Low Molecular Weight Polyacrylic Acid with Pendant Aminomethylene Phosphonic Acid Groups

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ABSTRACT: Low molecular weight poly(acrylic acid-*co*-vinyl aminomethylene phosphonic acid)s were prepared by consecutively applying the Hofmann degradation and the Mannich reaction to polyacrylamide and poly(acrylamide-*co*-acrylic acid)s. ^{1}H-NMR, ^{31}P-NMR, and microanalysis were used for structural analyses. These polymers were tested as anti-scalent and they showed better anti-scalent effect than commercial poly(acrylic acid)s. The scale inhibition properties of copolymers increased with increasing amount of aminomethylene phosphonic acid groups. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 870–874, 2000

Keywords: poly(acrylic acid); poly(vinyl amine); anti-scalent; aminotri(methylene phosphonic acid)

INTRODUCTION

Low molecular weight poly(acrylic acid)s are used for scale inhibition in water boilers. Their molecular weights are in the range of 1.000–10.000. The mechanism of anti-scaling effect of polyacrylic acid and simple compounds such as amino tri (methylene phosphonic acid) (ATMP) can be described briefly as follows. The anti-scalent is adsorbed on the growth sites of the scalent crystal altering its growth pattern so that the crystals are formed more slowly and highly distorted. Besides, adsorbed anti-scalent reinforces the repulsion between the particles thus it disperses solids and prevents precipitated crystals from agglomerating and depositing on surfaces.

ATMP and polyacrylic acids are usually used for scale inhibition and dispersion, respectively. ATMP is very effective for preventing $CaCO_3$ scale formation. The low molecular weight poly(acrylic acid)s are sometimes mixed with aminomethylene phosphonic acids such as ATMP for better anti-scalent properties since the mixture shows some synergism. Recently, low molecular weight poly(acrylic acid) with amino di(methylene phosphonic acid) chain-end was shown to have much better scale inhibition effect than commercial low molecular weight poly(acrylic acid)s.[1] However, amino di(methylene phosphonic acid) content of this poly(acrylic acid) was limited because it was only at the polymer chain-ends.

In this work, poly(acrylic acid-*co*-vinyl amine) copolymers were prepared from poly(acrylamide-*co*-acrylic acid)s by the Hofmann degradation and controlled amount of aminomethylene phosphonic acid groups were introduced as side groups by the Mannich reaction and their scale inhibition effects are elucidated.

EXPERIMENTAL

Materials and Spectroscopic Analysis

2,2′-Azobisizobutyronitrile (AIBN) was recrystallized from methanol. H_3PO_3, acrylic acid, and 2-mercaptoacetic acid (all from Fluka, Switzerland), were used without purification. Fourier transform infrared (FTIR) spectra were obtained on a JASCO-5300 spectrometer. KBr pellets were

prepared and KBr was used as a background reference. ^{1}H-NMR and ^{31}P-NMR spectra were recorded with a Bruker 320 spectrometer at 200 and 161 MHz, respectively, using D_2O as solvent and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as internal standard. Nitrogen/carbon (N/C) was obtained from microanalysis.

Synthesis of Low Molecular Weight Polyacrylamide (A11)

Under nitrogen atmosphere, a mixture of acrylamide (10 g; 140.8 mmol), thioglycolic acid (0.19 g; 1.84 mmol), and tetrahydrofuran (THF) (20 mL) were placed in a 100-mL flask equipped with a reflux condenser. Polymerization was performed for 2 h. The polyacrylamide was isolated and reprecipitated by pouring its water solution into methanol. It was then dried *in vacuo* and stored under nitrogen.

Synthesis of Low Molecular Weight Poly(acrylamide-*co*-acrylic acid) (A21 and A31)

In a 100-mL three-necked flask, equipped with a reflux condenser and a mechanical stirrer, acrylamide (2.9 g; 40.8 mmol), acrylic acid (7.056 g; 100.8 mmol), AIBN (0.12 g; 0.75 mmol), and thioglycolic acid (0.19 g; 2.06 mmol) were dissolved in THF (20 mL) and 5 mL of water was added. The solution was stirred under nitrogen at 60°C for 1 h. The resulting copolymer (A21) was precipitated by pouring the solution into methanol and then purified by pouring its water solution (pH = 10) into methanol. For the synthesis of A31, a similar experiment was performed by taking 1.5 g of acrylamide and 8.5 g of acrylic acid.

The Hofmann Degradation of Low Molecular Weight Polyacrylamide and Poly(acrylamide-*co*-acrylic acid) (A12, A22, and A32)

Into a thermostated jacketed reactor equipped with a mechanical stirrer, 1.54*M* NaOCl (164 mL; 0.25 mol) and 15*M* NaOH (20 mL; 0.3 mol) were added and cooled to approximately −10°C. A solution of poly(acrylamide-*co*-acrylic acid) in water (294 mL: 0.28 mol of amide function) was cooled to 0°C and added into the reactor under vigorous stirring. After 1 1/2 h, 11*M* NaOH (640 mL; 7.04 mol) solution that was cooled to −10°C was added and the reactor was kept at −10°C for 5 1/2 h and then at 0°C for 17 h. The copolymer was reprecipitated by pouring its water solution (pH = 2) into a mixture of methanol and acetone and drying *in vacuo*.

The Mannich Reaction (Formation of A13, A23, A33)

Into a three-necked flask equipped with a thermometer, a stirrer, a condenser, and a dropping funnel, 0.5 mol of the Hofmann degradation product, 82 g of crystalline phosphorous acid dissolved in 100 mL of water, and 100 mL of concentrated HCl were added, then the mixture was heated to reflux. In the course of about 1 h, 160 mL of 37% aqueous formaldehyde solution was added dropwise, and the reaction mixture was kept at reflux temperature for one additional hour. Upon cooling to room temperature, the product precipitated. It was washed with a mixture of acetone and ethanol and then dried at 60°C *in vacuo*.

Viscosimetry

Molecular weight of polyacrylamide was calculated from a single point viscosity measurement at 25°C using an aqueous solution and making use of the following equations[2,3]:

$$[\eta] = \frac{\eta_{sp}}{1 + 0.28 \times \eta_{sp}}$$

$$[\eta] = 6.8 \times 10^{-4} \times Mn^{0.66}$$

Scale Inhibition Effect

Stock solution I: 3.25 g/L $CaCl_2 2H_2O$ (pH 8.5); stock solution II: 2.48 g/L Na_2CO_3 (pH 8.5). One milliliter of 0.1% copolymer solution was added into 50 mL of stock solution I then pH was adjusted to 8 with dilute NaOH solution. The solution II (50 mL) was added to this content. The flask was kept at 85°C for 1 h in a water bath then cooled to room temperature. The content of flask was filtered from filter paper and 4 mL concentrated HCl was added to 25 mL of filtrate then let to stand for 15 min. This content was diluted to 50 mL and 3 mL of 50% NaOH solution was added. The soluble calcium was titrated with EDTA (0.01*M*) to a bright violet end point using murexide as indicator. Sufficient indicator should be added to turn the solution to a bright rosy pink color. Inhibition is calculated from the following equation:

$$\text{Inhibition \%} = \frac{\text{S-B} \times 100}{\text{T-B}}$$

where S is milliliter EDTA for polymer treated mixture and kept in water bath; T is milliliter
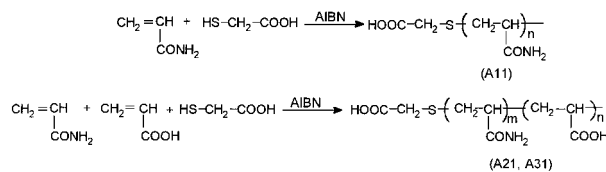
Scheme 1

EDTA for blank, untreated, and not kept in water bath; B is milliliter EDTA for blank, untreated, and kept in water bath.

Microanalysis

N/C ratios of polymers were determined by microanalysis. Phosphorous content was determined by ammonium phosphomolybdate method after the polymer samples were degraded by HNO_3 and $HClO_4$. Polymer and N/C, respectively: A11 (0.36), A12 (0.444), A13 (0.238), A21 (0.094), A22 (0.088), A23 (0.081), A31 (0.051), A32 (0.045), A33 (0.041).

RESULTS AND DISCUSSION

Low molecular weight polyacrylic acids with some pendant amino di(methylene phosphonic) acid groups were produced starting from low molecular weight polyacrylamide and poly(acrylamide-*co*-acrylic acid)s which were prepared by radical polymerization using AIBN as the initiator and thioglycolic acid as the chain transfer compounds (Scheme 1).

Chain transfer constant of thioglycolic acid for acrylic monomers was reported to be about 0.5.[4,5] The ratio of thioglycolic acid to acrylamide was about 0.013 and polyacrylamide with molecular weight of about 10.000 was produced.

From Table I, the chain transfer constant of thioglycolic acid for acrylamide polymerization was calculated as 0.5 which was the same for other acrylic monomers reported previously.[6] By taking the chain transfer constant of thioglycolic acid for both acrylamide and acrylic acid monomers as 0.5, low molecular weight poly(acryl-
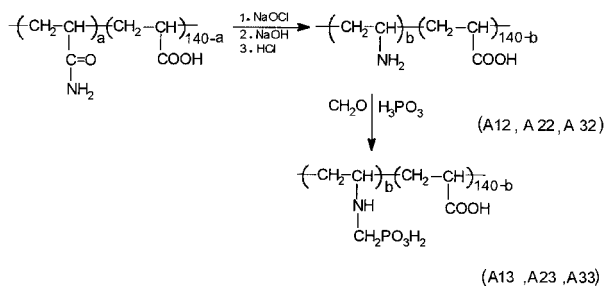
Scheme 2

amide-*co*-acrylic acid) copolymers were synthesized under the similar condition for the preparation of low molecular weight polyacrylamide.

Although initial reactive ratios of acrylamide and acrylic acid were $r_1 = 0.6$ and $r_2 = 1.43$, respectively, the average compositions of the produced copolymers should be in the range of initial mol ratios of acrylamide and acrylic acid monomers since the polymerization conversions were above 95%. Actual values of amide content of copolymers were calculated from N/C weight ratios. Experimental N/C ratios of poly(acrylamide-*co*-acrylic acid) (A21 and A31) were 0.094 and 0.051 that corresponded to 24% ($a = 34$) and 13% ($a = 18$) acrylamide contents, respectively (Scheme 1).

The Hofmann Degradation

The Hofmann degradation of polyacrylamide and poly(acrylamide-*co*-acrylic acid)s were performed under the conditions described previously[7] such that hypochlorite/amide ratio was about 1.3. This gave about 90% of amide converted into amine (Scheme 2). Amine content of poly(vinyl amine-*co*-acrylic acid)s was calculated from microanalysis values (N/C for A12: 0.444, for A22: 0.088, and for A32: 0.045). The values were between 88 and 91% of the theoretical amine values which were slightly lower than the values reported earlier.[7]

The Mannich Reaction

Poly(acrylic acid-*co*-vinyl amine)s containing vinyl amine groups ($b = 115$, $b = 31$, and $b = 16$ in

Table I Chain Transfer Constant

Monomer Concentration M (mol · l^{-1})	Thioglycolic Acid S (mol · l^{-1})	[S]/[M]	Mol Weight
6.97	—	0	195.000
6.97	0.091	0.0131	10.665

Table II   Conversion of Amine Groups into Aminomethylene Phosphonic Acid Groups

No.	Polymer	P/N Mol Ratio	Conversion (%)	Reference
—	Polyallyl amine	0.57	28	8
—	Polyethylene imine	—	50	9
—	Polyvinyl amine	0.6	30	10
A13	Poly(acrylic acid-*co*-vinylamine)	0.98	98	This work
A23	Poly(acrylic acid-*co*-vinylamine)	1.01	100	This work
A33	Poly(acrylic acid-*co*-vinylamine)	1.01	100	This work

the Scheme 2) were reacted with formaldehyde/phosphorous acid in the presence of HCl.

The Mannich reaction of amine groups on the polymer chain reported to give lower conversion. The conversion of amine groups of polyallyamine,[8] polyethylene imine,[9] and polyvinyl amine[10] to aminomethylene phosphonic acid groups were reported to be 28, 50, and 20–30%, respectively (Table II). These values were much lower than the values (95%) observed when simple organic amines such as octyl amine[11] was converted into amino di(methylene phosphonic)acid derivative. These lower yields of modifications may be due to high local amine concentration in the polymer solution and neighboring group effect on the polymer chain. To increase the yield of the Mannich reaction, polymer concentration in solution and local concentration of amine groups on the polymer chain should be lowered. This was achieved by both reducing molecular weight and preparing copolymers of vinyl amine and acrylic acid. By using low molecular weight poly(vinylamine-*co*-acrylic acid)s, the conversion of amine groups into aminomethylene phosphonic acid groups was successfully reached to about 100% (Scheme 2).

Spectroscopic Examination

Starting from polyacrylamide and poly(acrylamide-*co*-acrylic acid)s, the modified polymer products after the Hofmann degradation and the Mannich reaction were characterized by microanalysis and spectroscopic methods such as FTIR and NMR. Peaks due to characteristic groups were observed. FTIR spectrum of polyvinyl amine was similar to the spectrum reported previously.[12] After the Mannich reaction, all the polymers A13, A23, and A33 showed similar FTIR spectrum. P—OH stretching peaks appeared at about 2400 cm^{-1} and the peaks at 1190 cm^{-1}, 1000 cm^{-1}, and 950 cm^{-1} were due to P=O group.

^{1}H-NMR spectrum of polyacrylamide, poly(acrylamide-*co*-acrylic acid)s, poly(vinyl amine)s, and poly(vinyl amine-*co*-acrylic acid)s and the Mannich reaction products are summarized in the Table III. ^{31}P-NMR spectrum of poly(acrylic acid)s containing aminomethylene phosphonic acid groups (A13, A23, A33) showed peaks at about 23.5 ppm (singlet) and between 6.3–5 ppm a quartet (Table IV). Besides, very small signals at about 9 and 1 ppm were also observed. In one

Table III ^{1}H-NMR Spectrum of Polymers

Polymer	CH$_2$	CH—(COOH) or CH—(CONH$_2$)	CH—(NH$_2$)	—N—CH$_2$—PO$_3$H$_2$
A11	1.6–1.7	2.2–2.4	—	—
A21	1.4–1.7	2.1	—	—
A31	1.5–1.7	2.1	—	—
A12	2.0–2.5	—	3.88	—
A22	1.4	2.0	3.9	—
A32	1.6–1.8	2.2	3.2 + 3.8	—
A13	1.8–2.0	2.5	3.86	3.92
A23	1.8–2.0	2.5	—	3.2 + 3.6
A33	1.3–1.5	1.9	—	3.8

Table IV ^{31}P-NMR Spectrum of Poly(acrylic acid) with Pendant Aminomethylene Phosphonic Acids

Polymer			Peaks (δ) ppm		
A13	23.7	9		6.3–5	0.8
A23	23.3	18.8 9.5 8.7		5.45	1.03
		(3 peaks)			
A33	23.34			6–4.77	0.65
				(4 peaks)	

sample (A23), a small peak at about 18.8 ppm was also present.

Scale Inhibition Effect

Scale inhibition effect of low molecular weight poly-(acrylic acid)s with pendant amino methylene phosphonic acid groups were compared with commercial poly(acrylic acid) and ATMP. The results are shown in the Table V. All poly(acrylic acid)s containing aminomethylene phosphonic acid pendant groups showed much better $CaCO_3$ anti-scaling effects than commercial polyacrylic acids and poly(alkenyl) phosphonic acid[13] such as polyizopropenyl phos-

Table V   Anti-Scaling Effects of Poly(acrylic acid)s

Product	Concentration of the Product (ppm)	Scale Inhibition (%)
A13	2	41
	8	100
A23	2	23
	8	100
A33	2	30
	8	100
Commercial polyacrylic acid M_w = 1500 g/mol	2	0
	8	35
ATMP	2	23
	8	100
Polyizopropenyl phosphonic acid[a]	3	32
	5	38
Poly-α-n-hexyl vinyl phosphonic acid[a]	3	5
	5	31

[a] Reference 11.

phonic acid and poly-α-n-hexyl vinyl phosphonic acid. This is probably due to synergetic effects of the polyacrylic acid and ATMP-like pendant groups belonging to the same polymer molecule. The synergism is usually observed when physical mixture of polyacrylic acid and ATMP is used for scale inhibition. Besides, ATMP-like pendant groups which contain strong negative charge increase considerably the negative charge of the carboxylate groups adsorbed onto particles preventing them from effectively aggregating into larger particles and depositing on surfaces.

CONCLUSIONS

Low molecular weight poly(acrylic acid)s containing some aminomethylene phosphonic acid pendant groups showed much better anti-scaling effect than commercial poly(acrylic acid). The anti-scaling effect increased with increasing pendant aminomethylene phosphonic acid content.

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