Fluorescent-Tagged No Phosphate and Nitrogen Free Calcium Phosphate Scale Inhibitor for Cooling Water Systems

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ABSTRACT: Allyloxy polyethoxy ether (APEO) and chloracetic acid were used to prepare allyloxy polyethoxy carboxylate (APEC). 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt was reacted with allyl chloride to produce fluorescent monomer 8-allyloxy-1,3,6-pyrene trisulfonic acid trisodium salt (AP). APEC and AP were copolymerized with maleic anhydride (MA) to synthesize AP tagged no phosphate and nitrogen free calcium phosphate inhibitor MA-APEC-AP. Structures of AP, APEO, APEC, and MA-APEC-AP were carried out by FTIR and ^{1}H-NMR. Different MA : APEC mole ratios were employed for the manufacture of MA-APEC-AP to study the effect of mole ratio on performance of MA-APEC-AP. Relationship between MA-APEC-AP's fluorescent intensity and its dosage was studied. MA-APEC-AP's calcium phosphate inhibition was compared with the down to date calcium phosphate inhibitor (MA)-ammonium allylpolyethoxy sulphate (APES). The results indicate that capability of MA-APEC-AP is heavily depended on the mole ratio of MA : APEC. Correlation coefficient r of MA-APEC-AP's fluorescent intensity and its dosage is 0.9983, and detection limit of MA-APEC-AP is 2.03 mg L^{-1}. MA-APEC-AP can be used to accurately measure polymer consumption on line besides providing excellent calcium phosphate inhibition. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1966–1974, 2009

Key words: copolymerization; fluorescence; synthesis; water-soluble polymer; surfactants

INTRODUCTION

The potential for corrosion and scale formation continues to be by far the most operating problem in cooling water systems.[1–3] Corrosion inhibition required chromate treatment in the olden days.[4,5] But it was prohibited on account of toxic pollutant discharge. Orthophosphates, polyphosphates compounds, etc were used to form protective barrier to provide corrosion protection through cathodic action.[6–8] However, the phosphate programs did not provide the passive oxide film induced by chromate. Godlewski discovered inorganic orthophosphate together with acrylic acid (AA)-hydroxy lower alkyl acrylate to establish the elusive passive oxide film on metallic surfaces.[9–11] Because of the popularity of using high levels of orthophosphate to promote passivation, it has become critically important to control calcium phosphate crystallization so that relatively high levels of orthophosphate may be maintained to achieve effective carbon steel corrosion control.

Recently, there is a new project which identified phosphate deposit control agent. It is MA-ammonium allylpolyethoxy sulphate (APES) copolymer. It offers twice as effective relative to all available phosphate inhibitor and it is no-phosphate.[12–14]

Unfortunately, it is quite difficult to test for MA-APES by traditional way because there is no phosphate active component in it. Improper feed rate of treating agent leads to serious problems. Another shortcoming of MA-APES is that it still contains nitrogen nutrition. Researches show that N is the key limiting element for the occurrence of algal blooms which leads to great economic loss. In despite of low P level in lake water, N becomes the limited factor of alga blooms when the ratio of N to P in lake water is lower than in the alga.[15,16]

Fluorescence methods provide direct measurement and control of a wide array of treatment actives. The concentration of a fluorescent tracer is directly determined from a calibration curve of tracer concentration versus emission. Fluorescent tracer permits the determination of the concentration of scale inhibitor range from parts per million (ppm) to parts per billion (ppb), and its compounds are environmentally

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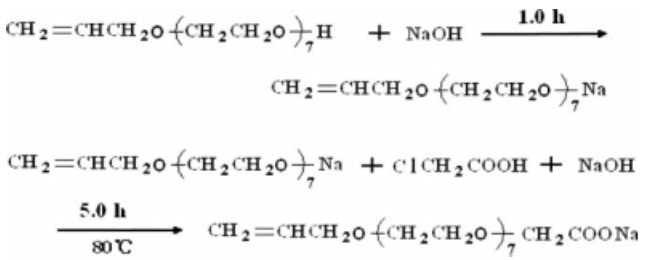


Scheme 1 Synthesis of APEC.

acceptable, and are available at low cost. Moriarty performed 8-allyloxy-1,3,6-pyrene trisulfonic acid trisodium salt (AP) fluorescent monomers. Hydrophilic of AP is strong because of sulfoacid hydrophilic groups.[17–20]

Alkyl epoxy carboxylate (AEC) is a no-phosphate calcium carbonate inhibitor. Its calcium carbonate control is superior to phosphonate technology.[21–23] One of the methods to prepare AEC is carboxy methylation, that is chloroacetic acid reacts with fatty alcohol-polyoxyethylene ether under alkaline conditions.[24–26] There is another no phosphate and nitrogen free calcium phosphate inhibitor AA/acetate-capped allyloxypolyethyleneglycol.[27,28] The step is preparing acetate-capped allyloxypolyethyleneglycol by reacting acetylating agent with allyloxypolyethyleneglycol and then react AA with acetate-capped allyloxypolyethyleneglycol. But the acetylation reaction needs 160°C, whereas carboxy methylation only needs 80°C to prepare same type monomer. Secondly, the acetylated allyloxypolyethyleneglycol was obtained from stripped the reactant at least 1 mm Hg or lower for 5.0 h at 120°C. Producing of carboxy methylation is obtained just natural cooling. Finally, excess unreacted acetic anhydride and acetic acid which are volatile components must be recovered or they cause pollution. Producing of carboxy methylation need not recover and no waste discharge. When compared with the two methods, carboxy methylation is obviously better.

On the basis of all these information, the study offers a new calcium phosphate inhibitor. Synthesized allyloxy polyethoxy carboxylate (APEC) by carboxy methylation and prepared fluorescent-tagged no phosphate and nitrogen free inhibitor MA-APEC-AP by free copolymerization. MA-APEC-AP compensates the weaknesses of MA-APES which contain nitrogen and cannot be monitor. Results of the study demonstrate that calcium phosphate inhibition of MA-APES and MA-APEC-AP is very basic.

EXPERIMENTAL

Materials

Ammonium allylpolyethoxy sulphate was synthesized according to Steckler.[29] 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (pyranine) was purchased from Xuhua Chemical (Shanghai, China). Allyloxy polyethoxy ether (APEO) was purchased from Zhongshan Chemical (Nanjing, Jiangsu, China). Other reagents such as maleic anhydride, potassium peroxydisulfate, allyl chloride, ammonium persulfate, of AR grade were obtained from Zhongdong Chemical Reagent (Nanjing, Jiangsu, China). Distilled water was used for all the studies.

Measurements

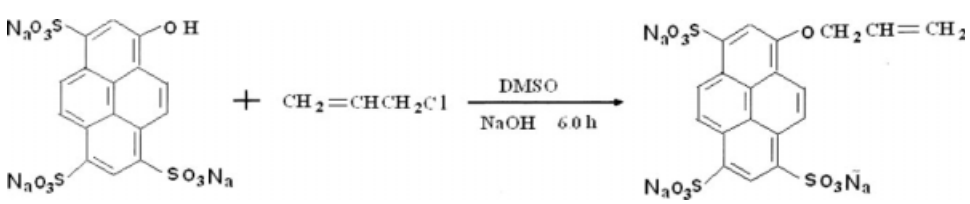
FTIR (VECTOR-22, Bruker, Germany) was employed to investigate the structures of AP, APEO, APEC, and MA-APEC-AP, in the form of a KBr pellet (compressed powder).

Structures of AP, APEO, APEC, and MA-APEC-AP were also explored by a Bruker NMR analyzer (AVANCE AV-500, Bruker, Switzerland) operating at 500 MHz.

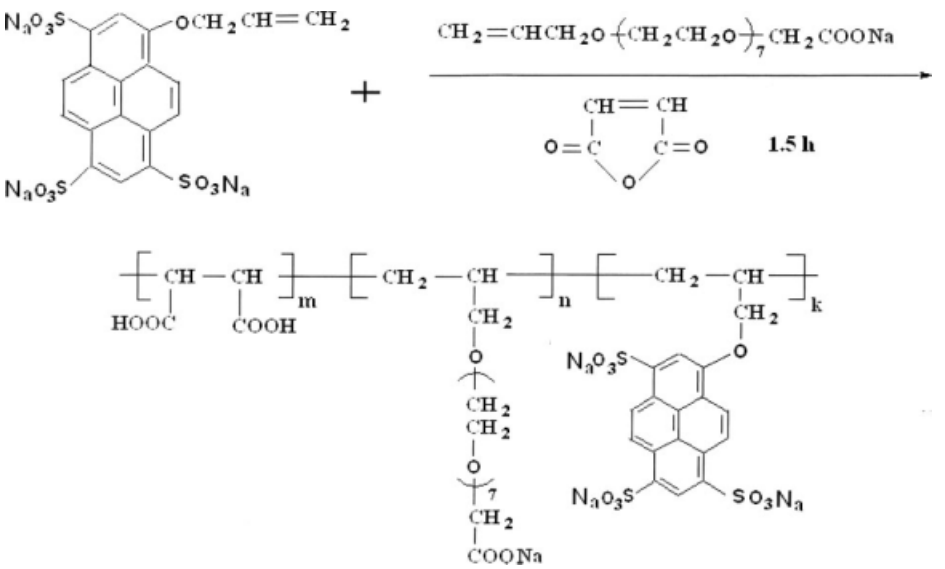
Fluorescence measurements were carried out on a luminescence spectrometry (LS-55, Perkin-Elmer, UK) with a xenon lamp as a light.

Synthesis of APEC and AP

The reaction flask was fitted with the accessories as was done for the synthesis of APEC. One hundred gram (0.25 mol) of APEO and 6 g (0.15 mol) NaOH was mixed in the flask. The mixture was sparged with nitrogen and under vigorous stirring at room temperature for 1.0 h. After that, 6 g (0.15 mol) NaOH and 20 g (0.21 mol) chloracetic acid were added and then the reaction mixture was heated at 80°C for 5.0 h. After natural cooling, the polymerization reactant was poured a large amount of alcohol. The solution was then filtered and the filtrate was recovered by stripping off alcohol. The filtrate



Scheme 2 Synthesis of AP.



Scheme 3 Synthesis of MA-APEC-AP.

product was dried in vacuum oven to give the desired APEC as a clear reddish solution.

The synthesis procedure of APEC from allyloxy polyethoxy ether, NaOH, and chloracetic acid is shown in Scheme 1.

AP was synthesized according to Moriarty.[17] The product was light yellow power. Synthesis procedure of AP from pyranine and allyl chloride is shown in Scheme 2.

Synthesis of MA-APEC-AP

Ninety gram (5 mol) distilled water, 9.8 g (0.1 mol) MA, and 16 g (0.03 mol) APEC (the mole ratio of MA and APEC was 3 : 1) were mixed together in a 250 mL 5-neck round-bottom flask fitted with a thermometer, and a magnetic stirrer. The mixture was heated to 70°C with stirring under nitrogen atmosphere. Around 0.66 g, 1 mmol of AP (the amount of AP in the tagged copolymers is 2.5 weight percent) in 20 g distilled water, 1.0 g ammonium persulfate in 20 g distilled water and 1.0 g sodium metabisulfite in 20 g distilled water were added dropwise in the 250 mL round-bottom flask over a period of 1.0 h at 70°C. And then, the reactant was heated with stirring at 80°C for 2.0 h under nitrogen atmosphere. The mixture was subsequently cooled and the polymer was then isolated by successive precipitations in a large volume of acetone. The insoluble product was filtered, collected, and extracted in a soxhlet extractor for 16.0 h to remove the unused MA and APEC. The crude product was dried in vacuum oven until constant weight, and re-crystallized from water-acetone mixture (3 : 7 V/V) to remove the residual AP and gain MA-APEC-AP as a white solid.

The synthesis procedure of MA-APEC-AP from MA, APEC, and AP is shown in Scheme 3.

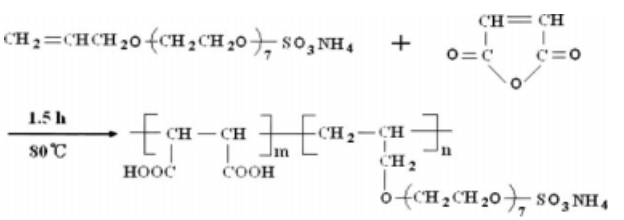
Prepare MA-APEC-AP and MA-APES at different MA : APEC and MA : APES mole ratio

MA-APEC-AP was radical polymerized at feed MA : APEC mole ratios of 3 : 2, 1 : 1, 2 : 3, and 1 : 3 to study the effect of different mole ratio of MA: APEC on MA-APEC-AP's phosphoric inhibition. The process was the same as initial feed mole ratio of MA : APEC was 3 : 1 in synthesis of MA-APEC-AP while kept the usage of AP at 2.5 weight percent in MA-APEC-AP.

MA-APES was synthesized according to Chen and Kolson.[14] To investigate the effects of MA : APES mole ratio on MA-APES phosphoric inhibition, the mole ratio of MA and APES in initial feed was also 3 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 3, respectively. Synthesis means of MA-APES is given in Scheme 4.

Methods to examine calcium phosphate inhibition of MA-APEC-AP and MA-APES at different mole ratio of MA : APEC and MA : APES

Calcium phosphate inhibition performance of MA-APEC-AP on different mole ratio of MA : APEC were evaluated at dosages of 5 mg L^{-1}. The test



Scheme 4 Synthesis of MA-APES.

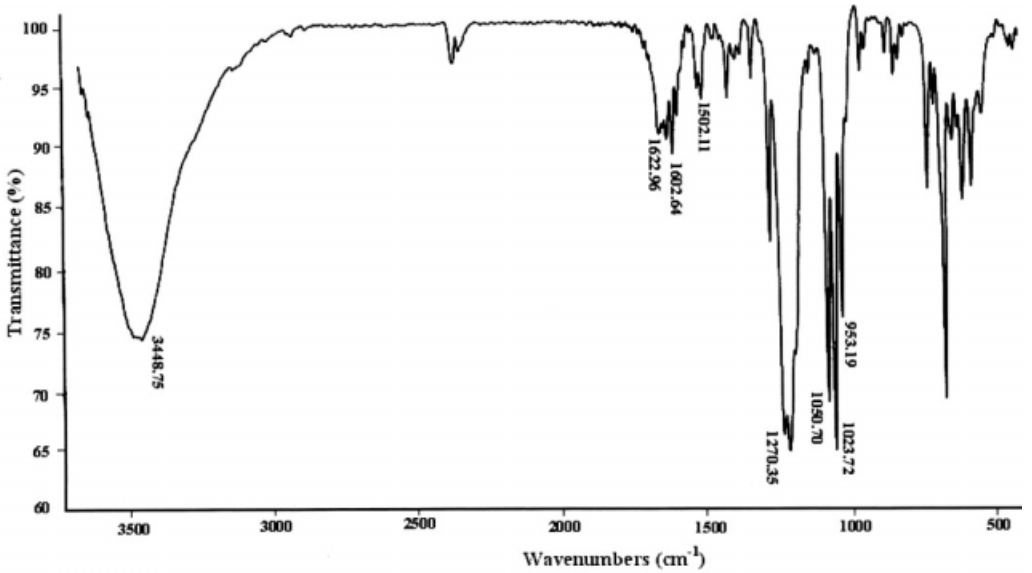


Figure 1 FTIR spectra of AP.

water contained 250 mg L^{-1} Ca^{2+}, 5 mg L^{-1} PO_4^{3-}, and 5 mg L^{-1} MA-APEC-AP. Each test water was pH adjusted to 9.0 and placed in a water bath controlled at 80°C for a 10.0 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.

MA-APES was also measured at 5 mg L^{-1}. The evaluation means of influence of MA-APES samples in different mole ratio of MA : APES on their calcium phosphate inhibition was the same as influence of MA-APEC-AP samples in different mole ratio of MA : APEC.

Calcium phosphate inhibition test of MA-APEC-AP and MA-APES at the same dosage

Calcium phosphate inhibition performance of MA-APEC-AP and MA-APES was compared, using the MA-APEC-AP and MA-APES samples which have the best mole ratio of MA : APEC and MA : APES. MA-APEC-AP and MA-APES samples were both evaluated at dosage of 4, 6, 8, 10, and 12 mg L^{-1}.

Excitation and emission wavelength measurement of AP and MA-APEC-AP

Excitation and emission wavelengths of AP and MA-APEC-AP were all measured at $\beta_{ex} = 460$ nm (10 nm slidwidth) and $\beta_{em} = 510$ nm (5 nm slidwidth), respectively. The excitation and emission wavelengths were chose the same as the excitation and emission wavelength of pyranine. 5×10^{-8} mol L^{-1} AP distilled water solution was prepared and MA-APEC-AP was dissolve in quantum sufficient distilled water and concentration of AP in MA-APEC-AP solution was also 5×10^{-8} mol L^{-1}.

Detection of MA-APEC-AP fluorescent intensity with different concentration

Use of inert fluorescent tracers and on-line fluorometer provides accurate control of treatment dosage and immediate response to changes in treatment dosage. Fluorescent light is emitted that ought to directly proportional to the dosage of treatment in the water, which translates into reliable control of treatment dosage. A serial concentration of MA-APEC-AP sample should reflect a corresponding serial of the fluorescence intensity. Prepared for 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 mg L^{-1} MA-APEC-AP aqueous solution samples which has the best mole ratio of MA : APEC in MA-APEC-AP. Estimated MA-APEC-AP fluorescent intensity response to their concentration.

RESULTS AND DISCUSSION

FTIR measurements

The FTIR spectra of AP are exhibited in Figure 1.

AP (FTIR, cm^{-1}): 953.19 (C—H plane deformation vibration of $=CH_2$), 1023.72 (C—H plane deformation vibration of $=CH_2$), 1050.70 (alkyl oxide characteristic absorption of AP), 1270.35 (fragrant ether characteristic absorption), 1502.11 (benzene nuclear absorption band), 1602.64 (benzene nuclear absorption band), 1622.96 (C=C stretching), 3448.75 (C—H stretching vibration of $=CH_2$).

The characteristic vibration bands of 1270.35 cm^{-1} is the fragrant ether characteristic absorption, the

alkyl oxide characteristic absorption of AP shows an intense peak at 1050.70 cm^{-1}. Presently two bands both exist prove the monomer structure includes alkyl aryl ether.[30] The C=C stretching shows a sharp intense peak at 1622.96 cm^{-1}. The FTIR proves the synthesized monomer has the anticipated structure.

The FTIR spectra of APEO (a), APEC (b), and MA-APEC-AP (c) are exhibited in Figure 2.

APEO (FTIR, cm^{-1}): 1104.10 (—OCH_2CH_2—, stretching vibration), 1459.74 (—CH_2—, asymmetric bending), 1643.59 (—C=C—, stretching vibration), 2872.45 (—CH_2—, symmetric stretching), 3446.71 (—OH, intramolecular H-bonds, single bridge stretching). [Figure 2(a)].

APEC (FTIR, cm^{-1}): 1113.60 (—OCH_2CH_2—, stretching vibration), 1452.81 (—CH_2—, asymmetric bending), 1642.09 (—C=C—, stretching vibration), 1726.17 (C=O, saturated stretching), 2920.63 (—CH_2—, symmetric stretching), 3420.70 (—OH, H-bonded in dimerized acids stretching). [Figure 2(b)].

The 1726.17cm^{-1} strong intensity absorption peak clear reveals that APEC has been synthesized successfully.

MA-APEC-AP (FTIR, cm^{-1}): 1097.99 (—OCH_2 CH_2—, stretching vibration), 1401.61 (—CH_2—, asymmetric bending), 1723.74 (C=O, saturated stretching), 2874.18 (—CH_2—, symmetric stretching), 3429.96 (—OH, H-bonded in dimerized acids stretching). [Figure 2(c)].

The (—C=C—) stretching at 1643.59 and 1642.09 cm^{-1} in (a) and (b) is absent in (c), indicating that all of monomers have participated in the polymerization reaction.

^{1}H-NMR studies

Figure 3 is ^{1}H-NMR of AP (a), APEO (b), APEC (c), and MA-APEC-AP (d).

AP (($(CD_3)_2SO$, δppm): 2.30–2.55 (solvent residual peak of $(CD_3)_2SO$), 4.96–6.32 (CH_2=CH—CH_2—, propenyl protons), 8.08–9.45 (six protons of benzene ring in AP). [Figure 3(a)].

AP has two different types of protons, the propenyl and benzene ring protons corresponding position in two absorption peaks, and the figure shows the integral structure consistent with the area. It certifies that the product has expected structure.

APEO (($(CD_3)_2SO$, δppm): 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.15–3.65 (—OCH_2CH_2—, ether groups), 3.88–4.02 (CH_2=CH—CH_2—, propenyl protons), 4.45–4.60 (—OH, active hydrogen in APEO), 5.11–5.85 (CH_2=CH—CH_2—, propenyl protons). [Figure 3(b)].

APEC (($(CD_3)_2SO$, δppm): 1.04–1.23 (—CH_2—, protons in —CH_2—COONa), 2.50 (solvent residual peak of $(CD_3)_2SO$), 3.21–4.03 (—OCH_2CH_2—, ether groups), 4.08–5.95 (CH_2=CH—CH_2—, propenyl protons). [Figure 3(c)].

The δ4.52–4.54 ppm (—OH) active hydrogen in (b) disappeared completely and (—CH_2—) protons in —CH_2—COONa appears obviously in δ1.04–1.23 ppm in (c). It proves that -OH in APEO has been entirely replaced by O—CH_2—COONa.

MA-APEC-AP (($(CD_3)_2SO$,δ ppm): 1.02–1.46 (—CH, —CH_2 and —CH_2—COONa protons of MA-APEC-AP), 2.08–2.63 (solvent residual peak of $(CD_3)_2SO$), 3.32–4.19 (—OCH_2CH_2—, ether groups), 8.00–9.58 (6 protons of benzene ring in AP), 9.80–14.00 (—COOH groups in MA-APEC-AP). [Figure 3(d)].

δ3.93–3.98, δ5.11–5.85 ppm in (b) and δ4.10–5.95 ppm in (c) double bond absorption peaks completely disappeared in (d). This reveals that free radical polymerization among APEC, MA, and AP has happened.[31] From FTIR and ^{1}H-NMR analysis, it can conclude that synthesized MA-APEC-AP has anticipated structure.

Presently, fluorophore in fluorescent monomer usually contains benzene ring or heterocyclic, and their structure is rigid planar, so the fluorescence chromophore are hydrophobic. It makes the process of preparation fluorescent-tagged water-soluble copolymer agent more complex. McCormick prepared copolymers of acrylamide (AM) and *N*-alkylacrylamides by micellar copolymerization in aqueous solution utilizing sodium dodecyl sulphate as a surfactant to solubilize hydrophobic monomer and decrease the adverse effects of solvents.[32] Lei et al. described a fluorescent-tagged water-soluble copolymer [4-methoxy-*N*-(2-*N*′,*N*′-dimethyl aminoethyl) naphthalimide allyl chloride quaternary ammonium salt] (FM)-acrylamide (AM).[33] They prepared the copolymer by reverse microemulsion because FM is a hydrophobic monomer. The step is that firstly allocated proper amount Span80 and Tween80 to certain HLB value and dissolved it in isooctane to get oil phase with concentration of 200 mg L^{-1}. FM and AM with certain ratio were dissolved in distilled water to get water phase.

Then, 50 mL Span80-Tween80 was added to 100-mL beaker. One hundred microlitre of FM and AM water solutions were added to the 100-mL beaker for every 20 min to determine the conductivity of the mixed solution until obtained stable reverse microemulsion system. After that, add 50 mL microemulsion to a four port flask and the four port flask was placed in a water bath controlled at 50°C for 3.0 h copolymerization.

Broke the emulsion by methanol and centrifugalized it after demulsification. The sediment was washed by acetone and dried in vacuum oven to get the final product.

Either micellar copolymerization or reverse microemulsion copolymerization requires to at least the

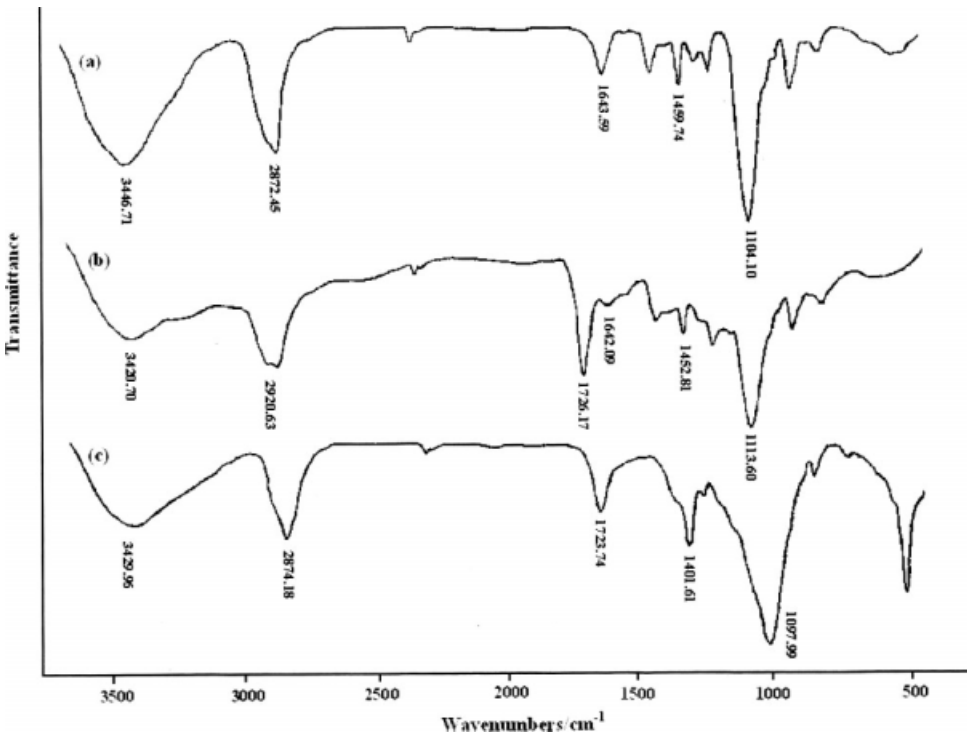


Figure 2 FTIR spectra of APEO (a), APEC (b), and MA-APEC-AP (c).

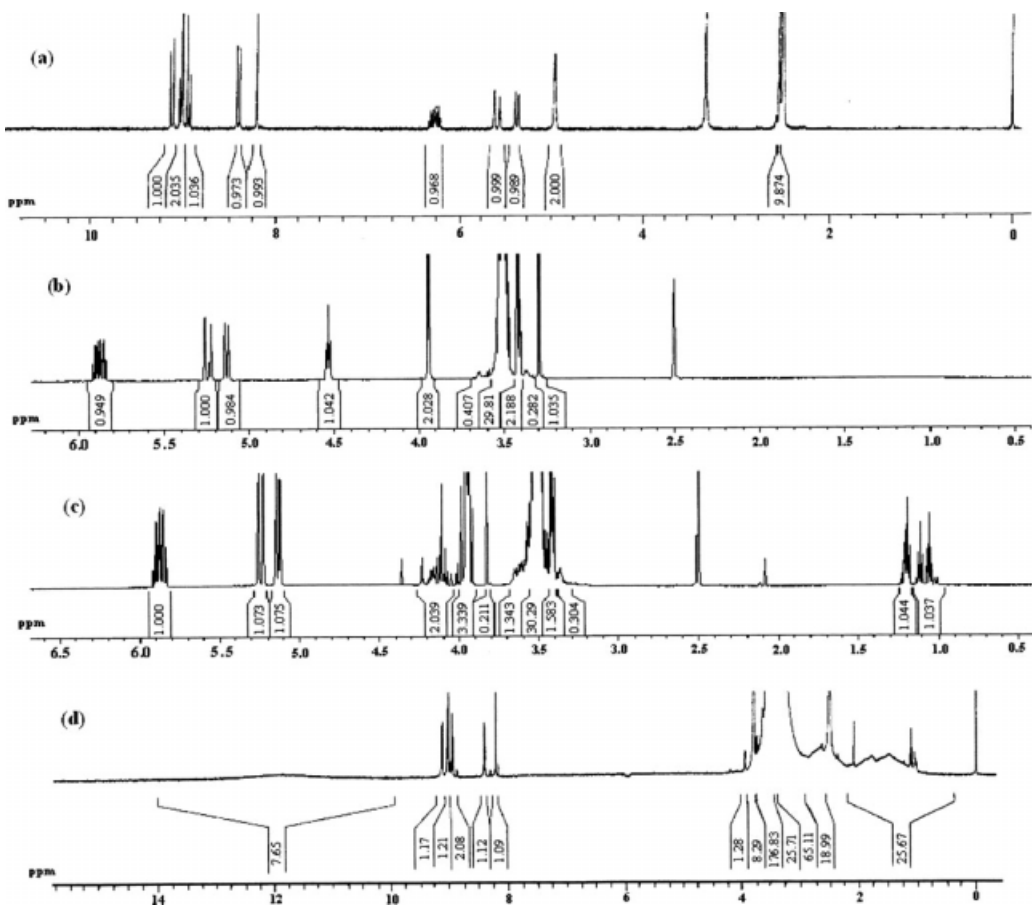


Figure 3 ^{1}H-NMR spectra of AP (a), APEO (b), APEC (c), and MA-APEC-AP (d).

procedure of demulsification, lavation, and drying to get the final product and the cost of production is comparatively high. In addition, emulsifier and other impurities in the product is not easily to be removed clearly thus decrease scale inhibition property of copolymer. It is obviously that obtain water-soluble fluorescent monomer is important and aqueous solution polymerization is a better way to prepare fluorescent-tagged copolymer than micellar copolymerization or reverse microemulsion.

Calcium phosphate inhibition of MA-APEC-AP and MA-APES at different mole ratio of MA : APEC and MA : APES

The properties of MA-APEC-AP and MA-APES prepared at different MA : APEC and MA : APES mole ratio is summarized in Table I.

The results demonstrated that mole ratio has large impact on the properties of polymers. Conversion rate of the reaction will be different when monomer ratio of MA : APEC and MA : APES is different, thus affects chain sequence structure and molecular structure of the macromolecular polymer. Copolymers can have very different properties with the same composition but different sequence structure.[34] At the same time, the proportions of functional groups in the long chain polymer macromolecules are also different. Polymers have good scale performance only when the proportions of functional groups in long chain macromolecules are appropriate. On the other hand, there is a best molecular weight for calcium phosphate scale inhibition. Monomer ratio changes of MA : APEC and MA : APES in MA-APEC-AP and MA-APES have relative impact on their molecular weight.

The calcium phosphate inhibition testing results manifest that MA-APEC-AP and MA-APES which mole ratio of MA : APEC and MA : APES are 1 : 1 show superior efficacy in calcium phosphate inhibition than other mole ratio.

TABLE I
Influence of Mole Ratio of MA : APEC and MA : APES on Calcium Phosphate Inhibition of MA-APEC-AP and MA-APES at 80°C

Mole ratio of MA : APEC and MA : APES	Calcium phosphate inhibition of MA-APEC-AP (%)	Calcium phosphate inhibition of MA-APES (%)
3 : 1	71.29	48.53
3 : 2	62.47	63.59
1 : 1	80.57	81.32
2 : 3	51.67	72.61
1 : 3	40.72	75.25

TABLE II
Calcium Phosphate Inhibition of MA-APEC-AP and MA-APES

Dosage of MA-APEC-AP and MA-APES (mg L^{-1})	Calcium phosphate inhibition of MA-APEC-AP (%)	Calcium phosphate inhibition of MA-APES (%)
4	70.68	62.56
6	90.57	85.84
8	91.33	92.08
10	96.87	94.45
12	100.0	98.16

Calcium phosphate inhibition testing results of MA-APEC-AP and MA-APES at same dosage

Efficiency of calcium phosphate inhibition of MA-APEC-AP and MA-APES are tabulated in Table II.

The results clear indicate that performance of calcium phosphate inhibition of MA-APEC-AP and MA-APES is equivalent. MA-APEC-AP and MA-APES have high molecular weight, and the (—SO_3NH_4) or (—COONa) anionic active groups are at the lateral and exposed. They have large extension in water because of electrostatic repulsion and chelate calcium ion. Next to chelate calcium ion, they adsorb in calcium phosphate micro-crystal particles surface and then increase negative charge density of the particles. It makes the electrostatic repulsion force increasing between particles thus prevents grow up of calcium phosphate micro-crystal particles. Furthermore, copolymer particles can be embedded in the lattice of calcium phosphate micro-crystal particles. Particles of MA-APEC-AP, MA-APES and calcium phosphate micro-crystal particles have different sizes. This enables MA-APEC-AP and MA-APES particles set in calcium phosphate crystal and prevent calcium phosphate micro-crystal growth in the lattice. In addition, ether structure and (—SO_3NH_4) or (—COONa) functional groups of MA-APEC-AP and MA-APES are similar to some anionic surfactants.[35] Only one hydrophilic group needed to perform hydrophilicity. (—SO_3NH_4) and (—COONa) are water soluble functional groups, the oxygen atoms in ether bond formed weak hydrogen bonds with hydrogen atoms in water. Strong hydrophilic makes MA-APEC-AP and MA-APES attach to one end or adsorbed on all calcium phosphate micro-crystal particle surface so both proved to be quite robust and superior efficiency in phosphoric inhibition.

Excitation and emission properties of AP and MA-APEC-AP

Excitation and emission wavelength of AP (a) and MA-APEC-AP (b) are represented in Figure 4.

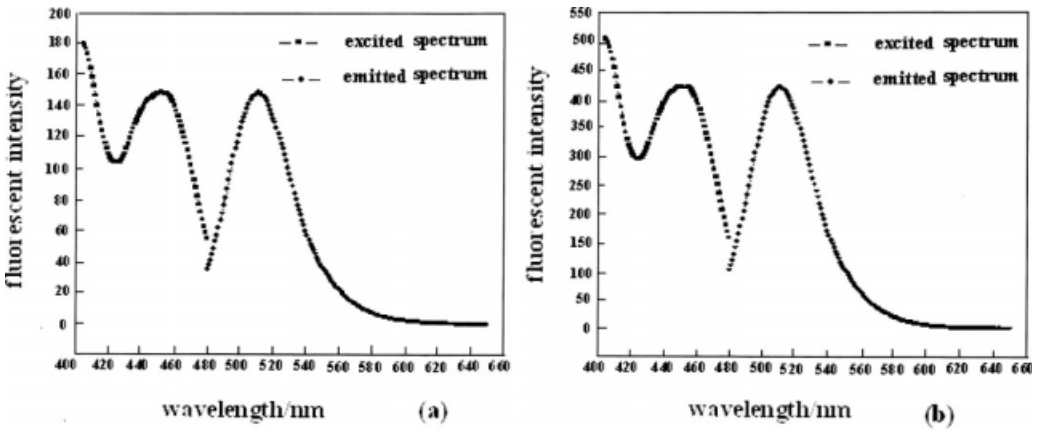


Figure 4 Excitation and emission wavelength of AP (a) and MA-APEC-AP (b).

It can be achieved by the figure that excitation and emission wavelengths of AP and MA-APEC-AP are also 460 nm and 510 nm. Chromophore of AP and MA-APEC-AP are all pyranine so MA-APEC-AP and AP have the same excitation and emission wavelengths as pyranine. Excitation spectra and emission spectra of MA-APEC-AP show good mirror-image relationship as AP. It demonstrates that molecule structure of fluorescent configuration changed a little from monomer to copolymer.

The fluorescence intensity of MA-APEC-AP increased compared with AP after copolymerization because of the form of hydrogen bond. The lowest singlet excited states of aromatic carbonyl compounds such as AP is (n, π^*). The excited state possess (n, π^*) character in nonpolar and weakly hydrogen bonding solvents but they exhibits enhanced (π^*, π^*) character in very polar hydrogen bonding solvents. (π^*, π^*) states are, or become, the energetically lowest states after copolymerization. The yields of fluorescence grow in quantity in (π^*, π^*) states than in (n, π^*) states.[36,37]

Response of fluorescent intensity over a range of MA-APEC-AP

Result of linearity testing between MA-APEC-AP fluorescence intensity and their concentration is shown in Figure 5.

The relationship between MA-APEC-AP concentration and fluorescence intensity provided exceptionally linear response [correlation coefficient r = 0.9983, where perfect line = 1.0000]. This positive linear relationship can be used to quantitatively measure the concentration of MA-APEC-AP. The dosage change of MA-APEC-AP is pointed out by the fluorescence spectra of MA-APEC-AP. This optical technique is able to characterize early corrosion and to quantify corrosion defects. The detection limit of MA-APEC-AP is 2.03 mg L^{-1} according to the detection limit formula: $D_r = 3\sigma/k$, where σ is 11 times determination of blank solution's standard deviation and k is slope of calibration curve.[38]

CONCLUSIONS

Water-soluble monomer APEC was produced from APEO and chloracetic acid by carboxy methylation method. Fluorescent monomer AP was prepared from pyranine and allyl chloride. Structures of APEC and AP were identified by FTIR and ^{1}H-NMR.

Fluorescent-tagged no phosphate and nitrogen free calcium phosphate inhibitor MA-APEC-AP was successfully synthesized by free polymerization of MA, APEC, and AP. FTIR and ^{1}H-NMR identified that MA-APEC-AP has the expected structures.

The most suitable of MA : APEC in MA-APEC-AP for its calcium phosphate inhibition is 1 : 1 by investigation of the effects of MA : APEC mole ratio on MA-APEC-AP performance. MA-APEC-AP provides calcium phosphate inhibition comparable to the up to date calcium phosphate inhibitor MA-APES under laboratory conditions.

Excitation and emission spectra of AP and MA-APEC-AP have been detected readily with a

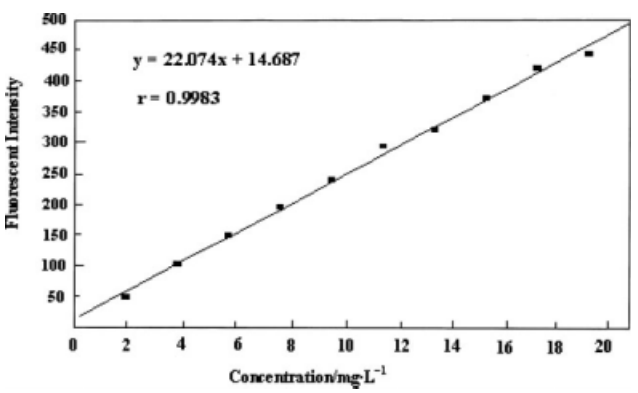


Figure 5 Linearity of fluorescent intensity and concentration of MA-APEC-AP.

fluorospectrophotometer and they show good mirror symmetry relations. MA-APEC-AP detection limit is 2.03 mg L^{-1} according to the detection limit formula. Good relationship between MA-APEC-AP fluorescent intensity and its dosage (the correlation coefficient $r = 0.9983$) ensures that MA-APEC-AP is a valuable indicator for cooling water system performance. The new active polymer test method provides an easy, quick, and accurate method to determine polymer consumption.

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