	10	9
TOC (ppm)	4.15	2.02	1.78	2.12	1.86	2.19
Chloride (ppm)	4	4	4	4	4	4
Sulfate (ppm)	5	11	11	11	11	11
Res. aluminum (ppm)	0.00	0.25	0.14	0.28	0.26	0.26
Floc size ^b	—	d_4	d_4	d_3	d_3	d_3
Settling rate	—	Fast	Fast	Medium	Medium	Medium

^a A = Poly(Na 6-AAC), B = Poly(Na 11-AAU), C = Poly(Na 11-MAAU), D = Poly(Na 11-EAAU), E = Hyperfloc CP753.^b d_3 = 0.75–1.0 mm; d_4 = 1.0–1.5 mm.

increased to a maximum and then decreased on further addition of the polyelectrolyte. The concentration of each polyelectrolyte required to produce the maximum turbidity was generally 1–2 ppm lesser than that needed for obtaining the minimum conductance in each solution (Fig. 6). This indicates that the increase of turbidity might not be solely due to coagulation of the colloidal particles by charge neutralization. It could also be due to flocculation via bridging the colloidal particles. It seems that poly(Na 11-MAAU) and poly(Na 11-EAAU) were more effective in forming alum flocs, as judged by their higher maximum turbidities, than those of poly(Na 6-AAC) and poly(Na 11-AAU).

Raw water from a river is known to contain negatively charged colloidal particles of silts, clay, and organic particulates. In water treatment, raw water was buffered by lime followed by addition of alum and polyelectrolyte. Table III shows the results of conductivity and zeta potential of raw and the treated water samples. As the dosage of alum was increased from 5 to 20 ppm, the conductivity increased slightly from 43 to 51.5 $\mu\text{S cm}^{-1}$, but its zeta potential changed substantially from -20.1 to $+7.6$ mV. The change of sign in zeta potential occurred in the range of 15–20 ppm dosage of alum. The charge neutralization between alum and the negatively charged colloidal particles prevailed in the alum-added water. On addition of 0.5 ppm of poly(Na 11-AAU) or poly(Na 6-AAC) to the water sample containing 15 ppm alum, the zeta potential changed significantly from -6.0 to -12.3 mV for the former and to -10.1 mV for the latter, while their conductivities only increased slightly. This clearly indicates that the anionic polyelectrolyte chains anchored onto the slightly negatively charged colloidal particles. Thus the flocculation of the colloidal particles by these anionic polyelectrolytes is deemed to proceed via the bridging mechanism²⁶ by adsorption of the polymer segments linked to many colloidal particles.

The performances of four anionic poly(Na-acrylamidoalkanoate)s as coagulant aids were assessed by the jar tests in terms of supernatant quality of the treated water, the floc size, and the settling rate of the flocs. The results obtained from the optimum dosages of alum and polyelectrolyte are shown in Table IV. A commercial product of cationic polyamine organic coagulant (Hyperfloc CP753 from Chemlab, Singapore) was also used for comparison. The synthesized anionic poly(Na-acrylamidoalkanoate)s performed as good as that of the commercial one. In terms of the floc settling, the

effect of poly(Na 11-AAU) and poly(Na 6-AAC) were superior to the other three polyelectrolytes investigated. The shortcoming of low molecular weight poly(Na 6-AAC) might be compensated by its high charge density and large radius of gyration (Table II). It is encouraging to note that the anionic poly(Na-acrylamidoalkanoate)s are effective in water treatment when they are used as coagulant aids in conjunction with alum.

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