

Low-Phosphorus Maleic Acid and Sodium ρ -styrenesulfonate Copolymer as Calcium Carbonate Scale Inhibitor

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Received 24 January 2009; accepted 15 August 2009

DOI 10.1002/app.31300

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, a multifunctional and environment-friendly agent for industry circulation cooling water, maleic acid and sodium ρ -styrenesulfonate copolymer containing low-phosphorus was synthesized in aqueous solution with hypophosphorous acid/hydrogen peroxide as redox initiators. The effects of monomer feed ratio, temperature, dose of hypophosphorous acid, and drop speed of hydrogen peroxide on calcium carbonate inhibition were investigated, and the experimental conditions were optimized using orthogonal method. The composition and structure of the copolymer were analyzed by energy-dispersive X-ray analysis, fourier transform infrared spectroscopy, and nuclear magnetic resonance spec-

troscopy. The results of the static scale inhibition tests showed that the copolymer was effective in inhibiting the formation of calcium carbonate scale. The calcium carbonate precipitates formed in the static tests were examined by scanning electronic microscopy and X-ray diffraction spectra. The results indicate that in the presence of the copolymer the calcium carbonate precipitate is the mixture of calcite and vaterite that could be stabilized kinetically in the presence of the copolymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2149–2155, 2010

Key words: copolymerization; water-soluble polymers; phosphonate; scale inhibition; cooling water

INTRODUCTION

Open recirculating cooling water systems are frequently used because they not only provide economical heat removal but also recirculation of water conservation is accomplished with substantial cost reductions. The cooling water circulates to operating units where it picks up heat and the resulting warm water is cooled through vaporization by returning to the cooling tower. Dissolved and suspended matter contained in the water is concentrated in cooling water recirculation. The precipitation of calcium carbonate scale on heat transfer surfaces widely occurs, which involves the deposition of an insulating layer onto the internal walls owing to its inverse temperature-solubility characteristics.^{1–3} Deposits formation may cause severe corrosion and deterioration of heat exchange. The study of the mechanism of calcium carbonate crystal growth inhibition is an important theme for developing an effective technique to prevent scale formation. The most common and effec-

tive method of scale controlling is the use of chemical additives as scale inhibitors that retard or prevent scale formation even in very small concentrations.^{4,5} Several studies about calcium carbonate scale formation in the absence and presence of inhibitors have been carried out.^{6–10}

Copolymer has been used satisfactorily as a specific scale inhibitor in the circulating cooling water systems is developed in the late 1970s¹¹ because of its strong complexation of multifunctional groups and superior dispersion characteristic of macromolecule. This kind of chemical inhibitors is applied widely in circulating cooling water treatment contribute to their excellent performances such as inhibiting formation of calcium carbonate scale, dispersing ferric oxide (Fe_2O_3), and stabilizing Zn^{2+} in water. In addition, some of them can perform as a metal corrosion inhibitor. With the improvement of environmental consciousness, the content of phosphorus in water treatment agent has been of rigorous control. Concerning over accelerated aquatic eutrophication, the popularity of inhibitors containing high phosphorus is diminishing. As a result, the current trend for inhibitor usage is toward more environmentally friendly “green” chemicals.

In this article, a maleic acid–sodium ρ -styrenesulfonate (MAC-SS) copolymer containing low-phosphorus was prepared in aqueous solution with redox

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Contract grant sponsor: Research Award Program for Yong Scientists in Shandong Province; contract grant number: 2008BS09021.

system of hypophosphorous acid and hydrogen peroxide as initiator. The experimental factors of monomer feed ratio, reaction temperature, dosage of hypophosphorous acid, and drop speed of hydrogen peroxide were investigated. Elemental composition of the optimization copolymer was analyzed with energy-dispersive X-ray analysis (EDX), and infrared spectroscopy was used to study the structure of the copolymer, and the chain structure of the copolymer was identified by ^{31}P -NMR and ^{13}C -NMR spectra. In addition, the viscosity-average molecular weight of the copolymer were calculated. The CaCO_3 scale inhibition performance of the optimization copolymer in the artificial cooling water was studied through static scale inhibition tests,¹² and the effect on formation of CaCO_3 was investigated with scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD), respectively.

There are few reports of low-phosphorus copolymer of MAc-SS used as scale inhibitor in cooling water.^{11,13,14} It is believed to represent a potentially new environmentally safe water treatment agent suitable for cooling water systems because of its low-phosphorus and decreasing eutrophication.

EXPERIMENTAL

Materials

All reagents were commercially available and were used without further purification. Maleic anhydride (MA), hydrogen peroxide, sodium hydroxide, calcium chloride, and sodium bicarbonate were analytical reagent grade purchased from Sinopharm Chemical Reagent Beijing. Sodium ρ -styrenesulfonate (SS) was industrial grade afforded by Zibo Xingzhilian Chemical, and hypophosphorous (Guaranteed reagent) was supplied by Nanjing Chemical Reagent. All solutions were prepared using deionized water.

Synthesis of MAc-SS copolymer

A standard orthogonal array L_9 (3^4) was used to examine reaction conditions such as the ratio of MA to SS, reaction temperature, the ratio of H_3PO_2 to monomer, and the drop time of H_2O_2 in three levels. The four factors and the levels of the factors studied are shown in Table I. Accordingly, the optimal reaction conditions were determined by combining the levels of factors that had the highest main effect value.

The copolymerization reaction was carried out in 250-mL flasks with mechanical stirrer, reflux condenser, dropping funnel, and thermometer. A total of 10 g MA and 50 mL of deionized water were

mixed stirring continuously with nitrogen as protective gas. SS and hypophosphorous acid were added in definite proportion and heated to the reaction temperature. In fixed temperature and stirring conditions, hydrogen peroxide was added drop by drop. After hydrogen peroxide had been added, it was kept reacting for 60 min. Finally, the pH value of solution was adjusted to 7–8 by adding 20% NaOH solution.

To test the properties of the low-phosphorus MAc-SS copolymer as a recirculating cooling water treatment agent, inhibition of calcium carbonate scale efficiency was developed for controlling experimental parameters in orthogonal experiments. All the parameters were determined according to the standard method of static evaluation for circulating cooling water treatment agent.¹² All calculations were performed using Design Expert software (version 6.0.10, Stat-Ease, USA).

Inhibition test

The ability of the low-phosphorus MAc-SS copolymer to inhibit calcium carbonate scale was compared with that of the free-inhibitor in flask tests. The inhibition test was carried with artificial water, which was prepared by dissolving a certain quantity of CaCl_2 and NaHCO_3 in deionized water, and the initial total concentrations of Ca^{2+} ($C_{\text{Ca},i}$) and HCO_3^- ($C_{\text{HCO}_3,i}$) were $2.45 \times 10^{-3} \text{ mol L}^{-1}$ and $5 \times 10^{-3} \text{ mol L}^{-1}$, respectively. Hence, the ratio of initial concentrations, $R_i (= C_{\text{Ca},i} / C_{\text{HCO}_3,i})$, was 0.49. The artificial waters containing different dosages of the low-phosphorus MAc-SS copolymer were thermostated at 80°C for 10 h.

The concentrations of soluble calcium ions in different solutions were analyzed using a standard solution of EDTA. The inhibition efficiency φ was defined as:

$$\varphi = \frac{\rho_1(\text{Ca}^{2+}) - \rho_2(\text{Ca}^{2+})}{\rho_0(\text{Ca}^{2+}) - \rho_2(\text{Ca}^{2+})} \times 100\%$$

where $\rho_0(\text{Ca}^{2+})$ was the total concentrations of Ca^{2+} (mg L^{-1}), $\rho_1(\text{Ca}^{2+})$ was the concentrations of Ca^{2+} (mg L^{-1}) in the absence of the copolymer inhibitor, $\rho_2(\text{Ca}^{2+})$ was the concentrations of Ca^{2+} (mg L^{-1}) in the presence of the copolymer inhibitor. The morphologies of CaCO_3 precipitates were examined by SEM on a scanning electronic microscope (QUANTA 200, Netherlands). Precipitated phases were identified by XRD on an X-ray powder diffractometer (SHIMADZU XRD-600, Japan, using Ni-filtered $\text{CuK}\alpha$ radiation).

TABLE I
The Arrangement of Orthogonal Array L_9 (3^4) and Corresponding Results for Calcium Carbonate Scale Inhibition

Trial no.	MA /SS ratio	Reaction temperature ($^{\circ}\text{C}$)	H_3PO_2 /monomer ratio	Drop time of H_2O_2 (min)	Scale inhibition rate on calcium carbonate (%)
1	A ₁ (1 : 1.0)	B ₁ (65)	C ₁ (0.14 : 1)	D ₁ (60)	72.35
2	A ₁ (1 : 1.0)	B ₂ (80)	C ₂ (0.16 : 1)	D ₂ (90)	88.74
3	A ₁ (1 : 1.0)	B ₃ (95)	C ₃ (0.18 : 1)	D ₃ (120)	85.72
4	A ₂ (1 : 0.8)	B ₁ (65)	C ₂ (0.16 : 1)	D ₃ (120)	92.83
5	A ₂ (1 : 0.8)	B ₂ (80)	C ₃ (0.18 : 1)	D ₁ (60)	98.56
6	A ₂ (1 : 0.8)	B ₃ (95)	C ₁ (0.14 : 1)	D ₂ (90)	96.37
7	A ₃ (1 : 0.6)	B ₁ (65)	C ₃ (0.18 : 1)	D ₂ (90)	68.58
8	A ₃ (1 : 0.6)	B ₂ (80)	C ₁ (0.14 : 1)	D ₃ (120)	75.65
9	A ₃ (1 : 0.6)	B ₃ (95)	C ₂ (0.16 : 1)	D ₁ (60)	72.46
k_1	82.27	77.92	81.46	81.12	
k_2	95.95	87.65	84.68	84.56	
k_3	72.23	84.85	84.29	84.73	
R	23.72	9.73	3.22	3.61	

k , average of every factor scale inhibition rate on calcium carbonate, %; R, range; the copolymer concentration is 16 ppm.

Analysis

The low-phosphorus MAc-SS copolymer sample obtained under the optimal reaction condition was precipitated (not adjusted pH by adding NaOH solution) and purified with ethanol.

The intrinsic viscosity $[\eta]$ of the copolymer (0.005 g mL^{-1}) was measured in sodium thiocyanate aqueous solution (0.15 mol L^{-1}) with an Ubbelohde viscometer thermostated at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$, and the viscosity-average molecular weight was calculated by Mark-Houwink empirical equation¹⁵:

$$[\eta] = KM^{\alpha}$$

where $[\eta]$ is intrinsic viscosity, K is a Mark-Houwink constant, here $7.65 \times 10^{-6} \text{ mL g}^{-1}$ was adopted, α is the other Mark-Houwink constant, here 0.924 was adopted, M is molecular weight

The elemental compositions of the low-phosphorus MAc-SS copolymer were measured using X-ray Photoelectron Spectroscopy (EDAX, USA). Fourier Transform Infrared (FTIR) spectra were recorded by a Tensor 27 spectrophotometer (BRUKER OPTICS, Switzerland) using KBr pellet at room temperature. NMR spectra were acquired on BRUKER AVANCE600 spectrometer (BRUKER, Switzerland) at 300 K, and all the experiments were recorded using D_2O as solvent, The ^{13}C -NMR and ^{31}P -NMR spectra were operated at 150.90 MHz with DSS as an internal reference and at 242.93 MHz with 85% H_3PO_4 as an external reference, respectively.

RESULTS AND DISCUSSION

Results of orthogonal experiment

Table I presents the contribution of the four independent factors at different levels to calcium car-

bonate scale inhibition performance of the low-phosphorus sodium MAc-SS copolymers. MA/SS ratio has shown the highest positive impact on the calcium carbonate scale inhibition rate. The next most important factor is reaction temperature. The ratio of H_3PO_2 to monomer and the drop time of H_2O_2 rank the last. Therefore, the optimum parameter level for the calcium carbonate scale inhibition performance is $\text{A}_2\text{B}_2\text{C}_3\text{D}_1$. The optimal reaction conditions to synthesize the copolymer are 1.25 of MA/SS ratio, 0.18 of the ratio of H_3PO_2 to monomer, 80°C reaction temperature, and 60 min of H_2O_2 drop time.

Structure analysis of the copolymer

The viscosity-average molecular weight of the optimization low-phosphorus MAc-SS copolymer was calculated as 1.86×10^5 .

EDX was performed to get information about the elemental composition of the optimization low-phosphorus MAc-SS copolymer, including C, O, P, S, and Na. Importantly, the phosphorus content is 3.63% in weight. In fact, the actual phosphorus content should be lower than 3.63% because the hydrogen had been reckoned without in the EDX result. Consequently, the phosphorus content in the copolymer is lower than 4% for certain, which carried the points of low-phosphorus content and environment friendly.

The FTIR spectra of sodium p -styrenesulfonate (a) and the optimization low-phosphorus MAc-SS copolymer (b) were shown in Figure 1. In contrast to the spectrum of sodium p -styrenesulfonate, the characteristic absorption bands of alkene, i.e., out of plane bending vibration of CH_2 at 909 cm^{-1} , out of plane bending vibration of CH at 991 cm^{-1} , and $\text{C}-\text{H}_{\text{str}}$ at 3051 cm^{-1} all disappeared indicating that

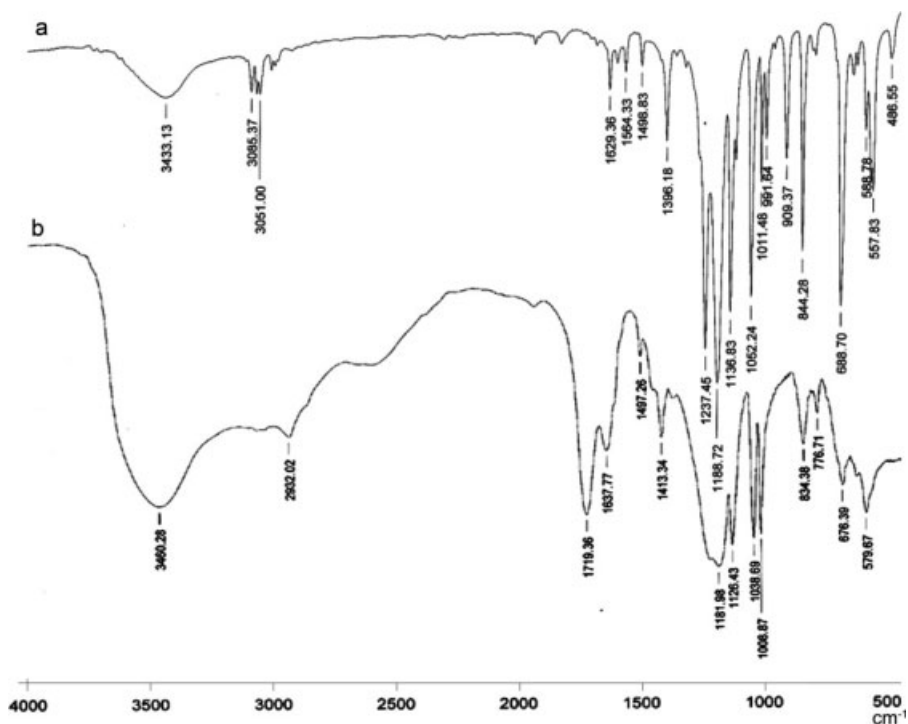


Figure 1 The FTIR spectrums of sodium *p*-styrenesulfonate (a) and the MAC-SS copolymer (b).

a polymerization reaction must be carried out. The slender peak at 776 cm^{-1} is attributed to $\text{P}-\text{C}_{\text{def}}$, 1126 cm^{-1} is attributed to $\text{P}=\text{O}_{\text{str}}$, 2309 cm^{-1} is attributed to $\text{P}-\text{O}_{\text{str}}$. These appearance can be explained by H_3PO_2 that had been concerned with the copolymerization. At the same time, another three visible peaks ($\text{C}=\text{O}_{\text{str}}$ at 1719 cm^{-1} , symmetri-

cal and asymmetrical stretching vibration of $\text{S}=\text{O}$ at 1038 cm^{-1} , and 1181 cm^{-1}) are observed in the FTIR spectrum, which reflects the copolymerization reaction between MAC and SS coming true. Therefore, the FTIR spectra revealed that the optimization MAC-SS copolymer contain multifunctional groups including carboxyl, phosphoric acid and sulfonic.

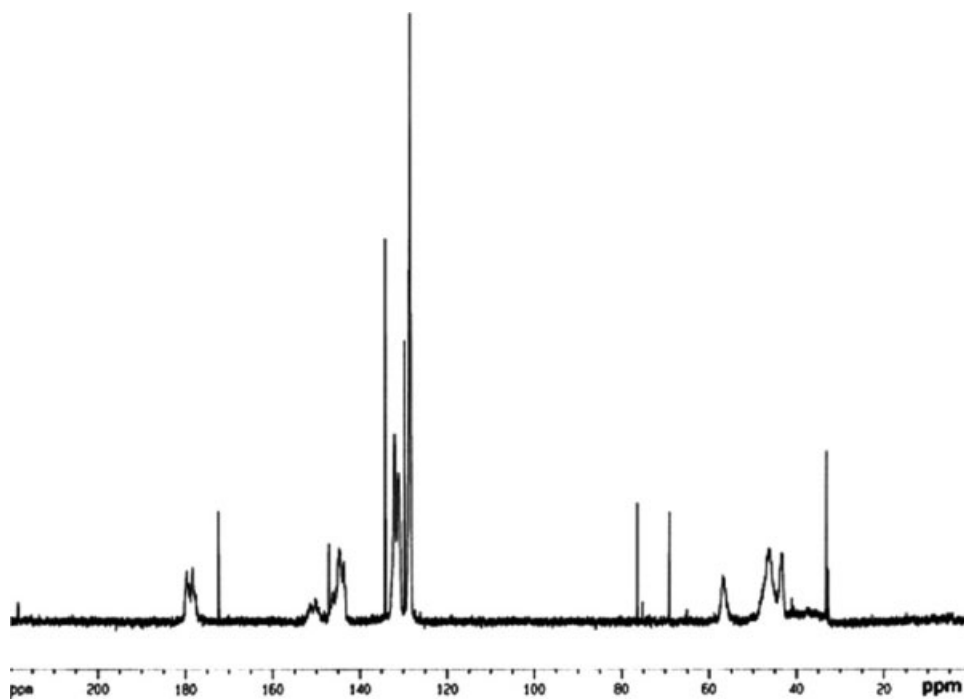


Figure 2 ^{13}C NMR spectra of the copolymer (ppm).

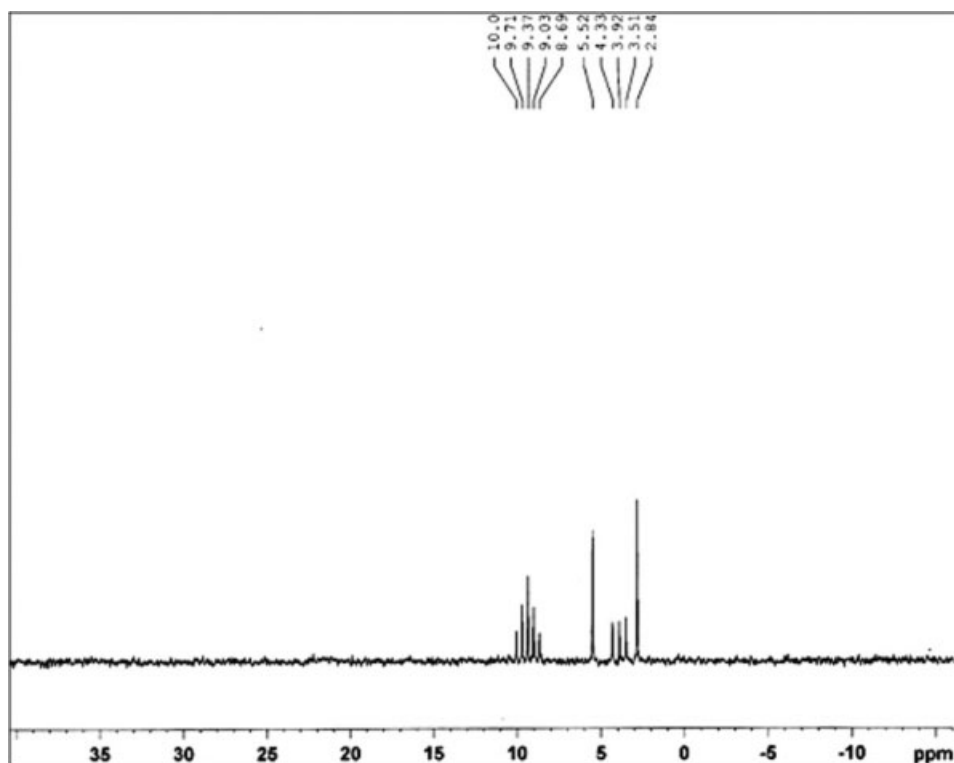


Figure 3 ³¹P NMR spectra of the copolymer (ppm).

These groups provide a base for its varied application properties such as inhibiting the formation of calcium carbonate, dispersing ferric oxide, and stabilizing Zn²⁺.

The ¹³C NMR spectrum and ³¹P NMR spectrum of the optimization low-phosphorus MAc-SS copolymer were shown in Figures 2 and 3, respectively. ¹³C NMR spectral analysis reveals that the copolymer produced in the copolymerization is an alternating copolymer with maleic acid and sodium *p*-styrenesulfonate. The peak at 179.7 ppm is assigned to the carbonyl carbon adjacent the phenyl. The chemical shifts in the region from 172.3 to 178.3 ppm are assigned to the carbonyl carbon away from the phenyl. The chemical shifts in the region from 136 to 139 ppm are assigned the phenyl carbon adjacent to the copolymer backbone. The presence of these peaks provides evidence that the copolymer backbone chain is the alternating units of maleic acid and sodium *p*-styrene sulfonate. The ³¹P-NMR

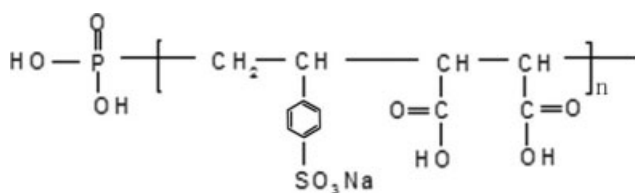


Figure 4 Diagram of the molecular structure of the copolymer.

spectra in Figure 3 implied that the chemical shifts in the region from 8.6 to 10.0 ppm are a terminal phosphoro-to-carbon bond in the copolymer molecular structure. Therefore, the molecular structure of the copolymer was presented in Figure 4.

Inhibition of the copolymer

The effect of the low-phosphorus MAc-SS copolymer as an antiscaling agent for calcium carbonate was

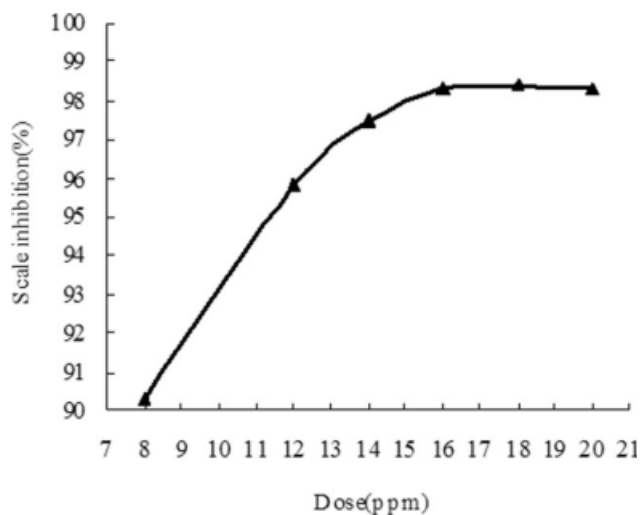


Figure 5 Influence of the copolymer concentration on the inhibition efficiency.

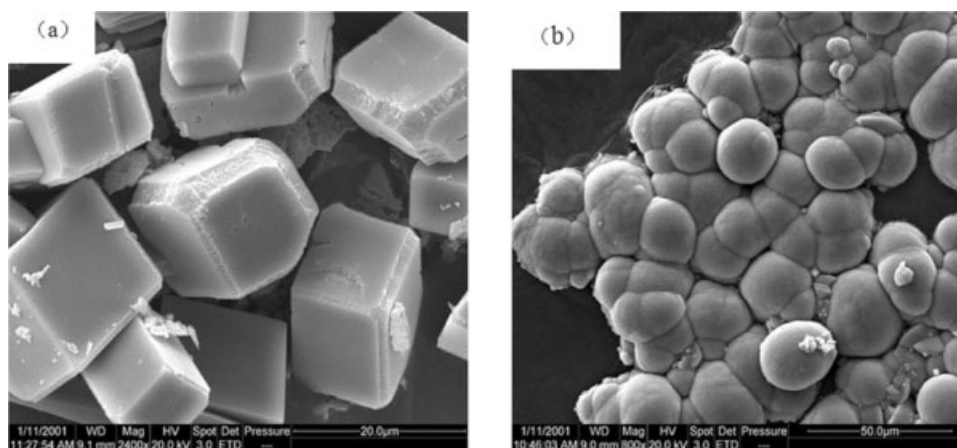


Figure 6 SEM micrographs of CaCO_3 precipitates. (a) In the absence of the low-phosphorus copolymer and (b) In the presence of 8 ppm the low-phosphorus copolymer.

shown in Figure 5. A series of artificial cooling water with different dosages of the low-phosphorus MAC-SS copolymer ranging from 8 to 20 ppm were heated at 80°C for 10 h, respectively. Figure 5 illustrates the ability of the low-phosphorus MAC-SS copolymer under identical conditions. When the copolymer concentration increased, the scale inhibition effect enlarged correspondingly. Noticeably, there is a sudden increase of scale inhibition when the concentration increases from 8 to 14 ppm, where the scale inhibition result is 90.3% at 8 ppm, but 97.4% for 14 ppm, and the curve has a tendency to moderate when the concentrations increase from 14 to 20 ppm, where reaches 98.2% at 16 ppm, and 98.4% for 20 ppm.

Figure 6 shows the SEM micrographs of CaCO_3 precipitate formed in artificial cooling water. As shown, in the absence of the low-phosphorus sodium MAC-SS copolymer, the form of CaCO_3 precipitates is essentially well-regulated orthorhombic calcite particles with average particle size of about

10 μm . In the presence of the low-phosphorus MAC-SS copolymer [Fig. 6(b)], obvious changes can be noted in distribution, size, and morphology of the CaCO_3 precipitate comparing with Figure 6(a). The CaCO_3 precipitate lost its sharp edges, and the form was distorted. In addition, the size was increased to 25–30 μm , larger than those deposited in uninhibited solution.

It is generally accepted that the inhibition of scale formation is influenced by both the location of the adsorbed inhibitor at the crystal surface and the extent of chemical bonding with the surface.^{16–18} The more effective the inhibitor is, the higher the surface binding capability. Organic phosphonic can strongly adsorb onto a CaCO_3 crystalline substrate owing to the high chelating ability of the $-\text{P}(\text{O})(\text{OH})_2$ group.^{19–21} The low-phosphorus MAC-SS copolymer contains both carboxyl and phosphorus groups in one molecule. Therefore, its surface-binding capability is stronger, and as a result, it possesses higher inhibition effect under identical

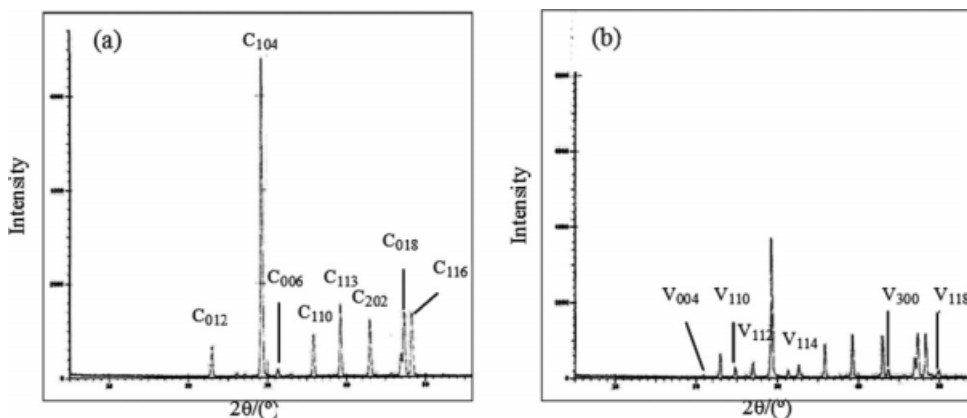


Figure 7 The XRD pattern of CaCO_3 precipitates. (a) In the absence of the low-phosphorus copolymer and (b) in the presence of the low-phosphorus copolymer.

conditions. The low-phosphorus MAc-SS copolymer adsorbs on CaCO_3 surfaces by binding the carboxylic or phosphonate anions to surface calcium ions.

The CaCO_3 precipitated phases were identified by XRD, and the spectra were shown in Figure 7. In the absence of the low-phosphorus MAc-SS copolymer, calcite is the main crystal form [Fig. 7(a)]. As indicated in Figure 7(b), in the presence of the low-phosphorus MAc-SS copolymer, there are a number of vaterite crystals interlarding.

It is well known that calcite is the most thermodynamically stable, and vaterite is the least stable form in the three polymorphic forms of CaCO_3 .^{1,22,23} Vaterite is the initial phase formed when CaCO_3 supersaturated; calcite can be formed from the transformation of aragonite or vaterite in the absence of inhibitors.^{24,25} Although calcite has the greatest thermodynamic stability under ambient conditions, the thermodynamically less stable aragonite and/or vaterite phase may be stabilized under certain conditions of temperature or in the presence of other ions or inhibitors.²⁶⁻²⁹ The calcium carbonate precipitate obtained from the artificial cooling water without the low-phosphorus MAc-SS copolymer has XRD patterns [Fig. 7(a)] corresponding to calcite. Figure 7(b) shows the X-ray diffraction spectrum for CaCO_3 precipitate in the presence of the low-phosphorus MAc-SS copolymer, in which there are the (004), (110), (112), (114), (300), and (118) weak peaks corresponding to vaterite, and a strong peaks for calcite. These results indicate that in the presence of the low-phosphorus MAc-SS copolymer the calcium carbonate precipitate is the mixture of calcite and vaterite. It was found that thermodynamically unstable vaterite could be stabilized kinetically in the presence of the low-phosphorus MAc-SS copolymer.

CONCLUSIONS

In this article, MAc-SS copolymer containing low-phosphorus was synthesized in aqueous solution with hypophosphorous acid/hydrogen peroxide as redox initiators to inhibit cooling water scale. Based on the earlier discussions, we reach the following conclusions:

1. The optimal reaction conditions to synthesize the copolymer are 1.25 of MA/SS ratio, 0.18 of the ratio of H_3PO_2 to monomer, 80°C reaction temperature, and 60 min of H_2O_2 drop time.
2. Phosphorus content in the copolymer is lower than 4% (mass percentage); the viscosity-average molecular weight of the copolymer obtained under the optimal reaction conditions is $1.86 \times 10^{-5} \text{ g mol}^{-1}$; the copolymer contains carboxyl group, sulfonic group, and terminal phosphonate group, and the main chain struc-

ture of the copolymer is the alternating units of styrene sulfonic acid and maleic acid.

3. The results of static scale inhibition test showed that the MAc-SS copolymer is effective in inhibiting calcium carbonate scaling. The MAc-SS copolymer sharply inhibited the formation of calcium carbonate scale with a lower dose in the solution. The adsorption of the MAc-SS copolymer on the crystal surface caused a deformation of the crystal morphology.

We would also like to thank Dr. Chu Libing for valuable discussions.

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