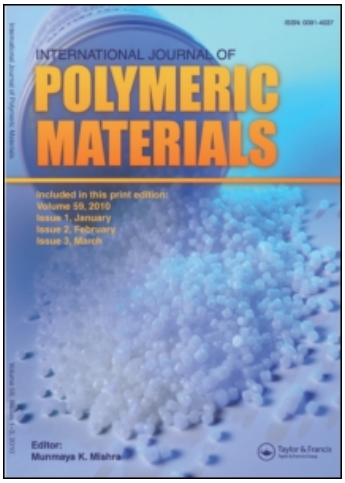

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Preparation and Properties of Polyether Scale Inhibitor Containing Fluorescent Groups

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Water soluble fluorescent monomer, 8-allyloxy-1,3,6-pyrenetrisulfonic acid trisodium salt (AP), was synthesized from 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt and allyl chloride. AP-tagged copolymer maleic anhydride (MA)–ammonium allyl polyethoxy sulfate (APES)-AP, which is a calcium phosphate inhibitor, was prepared and the structures of AP and MA-APES-AP were characterized by FTIR and ^{1}H-NMR. The influence of the mole ratio of MA:APES on a calcium phosphate inhibitor of MA-APES-AP was discussed. Fluorescent properties and scale inhibition performance of MA-APES-AP were also studied. The results indicate that monomer ratio has great impact on the performance of MA-APES-AP. Fluorescent intensity increases with the concentration of MA-APES-AP, with a correlation coefficient (r) of 0.9934 and MA-APES-AP limit of detection of 1.72 mg · L^{-1}. Calcium phosphate inhibition performance test results show that calcium phosphate inhibition of MA-APES-AP reaches 98.78 percent when the dosage is 12 mg · L^{-1} at 80°C.

Keywords: 8-allyloxy-1,3,6-pyrenetrisulfonic acid trisodium salt, ammonium allyl polyethoxy sulphate, calcium phosphate, fluorescent, polyether

INTRODUCTION

Corrosion inhibitors, scale inhibitors, dispersants, and biocides are key active components in water treatment programs [1]. Polymers

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act as particulate dispersants and scale inhibitors. The identification of particularly effective polymer technology allowed the use of relatively high phosphate concentrations in bulk cooling streams so that effective scale control could be maintained, while eliminating concern for phosphate deposition [2]. Over the last 20 years, the technology changed dramatically with the identification of acrylic acid copolymers which used elevated phosphate dosages to achieve chromate-like corrosion protection of mild steel. While performing these important functions, the active treatment species are adsorbed onto particulates and metal surfaces [3–4]. These treatments are widely utilized and provide both anodic and cathodic corrosion inhibition [5–8] and stabilized phosphate treatment programs have been the standard for cooling systems operation. But cooling systems operation has changed dramatically due to both discharge restrictions and water conservation efforts. High phosphate concentrations in the bulk cooling stream was restricted because of increased interest in environmental and pollution control. In accordance with the present research, it has been discovered that water-soluble copolymer of acrylic acid and ammonium allyl polyethoxy sulfate is effective in inhibiting corrosion in various aqueous systems [9–11]. Copolymer of acrylic acid and allyloxy polyethoxy sulfate was used as a powerful dispersant to prevent calcium phosphate deposition. It has proven to be twice as effective relative to all commercially available phosphate inhibitor technologies under laboratory conditions, and it is the latest generation of calcium phosphate scale inhibitors. Unfortunately, all these new treatment programs are quite difficult to test. Most conventional polymer analysis techniques require the preparation of calibration curves for each type of polymer employed, and the originally prepared calibration curves lose their accuracy if the polymer structures change [12]. Due to all the operating limitations and uncertainties in cooling water systems, the need to rapidly determine and continuously monitor the concentration of chemical treatments is evident.

In general, and in comparison, the concentration of an inert water soluble tracer such as a fluorescent tracer may be directly determined from a calibration curve of tracer concentration versus instrument response, permitting the determination of the concentration range from parts per million (ppm) to part per billion (ppb). In addition to being able to quantify complex combinations of the treatment feeds, fluorescent compounds are available which are environmentally acceptable and available at low cost. For over two decades, water-soluble polymers containing amide groups, such as polyacrylamide of high molecular weight and its derivatives containing anionic groups, cationic groups or hydrophobic groups, have been used in waste water treatment [13]. Acrylamide polymers can be modified in aqueous

solution with organic die molecules which can form stable carbo-cations reversible in water. But the modification of polyacrylamide in dilute aqueous or mixed solvent systems is not very practical compared with copolymerization with a fluorescent monomer to prepare tagged polymers [14–15]. However, conventional fluorescence monomers such as rhodamines, naphthalene, and anthracene are all hydrophobic fluorescent chromophores and their preparation would result in a complicated process and undermine the performance of scale inhibitors. Moriarty et al. [16–17] appear to reveal the use of 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (pyranine) fluorescent monomers for tagging polymers used in industrial waste water treatment systems as a means for determining the amount of the polymer treatment agent.

In the present investigation, we describe the synthesis of water-soluble fluorescence monomer 8-allyloxy-1,3,6-pyrene trisulfonic acid trisodium salt (AP) and a method of preparing maleic anhydride (MA)-ammonium allyl polyethoxy sulfate (APES)-AP, which is a calcium phosphate inhibitor containing AP fluorescent group, by free-radical polymerization methods. The MA-APES-AP overcame the drawback of MA-APES which could not be accurately detected and controlled. In addition, the hydrophilicity of MA-APES-AP was greatly enhanced compared with other fluorescent-tagged polymers because it contains sulfoacid which is a hydrophilic functional group. We inspected the relationship between the fluorescence intensity of MA-APES-AP and its concentration. The relationship between concentration of MA-APES-AP and its calcium phosphate inhibition performance was also investigated. Based on the results presented in this paper, monitoring of treatment program dosage and consumption in the treatment program through fluorescence analysis of inert tracers helps to optimize the cooling system operation and prevents phosphate deposition problems.

EXPERIMENTAL

Materials

Ammonium allyl polyethoxy sulfate was synthesized according to Steckler [18]. Pyranine was purchased from Xuhua Chemical Co. (China). Maleic anhydride, potassium peroxydisulfate, allyl chloride, and ammonium persulfate were all analytically pure grade and were supplied by Zhongdong Chemical Reagent Co. (Nanjing, China).

Instruments

Fourier-transform infrared (FTIR) spectra were taken on a Bruker FT-IR analyzer (VECTOR-22, Bruker Co., Germany) using the KBr

disc method. The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker NMR analyzer (AVANCE AV-500, Bruker Co., Switzerland). The structure of AP and MA-APES-AP was detected by ^{1}H-NMR and FTIR spectroscopy. Fluorescence measurements were carried out on a Varian spectrofluorophotometer (Cary Eclipse, Varian Co., USA) with a xenon lamp as a light source.

Synthesis of AP and MA-APES-AP

Synthesis of AP

A 500 mL round-bottom flask with magnetic stirrer was charged with (40 g, 76 mmol) pyranine, 50% sodium hydroxide solution and 200 mL of dry dimethylsulfoxide (DMSO). The stirred mixture was sparged with nitrogen for 40 min at room temperature. In one portion allyl chloride (7.0 g, 92 mmol) was added and stirring at room temperature continued for an additional 5 h. By-product sodium chloride was filtered off, and the residue was dumped and stirred in eight times volume of acetone. The insoluble product was filtered, collected and recrystallized from a mixed solvent of 1:3 water:ethanol to produce yellow crystals that were dried to give the desired AP (37.2 g, yield: 86%). The structure of the fluorescent monomer was characterized by means of FT-IR and ^{1}H-NMR. The synthesis scheme of AP from pyranine and allyl chloride is shown in Figure 1.

Synthesis of MA-APES-AP

A 5-neck round-bottom flask equipped with a thermometer and a magnetic stirrer was charged with 90 g (5 mol) distilled water, 9.8 g (0.1 mol) MA, and 16.6 g (0.033 mol) APES (the mole ratio of MA to APES was 3:1), and heated to 70°C. 0.528 g (0.1 mmol) of AP (the amount of AP in the tagged copolymers is 2 wt%), initiator solution 1 (3.0 g ammonium persulfate in 20 g distilled water), and initiator solution 2 (8.0 g sodium metabisulfite in 30 g distilled water) were added separately at constant flow rates over a period of 2 h under a nitrogen

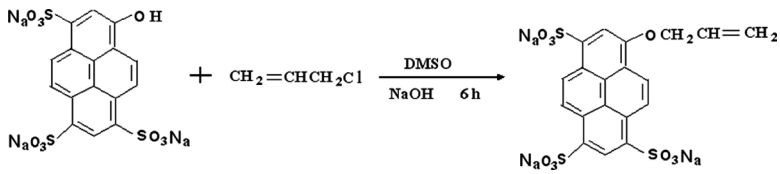

FIGURE 1 Scheme for synthesis of monomer 8-allyloxy-1,3,6-pyrenetrisulfonic acid trisodium salt (AP).

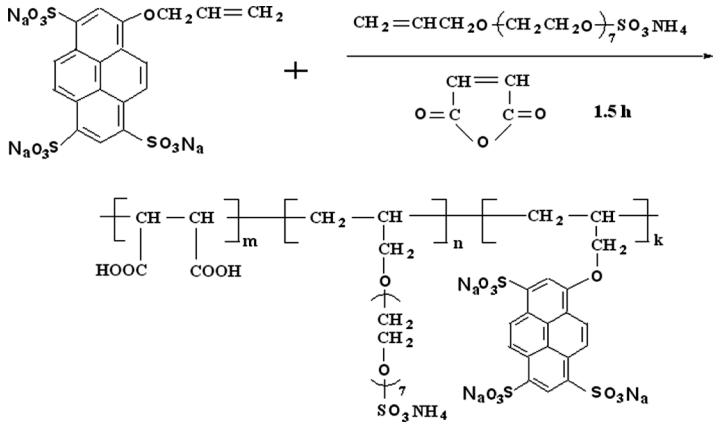

FIGURE 2 Scheme for synthesis of maleic anhydride (MA)–ammonium allyl polyethoxy sulfate (APES)–8-allyloxy-1,3,6-pyrenetrisulfonic acid trisodium salt (AP).

atmosphere. The reaction was then heated to 80°C and maintained for an additional 90 min period, ultimately affording an aqueous polymer solution containing approximately 35% solid. The product was dumped and stirred in ten times volume of acetone. The insoluble product was filtered, collected and recrystallized from 2:5 water:acetone to afford white crystals, and dried to give the desired MA-APES-AP as a white solid. The structure of MA-APES-AP was then characterized by means of FT-IR and ^{1}H-NMR. The synthesis of MA-APES-AP from MA, APES and AP is shown in Figure 2.

Excitation and Emission Wavelength Measurements of AP and MA-APES-AP

Excitation and emission wavelengths of AP and MA-APES-AP were measured. Their excitation wavelengths were measured at 460 nm (10 nm slidwidth) and emission wavelengths were measured at 510 nm (10 nm slidwidth). The excitation and emission wavelengths were chosen according to the excitation and emission wavelength of pyranine. AP distilled water solution was used at a concentration of $5 \times 10^{-8}\,\mathrm{mol \cdot L^{-1}}$. MA-APES-AP was dissolved in a sufficient amount of water to yield a concentration of $5 \times 10^{-8}\,\mathrm{mol \cdot L^{-1}}$ solution.

Synthesis of MA-APES-AP with Different Mole Ratios of MA:APES

In order to study the influence of different mole ratios of MA:APES on MA-APES-AP's phosphoric inhibition performance, the same

process of synthesis MA-APES-AP was repeated except that the mole ratio of MA:APES was 3:2, 1:1, 2:3, 1:3 and the usage of AP are kept at 2 wt% in the tagged polymers. Usage of initiator solution was the same as when the mole ratio of MA:APES was 3:1.

Influence of Mole Ratios of MA:APES on MA-APES-AP's Calcium Phosphate Inhibition Property

The influence of MA-APES-AP samples with different mole ratio of MA:APES on their calcium phosphate inhibition performance was evaluated at dosages of $5\,mg \cdot L^{-1}$. The test water contained $250\,mg \cdot L^{-1}$ Ca^{2+} and $5\,mg \cdot L^{-1}$ PO_4^{3-} and $5\,mg \cdot L^{-1}$ MA-APES-AP. Each solution was pH-adjusted to 9.0 and placed in a water bath controlled at 80°C for a 10 h period. The solutions were then filtered and analyzed for soluble phosphate. Percent inhibition of calcium phosphate was then calculated for each polymer relative to a control sample without treatment.

Fluorescent Intensity Measurements of MA-APES-AP

To determine the concentration of scale inhibition containing fluorescent groups within fluorescent detection, a serial concentration of MA-APES-AP samples should generate a corresponding series of the fluorescence intensity. After choosing the best mole ratio of MA:APES in MA-APES-AP for the copolymer's calcium phosphate inhibition performance, we have prepared a series of 2, 4, 6, 8, 10, 12, 14, 16, $18\,mg \cdot L^{-1}$ concentrations of MA-APES-AP aqueous solutions from the one that has the best mole ratio of MA:APES, and estimated their fluorescent intensity.

Calcium Phosphate Inhibition Test of MA-APES-AP and MA-APES

Calcium phosphate inhibition performance of MA-APES-AP was compared with MA-APES copolymer after choosing the best mole ratio of MA:APES. The MA-APES copolymer was synthesized and the ratio of MA:APES was the same as the best mole ratio of MA:APES at the process of synthesis MA-APES-AP. MA-APES and MA–APES-AP were both evaluated at dosages of 4, 6, 8, 10, and $12\,mg \cdot L^{-1}$.

RESULTS AND DISCUSSION

FTIR Measurements

The FTIR spectra of AP and MA-APES-AP are exhibited in Figure 3.

In (a), the characteristic vibration bands of $1270\,cm^{-1}$ is the ether characteristic absorption, the alkyl oxide characteristic absorption of

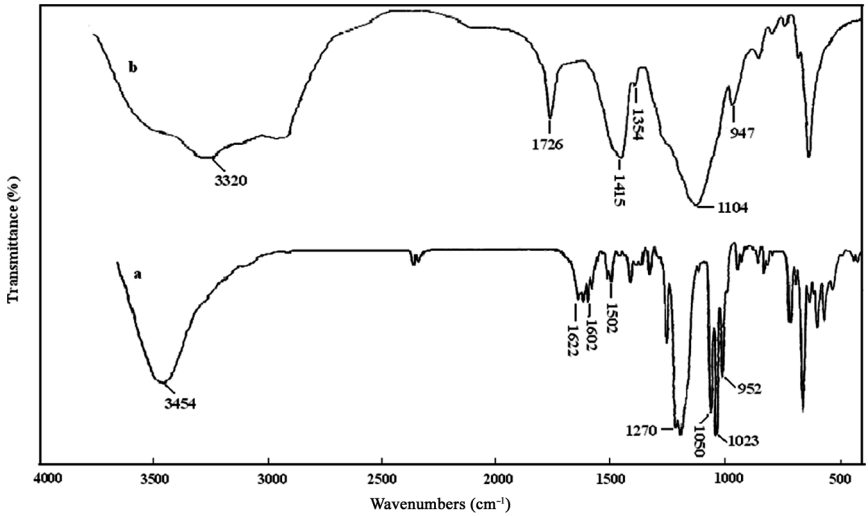

FIGURE 3 FTIR spectra of AP (a) and MA-APES-AP (b).

AP shows an intense peak at 1050 cm^{-1}. The coexisting two bands prove that the monomer structure includes alkyl aryl ether [19]. The C−H stretching vibration of $=CH_2$ is shown around 3454 cm^{-1}, the C=C stretching is shown as a sharp intense peak at 1622 cm^{-1}. 1023 cm^{-1} and 952 cm^{-1} for C−H plane deformation vibration of $=CH_2$. This 1602 and 1502 cm^{-1} absorptions are attributed to the existence of benzene nucleus. The FTIR proves that the synthesized monomer has the anticipated structure. In (b) the characteristic vibration band of 3320 cm^{-1} corresponds to N−H stretching vibration, 947 cm^{-1} corresponds to N−H out-of-plane deformation vibration, 1415 cm^{-1} is attributed to $-CH_2$ bending vibration while 1354 cm^{-1} is for SO_2 asymmetric bending. The C=O stretching, of saturated carboxylic acids is shown at 1726 cm^{-1}, and the CH_2–O–CH_2 stretch is shown as an intense peak at 1104 cm^{-1}. In comparison with (a) the 1622 cm^{-1} for C=C stretching, the 1023 cm^{-1} and the 952 cm^{-1} for C−H plane deformation vibration of $=CH_2$ have disappeared. This reveals that free radical polymerization among APES, MA and AP has happened.

^{1}H-NMR Analysis

500 MHz NMR spectra of solution of AP and MA-APES-AP samples were measured, using $(CD_3)_2SO$ as the solvent and TMS as an internal reference. ^{1}H-NMR spectra of AP and MA-APES-AP, respectively, are depicted in Figure 4.

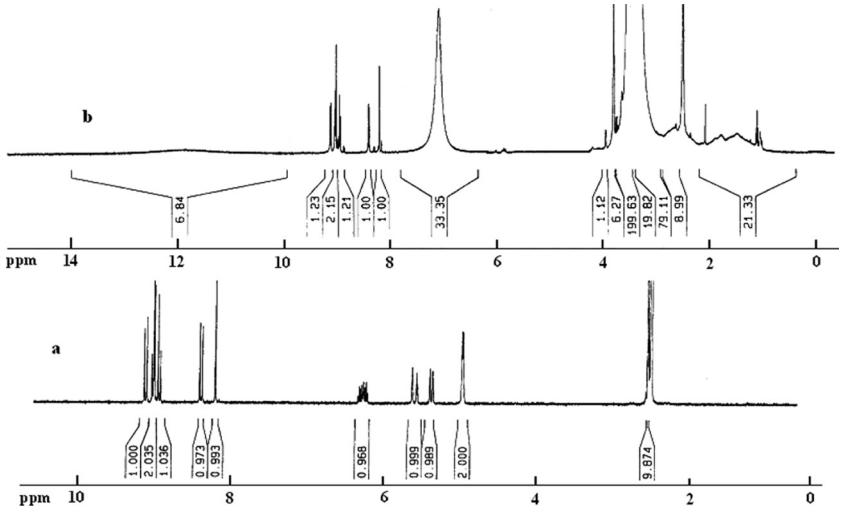

FIGURE 4 ^{1}HNMR spectra of AP (a) and MA-APES-AP (b).

In (a) the signal at δ 2.2–2.5 ppm, was previously assigned to the solvent residual peak of $(CD_3)_2SO$. The chemical shifts from the propenyl (CH_2=CH$-CH_2-$) protons appear in the region δ 4.8–6.4 ppm, and the 6 protons of the pyranine in AP in the region δ 8.1–9.4 ppm. AP has two different types of protons, whose the corresponding positions are two absorption peaks, and the figure shows that the structure is consistent with the integrated area. In (b): the chemical shifts from the methylene (CH_2) and methenyl (CH) protons of the MA-APES-AP copolymers are observed in the region δ 1.0–2.0 ppm, and the chemical shifts resulting from the ether (CH_2-O-CH_2) groups in these copolymers are observed in the region δ 3.2–4.0 ppm. At the chemical shift from δ 2.2–2.5 ppm, the residual solvent peak of $(CD_3)_2SO$ appears. The sulfate ammonium ($-SO_3NH_4$) proton resonance peak is seen at the chemical shift from δ 6.9–7.2 ppm. The chemical shifts for pyranine protons in AP extend from δ 8.1–9.4 ppm. The resonance peaks from the carboxylic acid groups in the copolymers appear in the δ 10.0–14.0 ppm region. MA-APES-AP structure has six different types of protons whose corresponding position appear in five absorption peak groups (methyl and methylene-H in the absorption peaks at δ 1–2 ppm overlap). The δ 5.0–6.5 ppm double bond absorption peaks which appear in (a) have disappeared in (b). FTIR measurements and ^{1}HNMR analysis confirm that the synthesizes monomer and copolymer have the expected structures.

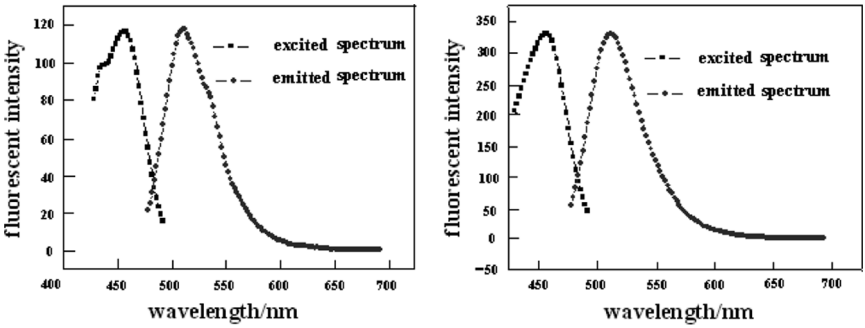

FIGURE 5 Excitation and emission wavelength of AP (a) and MA-APES-AP (b).

Excitation and Emission Properties of AP and MA-APES-AP

Excitation and emission wavelength of AP and MA-APES-AP are represented in Figure 5.

It can be seen that excitation and emission wavelengths of AP and MA-APES-AP are 460 nm and 510 nm. MA-APES-AP and AP have the same excitation and emission wavelengths as pyranine because the chromophore of AP and MA-APES-AP is pyranine too. MA-APES-AP excitation spectra and emission spectra show good mirror symmetry relations, indicating that the molecular structure of the fluorescent configuration changed little from monomer to copolymer.

Test Results of MA-APES-AP's Calcium Phosphate Inhibition Property with Different Mole Ratios of MA:APES

MA-APES-AP's calcium phosphate inhibition performance with different mole ratios of MA:APES is reported in Table 1.

From the results obtained so far, it seems that different monomer ratios of MA:APES have great impact on performance of MA-APES-AP. Polymerization has different conversion rates when monomer concentration and the mole ratio of monomer are different, while the polymer macromolecules contained a different proportion of the functional groups. The properties of the copolymers have been greatly affected because of the large effects on average size of the molecular weight, molecular weight distribution and sequence structure. It had been hypothesized that the presence of both strong acid and weak acid functional groups built into the polymer provides the best stabilizing properties [20]. The calcium phosphate inhibition test results clearly

TABLE 1 Influence of Mole Ratios of MA:APES on Calcium Phosphate Inhibition of MA-APES-AP at 80°C

Mole ratio of MA:APES	Calcium phosphate inhibition of MA-APES-AP (%)
3:1	68.53
3:2	74.59
1:1	84.43
2:3	80.90
1:3	75.25

indicate that the copolymer with MA:APES mole ratio of 1:1 shows superior efficacy in calcium phosphate inhibition relative to the other compositions.

Fluorescence Intensity Response to the Concentration of Scale Inhibition

The correlation of fluorescence intensity and the concentration of MA-APES-AP is illustrated in Figure 6.

Based on the information contained in this figure, one may conclude that the correlation coefficient ($r = 0.9934$) ensures a linear relationship between MA-APES-AP concentration and fluorescence intensity. This positive linear relationship, where an increase in fluorescence intensity is proportional to an increase in MA-APES-AP concentration, can be used to quantitatively measure the concentration of

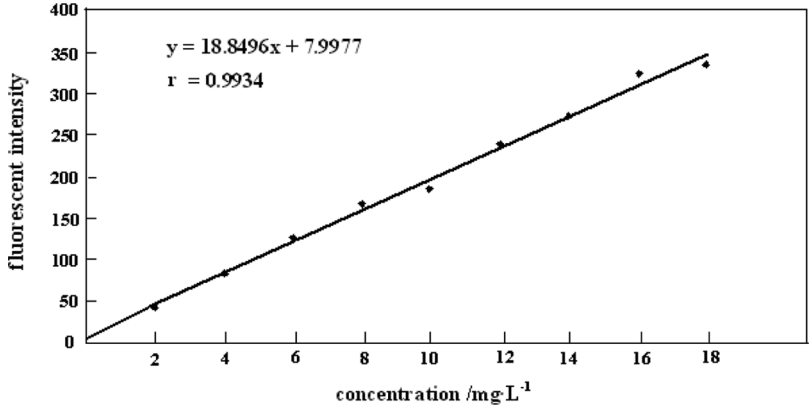

FIGURE 6 Correlation of fluorescent intensity and concentration of MA-APES-AP.

TABLE 2 Influence of Dosage on Calcium Phosphate Inhibition of MA-APES-AP and MA-APES at 80°C

Dosage of MA-APES-AP and MA-APES ($mg \cdot L^{-1}$)	Calcium phosphate inhibition of MA-APES-AP (%)	Calcium phosphate inhibition of MA-APES (%)
4	78.07	77.43
6	85.70	86.74
8	88.99	87.89
10	92.24	91.97
12	98.78	97.62

MA-APES-AP from its fluorescent intensity. The authors calculated that the sample limit of detection of MA-APES-AP is $1.72\,mg \cdot L^{-1}$ according to the formula of sample limit of detection: $D_r = 3\sigma/k$. σ is 11 times the size of blank solutions standard deviation, k is slope [21].

Test Results of MA-APES-AP and MA-APES Calcium Phosphate Inhibition Property

Calcium phosphate inhibition of MA-APES and MA-APES-AP under otherwise identical conditions is presented in Table 2.

The results clearly indicate that the performance of calcium phosphate inhibition from the two kinds of copolymers is very simillar. 12 ppm dosage of MA-APES-AP is required to reach 98.78 percent phosphoric inhibition whereas MA-APES reached 97.62 percent at the same condition. Both proved to be quite robust and of superior efficiency. But the quantity of MA-APES in water can not be ascertained and MA-APES-AP overcomes this the shortcoming. Copolymer concentration can be easily monitored by spectrofluorophotometer. The experimental results prove that fluorescence analysis methods and use of inert tracers are very useful in accomplishing calcium phosphate inhibition tasks.

CONCLUSIONS

1. Water-soluble fluorescent monomer AP has been prepared and characterized by ^{1}H-NMR and FTIR. The AP group shows strong fluorescence at 510 nm (ex 460 nm). AP tagged copolymer MA-APES-AP was prepared and the amount of AP was kept at 2 wt% in the tagged copolymers. Its structure was characterized through FTIR and ^{1}H-NMR. MA-APES-AP shows fluorescence at 510 nm and can be detected readily with a fluorospectrophotometer.

2. Calcium phosphate inhibition property of MA-APES-AP with different mole ratios of MA:APES was discussed, and the results show that MA-APES-AP provides the best stabilizing properties when the mole ratio of MA:APES is 1:1.
3. There is a good linear relationship between MA-APES-AP concentration and fluorescence intensity. The correlation coefficient (r) is 0. 9934 and MA-APES-AP limit of detection is $1.72\,mg \cdot L^{-1}$.
4. The calcium phosphate inhibition performance of MA-APES-AP is as good as the latest non-phosphorus scale inhibitor MA-APES. Its phosphoric inhibition reaches 98.78 percent when the dosage is 12 mg/L at 80°C while MA-APES phosphoric inhibition is 97.62 percent at the same conditions.

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