



# The effect of synthesized hydrolyzed polymaleic anhydride (HPMA) on the crystal of calcium carbonate

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## ABSTRACT

Precipitation of calcium carbonate followed by the adhesion of precipitates to equipment surfaces is the main problem of mineral scaling in cooling water systems. Many chemicals and antiscalants have been widely used to mitigate the mineral scaling problems. Hydrolyzed polymaleic anhydride (HPMA) was synthesized and used as antiscalant. The effect of Synthesized HPMA on the crystal of calcium carbonate was investigated through the calcium carbonate precipitation experiments. The synergetic effect of synthesized HPMA with 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and polyacrylic acid (PAA) was also investigated. It was indicated that the order of the ability to prevent the precipitation of  $\text{Ca}^{2+}$  from bulk solution was HEDP/HPMA/PAA > HEDP ≈ HPMA > PAA. The morphologies and the crystal structure of the precipitates were investigated using Scanning Electron Microscope (SEM) and X-ray Diffractometer (XRD). It was indicated that HPMA could change the morphologies and crystal structures of  $\text{CaCO}_3$  precipitates. The irregular framboid spherical shape and vaterite crystal was observed in the presence of HPMA. HEDP and PAA could enhance the effect of synthesized HPMA on the crystal of calcium carbonate. The synthesized HPMA together with HEDP and PAA showed higher antiscaling efficiency and synergetic effect on the crystal of calcium carbonate.

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## 1. Introduction

Water used in the cooling water systems usually contains particles, organic matters and scale-forming ions containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  [1]. The constituents could be concentrated many times (typically 4–8 times) because of the evaporative loss of water. The elevated concentration and high water temperature could cause severe mineral deposition and adhesion onto the heat transfer equipment surfaces (mineral scaling), along with the problems of corrosion and biofouling. It is well known that calcium carbonate, in particular, is the predominant mineral scale compound in cooling water systems [2]. The problem of scaling in cooling water systems during recirculation poses great challenges from both economical and technical points of view, decreasing system efficiency and increasing frequency of chemical cleaning.

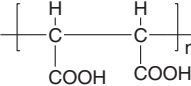
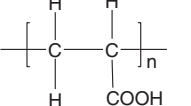
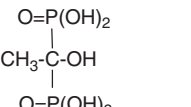
To mitigate the problem of mineral scaling, chemicals and antiscalants including but not limited to polyacrylic acid (PAA), polyacrylamide, hydrolyzed polymaleic anhydride (HPMA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and polyphosphates were widely used [3–9]. These antiscaling chemicals control mineral scale through mainly two antiscaling mechanisms: one is that antiscalants could

keep more scale-forming positive ions (e.g.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in the solution from being precipitated through complexation action [10]; the other is that the antiscaling chemicals could interact with mineral nuclei to disrupt the crystallization process and keep the crystal particles dispersed in the aqueous suspension, rendering them less prone to sedimentation or adhesion onto the equipment surfaces [10,11]. HEDP, HPMA and PAA have been widely used as scale inhibitors, corrosion inhibitors or dispersants. PAA has the “threshold effect” of  $\text{CaCO}_3$  inhibition could absorb the growing crystal phases of the nuclei and prevent vaterite transforming to aragonite or calcite, which results in the distortion and retardation of the crystal growth [3,12]. HEDP could modify the structure of calcium carbonate by incorporating into the crystals and thus decrease scale formation on the heat exchanger surfaces [13]. A. Martinod et al. investigated the effect of HPMA on the growth of calcium carbonate particles in the micrometer size range on stainless steel surface, HPMA could affect the growth of  $\text{CaCO}_3$  crystals due to adsorption of carboxylate ions on the nuclei of calcium carbonate [14]. Reports on the effect of HPMA on the morphologies and crystal structures of calcium carbonate precipitates are lacking. At present, reports on HPMA and the composition of multi-antiscalants are mostly limited to patents or personal communications. The synergetic effect of HEDP, HPMA and PAA on the crystal of calcium carbonate is still lacking.

In the present study, low molecular HPMA was synthesized and characterized, and the effect of HPMA on the crystal of calcium

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**Table 1**  
The structure of HPMA, PAA and HEDP.

Antiscalant	CAS no.	Structure	Supplier
HPMA	26099-09-02		Synthesized in lab.
PAA	9003-01-4		Nanjing Naco Water Treatment Technology Co., Ltd.
HEDP	2809-21-4		Nanjing Naco Water Treatment Technology Co., Ltd.

carbonate was investigated. The synergistic effect of synthesized HPMA with HEDP and PAA on the crystal of calcium carbonate was also investigated. The morphologies and crystal structures of precipitates were investigated using SEM and XRD.

## 2. Material and methods

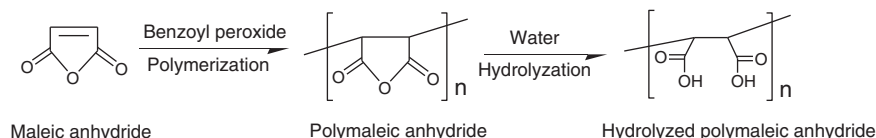
### 2.1. Chemicals and reagents

Calcium chloride, sodium bicarbonate, maleic anhydride, benzoyl peroxide, methylbenzene and methyl ethyl ketone were obtained from Sinopharm Chemical Reagent Co. Ltd. All the above chemicals are analytical reagents which were used as received from commercial suppliers without further purification, unless otherwise specified. HEDP and PAA were bought from Nanjing Naco Water Treatment Technology Co., Ltd. The structure of HEDP and PAA was shown in Table 1. Deionized water (DI water) was used throughout the experiments.

### 2.2. Synthesis of HPMA

As shown in Fig. 1, the polymaleic anhydride (PMA) was prepared by free radical solution polymerization with benzoyl peroxide as initiator. Maleic anhydride monomer and the initiator were dissolved in methylbenzene solvent respectively. The monomer solution was maintained at 70 °C for 10 min, and then the initiator solution was inlet into the monomer solution throughout the 5 min. The polymaleic anhydride deposition was obtained after 5 h polymerization reaction at 90 °C. Then the polymer was dissolved in methyl ethyl ketone and was made pure by methylbenzene three times. The PMA powder was placed in vacuum drying oven for other use.

Hydrolyzed polymaleic anhydride (HPMA) was prepared through hydrolysis of PMA and used as antiscalant. The details: 10 g PMA and 10 g DI water was added into the 50 mL beaker and then the solution was kept at 90 °C for 30 min under stirred condition. The HPMA solution was obtained with a solids content of 53%.



**Fig. 1.** Schematic diagram of HPMA preparation.

### 2.3. Characterization of PMA

Gel Permeation Chromatography (GPC, Agilent 1100) was used to investigate the molecular weight distribution of the synthesized PMA.

The FT-IR spectra were recorded for the synthesized PMA to confirm the functional groups that were responsible for the antiscaling property using Nexus FT-IR 670 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector in the pressed KBr pellets.

### 2.4. Evaluation of the synthesized HPMA

The calcium carbonate precipitation method was designed to provide a quantitative measure of the abilities of scale inhibitors to prevent the precipitation of  $\text{Ca}^{2+}$  from bulk solution. The details were described as follows: 250 mL of DI water and certain standard  $\text{CaCl}_2$  solution containing 120 mg of  $\text{Ca}^{2+}$  was firstly added into a 500 mL volumetric flask. Then various quantities of antiscalant solution needed and borax buffer solution was added into the volumetric flask in sequence. At last, the  $\text{NaHCO}_3$  standard solution containing 366 mg of  $\text{HCO}_3^-$  was added into the volumetric flask and it was filled to the tick mark with DI water. The control sample was prepared in the same way as mentioned above without adding antiscalants. The precipitation process was carried out in 500 mL conical flasks. To avoid the evaporation of the solution, the 40 cm long glass tube ( $\Phi = 3$  mm) plugged by the rubber stopper was used as a reflux condenser. Conical flasks were placed in a water-bath to keep static at 80 °C constantly for 24 h. The concentration of  $\text{Ca}^{2+}$  in the solution was quantified by 0.01 mol/L EDTA solution three times each sample. The antiscaling efficiency was calculated as:  $\eta = (m_1 - m_0) / (0.24 - m_0) \times 100\%$ , where  $m_1$  is the concentration of  $\text{Ca}^{2+}$  in the sample with antiscalant used;  $m_0$  is the concentration of  $\text{Ca}^{2+}$  in the control sample; 0.24 is the original concentration of  $\text{Ca}^{2+}$  in the bulk and  $\eta$  is the antiscaling efficiency.

The precipitates in the conical flask were carefully collected and dried in room temperature for morphology and crystal structure analysis. The XRD pattern was recorded on a Bruker D8 Advance X-ray diffraction instrument (Cu,  $K\alpha$ ), the diffraction angle ( $2\theta$ ) in the range of 20–80° was scanned (Bruker, Germany). SEM images were obtained using JEOL JSM-6380LV electron microscope (JEOL JSM-6380LV, Japan).

## 3. Results and discussion

### 3.1. Characterization of the synthesized HPMA

#### 3.1.1. Molecular weight determination

The molecular weight distribution (MWD) of the synthesized PMA was determined by GPC using tetrahydrofuran as solvent. In Fig. 2, GPC stands for the gel permeation chromatography (GPC) reading of the MWD calculated by computer [15]. The MWD was around 430 g/mol and covered from 200 g/mol to 800 g/mol. The average molecular weight is 526 g/mol. As calculated, the molecular weight of HPMA was around 625 g/mol, which could contribute to excellent antiscaling efficiency [16].

#### 3.1.2. FT-IR spectroscopy

The FT-IR spectra were taken for the synthesized PMA and were presented in Fig. 3. Functional groups were deduced from the characteristic peaks.

The bands at 1858  $\text{cm}^{-1}$  and 1780  $\text{cm}^{-1}$  could be assigned to the characteristic peaks of the anhydride groups [17]. The peak at

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