Desalination 345 (2014) 72–76

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

# Fluorescent polyaspartic acid with an enhanced inhibition performance against calcium phosphate

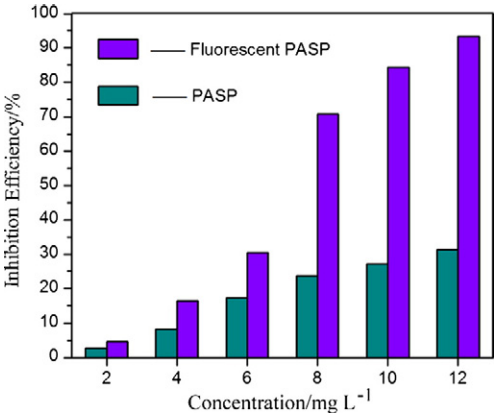
Jiuying Feng, Lijun Gao *, Rizhen Wen, Yiyi Deng, Xiaojun Wu, Shulin Deng

*Chemistry Science and Technology School, Development Center for New Materials Engineering & Technology in Universities of Guangdong, Zhanjiang Normal University, Zhanjiang 524048, PR China*

## HIGHLIGHTS

- A fluorescent polyaspartic acid scale inhibitor is synthesized.
- The fluorescence intensity is linearly related to the inhibitor concentration.
- The inhibitor concentration can be monitored conveniently and accurately.
- The inhibitor greatly improves calcium phosphate inhibition performance.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 5 December 2013
Received in revised form 2 April 2014
Accepted 15 April 2014
Available online 10 May 2014

*Keywords:*
Polyaspartic acid
Fluorescence
Scale inhibitor
Calcium phosphate

## ABSTRACT

Fluorescent polyaspartic acid (FPASP) used as a novel scale inhibitor was synthesized with partially ethanolamine-modified polysuccinimide, p-toluenesulfonyl chloride and 3-amino-9-ethyl carbazole. The products were characterized by $^1$H NMR, gel permeation chromatography and fluorescent spectra, respectively. The results show that carbazole groups, the fluorescent chromophore, were successfully incorporated into PASP. The relationship between the fluorescence intensity and the concentration of FPASP is linear. This provides a prerequisite for an automatic dosing of PASP by determining the concentration in situ using a fluorescence spectrometer with the help of computer technology. In addition, when the concentration was 12 mg $L^{-1}$, the inhibition efficiency of $Ca_3(PO_4)_2$ was improved from 31.3% of PASP to 93.3% of FPASP, which were determined using the static scale inhibition method. This improvement originates from the hydroxyl groups introduced into PASP.



## 1. Introduction

Large quantities of scale inhibitors are needed to prevent or minimize unfavorable events caused by deposits in cooling water systems, water desalination processes and oil field operations [1–4]. Biodegradable polymers such as PASP and polyepoxysuccinic acid have drawn much attention recently in view of environmental benefits [5,6]. In particular, PASP was widely studied as a representative in green scale inhibitors given its nontoxicity, good biodegradability and environmentally acceptability [7]. PASP exhibits excellent inhibition of $CaCO_3$ and $CaSO_4$ but a poor inhibition of $Ca_3(PO_4)_2$ [8], which limits its large-scale commercial application. Furthermore, $Ca_3(PO_4)_2$ scale has become more common in cooling

* Corresponding author. Tel.: +86 759 3183452.
*E-mail address:* gljtalk@163.com (L. Gao).

http://dx.doi.org/10.1016/j.desal.2014.04.019
0011-9164/

water systems because there is a tendency to run cooling systems at higher cycles and process operation at higher temperatures. Phosphates used often in the cooling water to prevent corrosion also increase calcium phosphate deposits [9]. In general, hydroxyl and/or sulfonic acid groups in polymers afford advantage for the $Ca_3(PO_4)_2$ inhibition, such as an itaconic acid/styrene p-sulfonic sodium/maleic anhydride/acrylamide copolymer and a double-hydrophilic block copolymer of maleic anhydride-allylpolyethoxy carboxylate and maleic anhydride-ammonium allylpolyethoxy sulfate [10,11]. 5-Aminoorotic acid was grafted onto PASP to improve $Ca_3(PO_4)_2$ inhibition of PASP [8].

What's more, it is desirable that scale inhibitor concentration is kept at the minimum value sufficient for exhibiting the effect. Several analytical methods such as colorimetric, turbidimetric, potentiometric, fluorescent tracer and spectrometric techniques were used to determine the concentration [12]. Among them, the fluorescence spectroscopy has become a hot spot of present research due to a high sensitivity, a good selectivity and a wide linearity. Fluorescent scale inhibitors therefore acquired a very significant interest. This method requires scale inhibitors to emit a strong fluorescence. However, these inhibitors reported were generally limited to the ones that were synthesized by radical copolymerization of a vinyl fluorescent monomer and the scale inhibiting monomers consisting of the specific groups such as unsaturated carboxylic acids or anhydrides, vinyl sulfonic acids or vinyl alcohols [13,14]. For preparing the fluorescent scale inhibitor like PASP, which is synthesized by non radical polymerization, the above strategy is not available. A few studies on fluorescence-labeling PASP were reported, for example, PASP was modified with 1-pyrenylmethylamine and 1-naphthymethylamine, which was not used for scale inhibitor [15].

Considering the strong fluorescence intensity of carbazole derivatives, we attempted to prepare fluorescent PASP by ammonization of polysuccinimide (PSI) with 3-amino-9-ethyl carbazole (AEC), which had already been a common synthetic strategy to prepare polyaspartamide derivatives, but failed due to the unfavorable steric hindrance and electron-withdrawing effect of carbazole group. Fortunately we successfully introduced the carbazole group into PASP by reacting of partially hydroxyl PSI (PHPSI) with N-(2,3-epoxylpropyl)carbazole (EPC) [16]. Nevertheless EPC is relatively expensive. In this report, we design a new synthetic strategy (Scheme 1), that is, first PHPSI sulfonic ester is obtained by reacting PHPSI with p-toluenesulfonyl chloride, and then the resultant sulfonic ester can react with AEC to form the target product FPASP. The fluorescent and scale inhibitive performance of FPASP was investigated extensively.

## 2. Experimental section

### 2.1. Materials

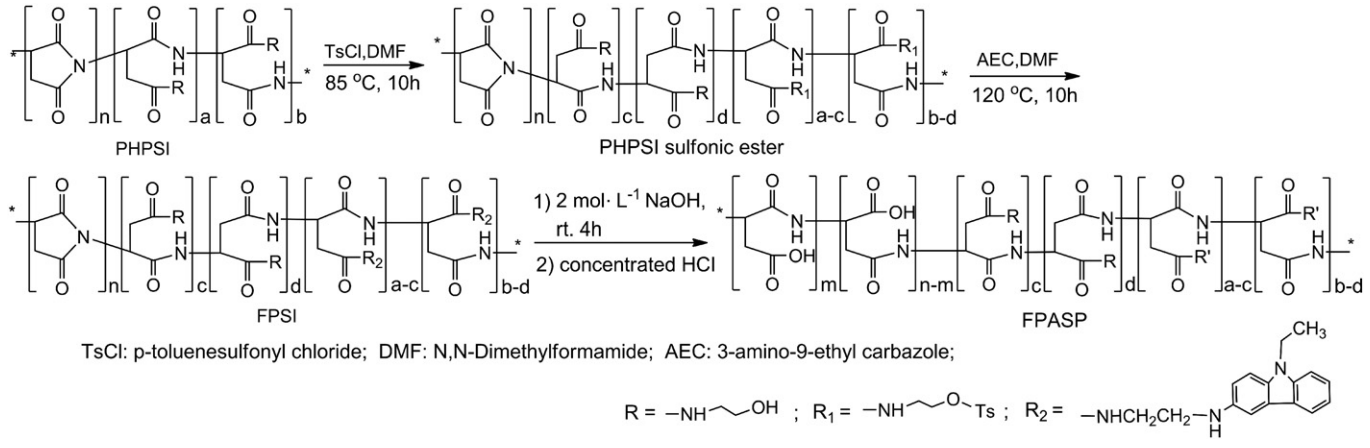
All reagents were purchased from Sinopharm Chemical Regent Co. Ltd and were of analytical grade unless noted. Deionized distilled water was used to prepare solutions. N,N-dimethylfomamide (DMF) and triethylamine were dried over Molecular Sieve 4A before use. PSI was prepared with maleic anhydride and ammonium hydroxide using a microwave according to the literature [17]. PHPSI was obtained by reacting PSI with ethynolamine using the previously reported method [16], in which the feed mole ratio was 1 to 0.52. The number average molecular weights ($M_n$) of PHPSI was determined to be 7, 330 g $mol^{-1}$ with the molecular weight distribution (MWD) of 2.09.

### 2.2. Synthesis of PHPSI sulfonic ester

PHPSI (1.84 g) was stirred and dissolved in DMF (10 mL). Then DMF (5 mL) solution of p-toluenesulfonyl chloride (3.38 g) and equimolar triethylamine (1.3 mL) was added dropwise through the constant-pressure funnel, and the mixture was stirred in oil bath at 85 °C for 10 h. Afterwards the mixture was poured into anhydrous ethanol (80 mL) to form the precipitate, which was filtrated, washed with anhydrous ethanol/ether (1:1, *v/v*) and finally dried at 80 °C under vacuum to yield 2.35 g brown PHPSI sulfonic ester ($M_n$ = 10, 852 g $mol^{-1}$ and MWD = 1.67).

### 2.3. Synthesis of FPASP

PHPSI sulfonic ester (1.41 g) and AEC (1.79 g) were dissolved in 10 mL of DMF in a two-necked flask. Potassium carbonate (1.39 g) was then added, and the reaction mixture was stirred at 120 °C in oil bath for 10 h. Then it was filtrated to remove solid salts. The mixture was precipitated with anhydrous ethanol (50 mL) and filtrated. This precipitate was washed with anhydrous ethanol/ether (1:1, *v/v*) until the unreacted AEC in the filtrate was not detected by thin-layer chromatography and was dried at 80 °C under vacuum to yield 1.76 g fluorescent PSI (FPSI) ($M_n$ = 19, 904 g $mol^{-1}$ and MWD = 1.56). FPSI (1.57 g) was then hydrolyzed in 2 mol/L NaOH solution (4.4 mL) at ambient temperature under stirring for 4 h. When the pH value was adjusted to 4–5 using concentrated hydrochloric acid, the mixture was poured into anhydrous ethanol (30 mL). After filtration, the precipitate was washed with anhydrous ethanol/ether (1:1, *v/v*), and dried at 80 °C under vacuum to yield 1.46 g FPASP ($M_n$ = 20, 022 g $mol^{-1}$ and MWD = 1.50).




**Scheme 1.** Synthesis of FPASP.