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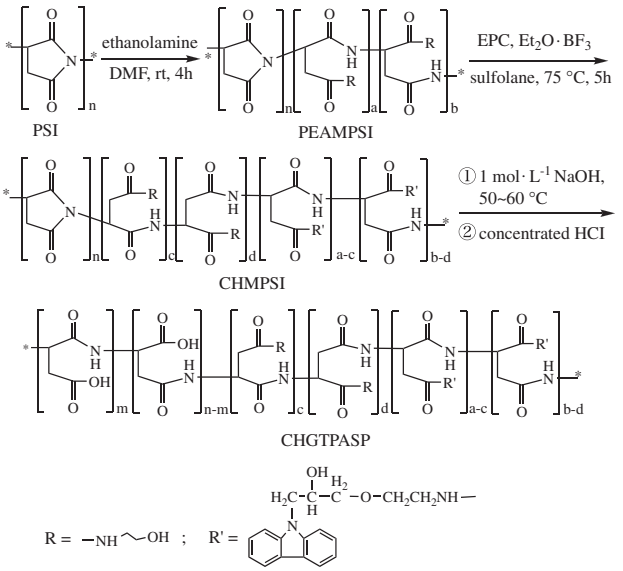
Carbazole and Hydroxy Groups-tagged Poly(aspartic acid) Scale Inhibitor for Cooling Water Systems

Li-Jun Gao, Jiu-Ying Feng,* Bei Jin, Qiu-Na Zhang, Tian-Qin Liu, Yang-Qing Lun, and Zhao-Jun Wu
Chemistry Science and Technology School, Development Center for New Materials Engineering and Technology in Universities of Guangdong, Zhanjiang Normal University, Zhanjiang 524048, P. R. China

(Received September 5, 2011; CL-110740; E-mail: fjy@zhjnc.edu.cn)

In order to conveniently monitor the concentration of poly(aspartic acid) (PASP) used as a green scale inhibitor in cooling water systems, and to improve calcium phosphate inhibition, carbazole and hydroxy groups-tagged PASP (CHGTPASP) was synthesized by ring-opening reaction of *N*-(2,3-epoxylpropyl)carbazole (EPC) with partially ethanolamine-modified polysuccinimide (PEAMPSI) followed by alkaline hydrolysis. CHGTPASP has good $Ca_3(PO_4)_2$ and $CaCO_3$ inhibition and its fluorescence intensity (*Fi*) is good linear to concentration. These multifunctional properties are of importance in industrial water processing economically and environmentally.

Various kinds of scale inhibitors had being added into industrial cooling water systems to prevent or minimize unfavorable events caused by mineral deposits.[1–3] In light of increasing environmental concerns and restrictions in law, biodegradable polymers such as PASP and poly(epoxysuccinic acid) were increasingly used.[4,5] PASP exhibits good inhibition on $CaCO_3$ and $CaSO_4$ but poor on $Ca_3(PO_4)_2$. In general, –OH and/or $–SO_3H$ groups in polymers can afford advantage for inhibition on $Ca_3(PO_4)_2$. It is desirable that scale inhibitors concentration is kept at the minimum value sufficient for exhibiting the effect. For the concentration determination several analytical methods such as colorimetric, turbidimetric, potentiometric, fluorescent tracer and spectrometric methods are available.[6] Among them, fluorescence spectrometric analysis has been becoming a hot spot of present research with a high sensitivity, a good selectivity, and a wide linearity. This method requires a strong fluorescence emitted by scale inhibitors. Therefore, a fluorescent multifunctional scale inhibitor acquires a very significant interest. Great efforts had being devoted to the synthesis of functional water-soluble polymers.[7] In general, there are two approaches to prepare fluorescent polymers. One is the copolymerization of a monomer containing a fluorescent chromophore and other monomer,[8] the other is chemical modification of polymers by fluorescent groups.[9] There exist some reports about the fluorescent scale inhibitors, generally focusing on polyacrylate, poly(maleic acid), and polyether.[10] For preparing fluorescent PASP, a few related works were reported. For example, PASP was modified with 1-pyrenylmethylamine and 1-naphthylmethylamine,[11] but it was not used for scale inhibitor. In this report, we present a feasible strategy to incorporate both carbazole and hydroxy groups into PASP's side chains and obtain a novel polymer, CHGTPASP. Therefore, we can expect CHGTPASP will exhibit good calcium carbonate and phosphate scale inhibition and have a good linearity between *Fi* and concentration. The synthetic route is shown in Scheme 1. First, the reaction of polysuccinimide (PSI) with ethanolamine



Scheme 1.

formed PEAMPSI, followed by ring-opening reaction between hydroxy groups of PEAMPSI and EPC catalyzed by 47% BF_3/ether, producing carbazole and hydroxy-modified PSI (CHMPSI). Finally, CHMPSI was hydrolyzed in sodium hydroxide solution to obtain the target product, CHGTPASP. The particular synthetic procedure was described in Supporting Information.[12]

The fluorescence performance of prepared CHGTPASPs was tested preliminarily. CHGTPASP with 0.01 g of EPC feed in preparing CHMPSI using 0.01 g of PEAMPSI had little fluorescence. One with 0.05 or 0.1 g of EPC feed exhibited strong fluorescence, but more EPC introduced should be unfavorable for scale inhibition properties for its poor water solubility, so the CHGTPASP sample with 0.05 g of EPC feed was only selected and was characterized by GPC and ^{1}H NMR.[12] In addition, its fluorescent and scale inhibitive properties were investigated extensively.

Based on the ^{1}H NMR spectra (Figures S1, S2, and S3),[12] the compositions of intermediate PEAMPSI and final product CHGTPASP, including ethanolamine molar fraction (f_{EA}) introduced in PEAMPSI, hydroxy groups molar fraction (f_{HG}) coming from ethanolamine and ring-opening reaction of EPC and carbazole groups molar fraction (f_{CG}) introduced in CHGTPASP were 49.3%, 49.5%, and 1.5% respectively. It is shown that the value of f_{EA} is approximately equal to one of f_{HG} because when a feed hydroxy in PEAMPSI consumes in epoxy ring-opening reaction, a new hydroxy forms simultaneously (Scheme 1).

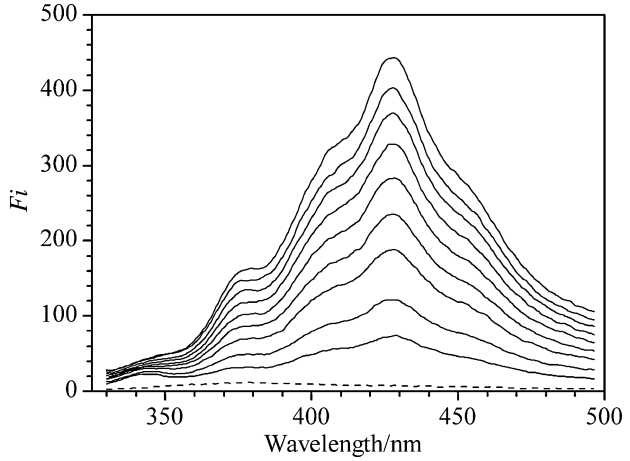


Figure 1. Fluorescence emission spectra of 1–9 mg L^{-1} CHGTPASP solutions (— from bottom to top) and 9 mg L^{-1} PASP solution (- - -) excited at 310 nm with excitation slit of 10 nm and emission slit of 5 nm.

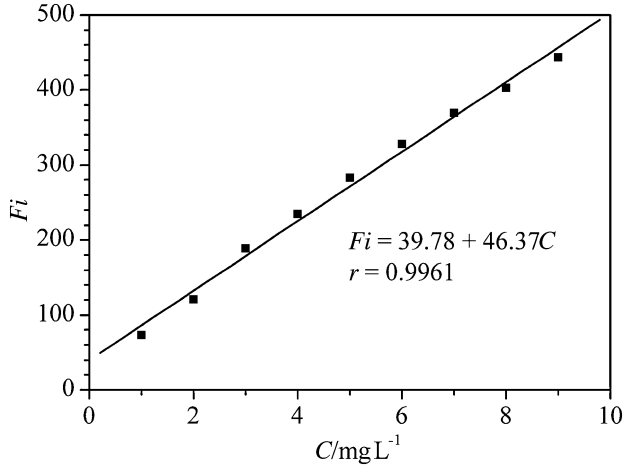


Figure 2. Linearity of the fluorescence intensity (*Fi*) with the concentration (*C*) of CHGTPASP.

GPC tests of CHGTPASP showed one strong peak and other two very weak peaks. The number average molecular weights (M_n) were 28564, 6141, and 987 with the molecular weight distribution (MWD) of 1.41, 1.07, and 1.13, respectively. This demonstrates that very small parts of the amido bonds in main chain of CHMPSI were hydrolyzed when transferred into CHGTPASP.

Fluorescence spectra of a serial concentration of aqueous CHGTPASP solutions were tested with water reference and compared to that of PASP. CHGTPASP exhibited a strong fluorescence peak at 428 nm while PASP had little fluorescence (Figure 1). Moreover, *Fi* was good linear to CHGTPASP concentration in the range of 2–10 mg L^{-1} (Figure 2) which is common dosage scope of scale inhibitors. The detection limit is 0.60 mg L^{-1} according to the formula: $D_r = 3\sigma/k$, where σ is standard deviation (SD) of 11 times *Fi* determination of water and k is slope of calibration curve. This positive linear relationship can be used to measure CHGTPASP concentration accurately.

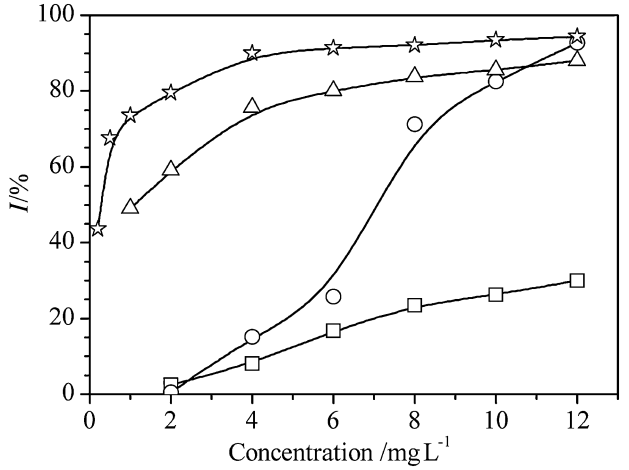


Figure 3. Scale inhibition of PASP on $Ca_3(PO_4)_2$ (open square), of CHGTPASP on $Ca_3(PO_4)_2$ (open circle), of CHGTPASP on $CaCO_3$ (open triangle), and of PASP on $CaCO_3$ (open star) at different concentrations of polymers respectively.

Scale inhibition of CHGTPASP on $Ca_3(PO_4)_2$ and $CaCO_3$ were tested and compared with unmodified PASP (Figure 3). The results revealed that CHGTPASP improved calcium phosphate inhibition robustly with inhibition of 92.8%, much better than 30% of PASP. This improvement is due to the incorporation of hydroxy groups. The dispersion effect of CHGTPASP is the mainly $Ca_3(PO_4)_2$ inhibitive mechanism compared to chelating solubilization effect because of very low solubility product of $Ca_3(PO_4)_2$. This conclusion is also supported by the facts that more quantity of CHGTPASP was needed for $Ca_3(PO_4)_2$ than $CaCO_3$ because dispersion achievement need more plenty of inhibitors. Absorbance of CHGTPASP on microparticles is prerequisite of the dispersion effect. So more hydrophobic hydroxy groups can heighten absorbance of CHGTPASP, and further improve inhibition. For $CaCO_3$ inhibition, CHGTPASP was weakly inferior to PASP, but 75.7% inhibition were obtained at the concentration of 4 mg L^{-1}. In addition, although carbazole groups are of poorly water-soluble, the incorporation of them had a negligible inhibitive effect either on $Ca_3(PO_4)_2$ or $CaCO_3$ because the molar fraction of 1.5% of carbazole groups in CHGTPASP is much lower as mentioned above and it is enough to work.

In conclusion, a novel multifunctional water-soluble polymer, CHGTPASP, was successfully synthesized. This polymer has very strong fluorescence, a good linearity with the concentration, and good scale inhibitive performance on calcium phosphate and carbonate. The work in this report would provide a strategy for multifunction and achievement of an accurate, convenient, and online measurement of commercially scale inhibitor, PASP.

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