Polyether copolymers containing fluorescent groups: a green inhibitor for calcium carbonate

Mengwei Xue, Changli Zhang, Qinpu Liu, Hui Yang and Guangqing Liu

ABSTRACT

A novel fluorescent-tagged scale inhibitor, linear-dendritic double hydrophilic block copolymer (acrylic acid (AA)/Allyloxy poly(ethylene glycol) polyglycerol (APEG-PG-(OH)n)/ 8-allyloxy-1, 3, 6-pyrene trisulfonic acid trisodium salt (PA) (MA/APEG-PG-(OH)n/PA) was synthesized by AA, APEG-PG-(OH)n and PA. Structures of APEG, APEG-PG-(OH)n and MA/APEG-PG-(OH)n/PA were carried out by ^{1}H NMR. The observation shows that the dosage and the *n* value of MA/APEG-PG-(OH)n/PA plays an important role on $CaCO_3$ inhibition. MA/APEG-PG-(OH)5/PA displays superior ability to inhibit the precipitation of calcium carbonate, with approximately 91% inhibition at a level of 8 mg/L. Relationship between AA/APEG- PG-(OH)5/PA's fluorescent intensity and its dosage was studied. Correlation coefficient R of MA/APEG-PG-(OH)5/PA's is 0.9991. The effect on formation of $CaCO_3$ was investigated with the combination of X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. MA/APEG-PG-(OH)5/PA can be used to accurately measure copolymer consumption on line besides providing excellent $CaCO_3$.

Key words | calcium carbonate, fluorescent, polyether copolymers, scale inhibitor

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INTRODUCTION

One of the main problems of industrial circulating cooling water systems is the scaling phenomenon, which has a great impact on economy and technology. Deposit formation may cause severe corrosion, deteriorate conditions of the heat exchange, decreased efficiency, and increased frequency of chemical cleaning (Amjad & Koutsoukos 2014; Wang *et al.* 2016). The clogging of pipes is the consequence of the scale formation, which leads to the shutdown of an industrial plant in the worst cases. Commonly, scales consist of calcium scales, zinc scales, magnesium hydroxide, ferric hydroxide, barium sulfate, etc., among which calcium carbonate scales are considered the most frequent in cooling water systems (Alimi *et al.* 2006; Hasson *et al.* 2011; Wang *et al.* 2016).

The most common and effective method of scale controlling is the use of chemical additives as scale inhibitors that retard or prevent scale formation even in very small concentrations (Chaussemier *et al.* 2015; Zhang *et al.* 2016). There are some small molecular organic phosphine compounds or phosphorus containing oligomer used as efficient scale inhibitors, but compounds containing phosphorus are harmful to the environment. In addition to organic phosphorus species, phosphates, a class of inorganic phosphorus species, are also commonly used as scale inhibitors. With the increase in discharging wastewater containing large amount of phosphorus to lakes and rivers, fresh-water pollution has been becoming a more and more serious problem. Under the pressure of worsening global ecological and environmental problems, the concept of 'green chemistry' was proposed and green scale inhibitors became a focus of water treatment technology.

In recent years, the phosphorus-free copolymers have attracted great interest, both in industry and in academia. Polycarboxylate such as polyacrylic acid (PAA), polymaleic acid (PMA) and polyepoxysuccinic acid (PESA) are environmentally benign inhibitors. But they will react with calcium ions to form insoluble calcium-polymer salts, so they have a

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low calcium tolerance (Wang *et al.* 2010). Thus, novel scale inhibitors should be further developed to offer a high calcium tolerance and should be environmentally acceptable water additives.

In our previous work, no phosphate and nitrogen free scale inhibitor (AA-APECn) which has a superior calcium tolerance were prepared from allyloxy polyethoxy ether, NaOH, and chloracetic acid (Du *et al.* 2009; Fu *et al.* 2011). But chloracetic acid is toxic, and harmful to the human body. In addition to this, it is quite difficult to test for AA-APECn in the traditional way because there is no phosphate active component in it. Improper feed rate of the treating agent leads to serious problems.

Fluorescence methods provide direct measurement and control of a wide array of treatment actives (Gatti & Lotti 2011). 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 acceptable, and are available at low cost.

In the present work, a fluorescent-tagged polyether-typed scale inhibitor, linear-dendritic double hydrophilic block copolymer (MA/APEG-PG-(OH)n/PA) was synthesized. MA/APEG-PG-(OH)n/PA compensates the weaknesses of AA-APECn which should use chloracetic acid as raw material and cannot be monitored. In comparison with traditional scale inhibitor, MA/APEG-PG-(OH)n/PA derived from capped polyether, easily prepared with non-toxic, biodegradable, lower cost, reliable reproducibility and less dosages, have superior scale inhibitive performances. In addition, MA/APEG-PG-(OH)n/PA belongs to an environment-friendly scale inhibitor, only containing three elements of carbon (C), hydrogen (H), oxygen (O) and is non-phosphorous (P)- and nitrogen (N)- free, which are potential nutrients for algae.

EXPERIMENTAL

Materials

Allyloxy poly(ethylene glycol) (APEG) was supplied by Jianghai Environmental Protection Co., Ltd (Changzhou, Jiangsu, P.R. China). Glycidol (99%) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, P.R. China). Other reagents such as maleic anhydride, 8-allyloxy-1,3,6-pyrene trisulfonic acid trisodium salt, potassium peroxydisulfate, ammonium persulfate, of AR grade were obtained from Zhongdong Chemical Reagent Co., Ltd (Nanjing, Jiangsu, P.R. China). Commercial inhibitors were technical grade and supplied by Jianghai Environmental Protection Co., Ltd (Changzhou, Jiangsu, P.R. China). Distilled water was used in all the studies.

Measurements

^{1}H NMR spectra was recorded on a Mercury VX-500 spectrometer (Bruker AMX500) using tetramethylsilane (TMS) internal reference and deuterated dimethyl sulfoxide (DMSO-d6) as a solvent. Molecular weight of the polymers was investigated through gel permeation chromatography (GPC-Waters-2410). The X-ray diffraction (XRD) patterns of the $CaCO_3$ crystals were recorded on a Rigaku D/max 2400 X-ray powder diffractometer with CuKα ($\lambda = 1.5406$) radiation (40 kV, 120 mA). The shapes of calcium carbonate scales were observed with a scanning electron microscope (SEM, S-3400N, HITECH, Japan). Fluorescence measurements were carried out on a luminescence spectrometry (LS-55, Perkin-Elmer, UK) with a xenon lamp as a light.

Synthesis

Synthesis of APEG-PG-(OH)n (n = 3, 5, 7, 9, 11)

Synthesis of APEG-PG-(OH)n (n is the number of hydroxyl) were carried out in a reactor equipped with a mechanical stirrer and dosing pump under nitrogen atmosphere. 18 g of APEG was partially deprotonated (35%) with potassium methylate solution by distilling off excess methanol from the melt. A certain quantity of glycidol was slowly added at 60 °C, choosing the initiator amount according to the monomer/initiator ratio. The reaction mixture was heated to 80 °C and maintained at this temperature for a further 4.0 h, to ultimately obtain yellowish viscous liquid APEG-PG-(OH)n. The synthesis procedure of APEG-PG-(OH)5 is shown in Figure 1.

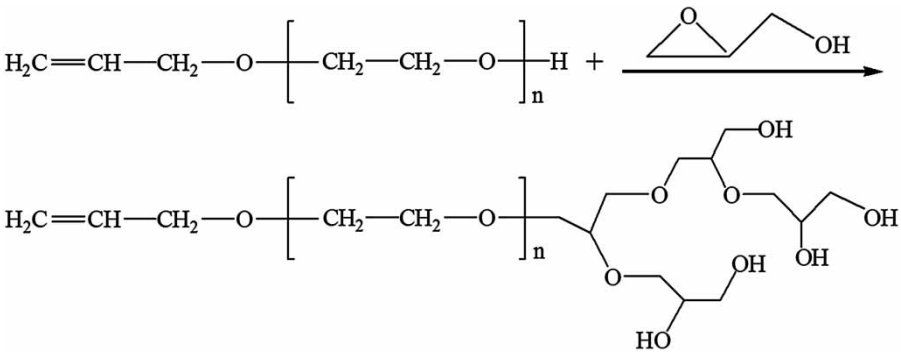

Figure 1 | Synthesis of APEG-PG-(OH)5.

Synthesis of MA/APEG-PG-(OH)n/PA (n = 3, 5, 7, 9, 11)

A 4-neck round-bottom flask equipped with a thermometer and a magnetic stirrer was charged with 25 mL of distilled water and 12 g of MA, and heated to 60 °C with stirring under nitrogen atmosphere. Subsequently, 18 g of APEG-PG-(OH)n and 0.12 g PA in 20 mL of distilled water (APEG-PG-(OH)n : MA : PA mass ratio = 1 : 1.5 : 0.01) and the initiator solution (0.8 g of ammonium persulfate in 30 mL of distilled water) were added separately at constant flow rates over a period of 1.0 h. The reaction mixture was heated to 70 °C and maintained at this temperature for a further 2.0 h, ultimately to afford an aqueous copolymer solution containing approximately 33% solid. The synthesis procedure of MA/APEG-PG-(OH)5/PA from AA, PA and APEG-PG-(OH)5 is shown in Figure 2.

Precipitation conditions

The ability of the MA/APEG-PG-(OH)5/PA copolymer to inhibit calcium carbonate scale was compared with that of the free-inhibitor in flask tests. The inhibitor dosages are given on a dry-inhibitor basis. Calcium carbonate was precipitated from supersaturated solutions prepared by mixing $CaCl_2$ and $NaHCO_3$ solutions according to the national standard of China concerning the code for the design of

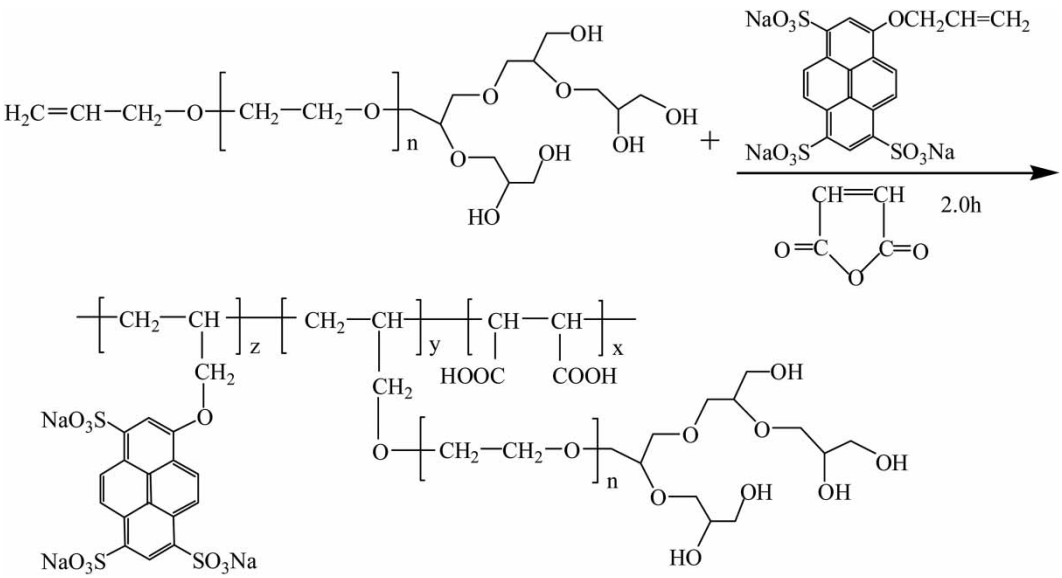

Figure 2 | Synthesis of MA/APEG-PG-(OH)5/PA.

industrial recirculating cooling-water treatment (GB/T 16632-2008). The salts of $CaCl_2$ and $NaHCO_3$ both were analytical reagents from Zhongdong Chemical Reagent Co., Ltd. The prepared solutions, 250 mL of $CaC1_2$ (480 mg/L Ca^{2+}) and 250 mL of $NaHCO_3$ (1,464 mg/L HCO_3^-), were kept in separate glass bottles at room temperature for 5 h to stabilize their temperature. After that time, at the beginning of experiments, these solutions were mixed in a flask of 500-mL capacity immersed in a temperature-controlled bath. To avoid the concentration of the solution by evaporation, especially at a high temperature, we condensed the vapor by means of a cooler. Precipitation of these calcium carbonate supersaturated solutions was monitored after these solutions were heated for 10.0 h at 60°C by analyzing aliquots of the filtered (0.22 μm) solution for Ca^{2+} ions. Concentration by using ethylenediaminetetraacetic acid (EDTA) complexometry titration according to the national standard of China concerning the code for the design of industrial recirculating cooling-water treatment (GB/T 15452-2009). The pH of the calcium carbonate supersaturated solutions was adjusted to 8.7 by using borax buffer solutions. Inhibitor efficiency as a calcium carbonate inhibitor was calculated by using the following equation:

$$\text{inhibition}(\%) = \frac{[Ca^{2+}]_{\text{final}} - [Ca^{2+}]_{\text{blank}}}{[Ca^{2+}]_{\text{initial}} - [Ca^{2+}]_{\text{blank}}} \times 100\%$$

where $[Ca^{2+}]_{\text{final}}$ is the concentration of Ca^{2+} ions in the filtrate in the presence of inhibitor after calcium carbonate supersaturated solutions were heated for 10.0 h at 60°C; $[Ca^{2+}]_{\text{blank}}$ is the concentration of Ca^{2+} ions in the filtrate in the absence of inhibitor after calcium carbonate supersaturated solutions were heated for 10.0 h at 60°C; and $[Ca^{2+}]_{\text{initial}}$ is the concentration of Ca^{2+} ions at the beginning of the experiment.

RESULTS AND DISCUSSION

^{1}H NMR measurements

The ^{1}H NMR spectra of APEG,APEG-PG-(OH)5 and MA/APEG-PG-(OH)5/PA are shown in Figure 3. ^{1}H NMR spectral analysis reveals that the ^{1}H NMR spectra of APEG and APEG-PG are almost the same, except the single peak at 4.5 ppm for active hydroxyl group of APEG (Figure 3(a)); while signals at 4.3–4.8 ppm belong to hydroxyl groups of APEG-PG-(OH)5 (Figure 3(b)). The number of hydroxyl groups was five, which means that on average four glycidol units were grafted to APEG chain. 8.10–9.15 ppm in Figure 3(c) belong to six protons of benzene ring in PA. 3.80–6.00 ppm in (b) double bond absorption peaks completely disappeared in Figure 3(c). This reveals that free radical polymerization among AA, APEG-PG-(OH)5 and PA has happened.

GPC analysis

The molecular mass distributions of MA/APEG-PG-(OH)5/PA copolymer was investigated via GPC. The weight-average molecular weight (Mw) is 9098, and the polydispersity index (PDI) is 2.5364, which strongly suggests that the monomers satisfactorily undergo copolymerization to produce uniform copolymers. The GPC response curve of MA/APEG-PG-(OH)5/PA shown in Figure 4 also indicates a typical low molecular weight product of copolymerization. Molar mass at the maximum peak (Mp), viscosity-average molecular weight (Mv) and the z-average molecular weight (Mz) were also obtained in the curve profiles. Their molecular weights are less than 1.0×10^5. Low molecular weight is an essential parameter for efficient scale inhibition which is achieved through careful control of the reaction rate and timely termination of chain propagation.

Response of fluorescent intensity over a range of MA/APEG-PG-(OH)5/PA

The fluorescence intensity spectra recorded for 2–20 mg/L aqueous solutions of MA/APEG-PG-(OH)5/PA at varying concentrations are shown in Figure 5(a). Also, the result of linearity testing between MA/APEG-PG-(OH)5/PA fluorescence intensity and their concentration is shown in Figure 5(b). Fluorescence intensity was good linear to MA/APEG-PG-(OH)5/PA concentration in the range of 2–20 mg/L which is common dosage scope to the inhibitors. The relationship between MA/APEG-PG-(OH)5/PA concentration and fluorescence intensity provided exceptionally linear response (correlation coefficient

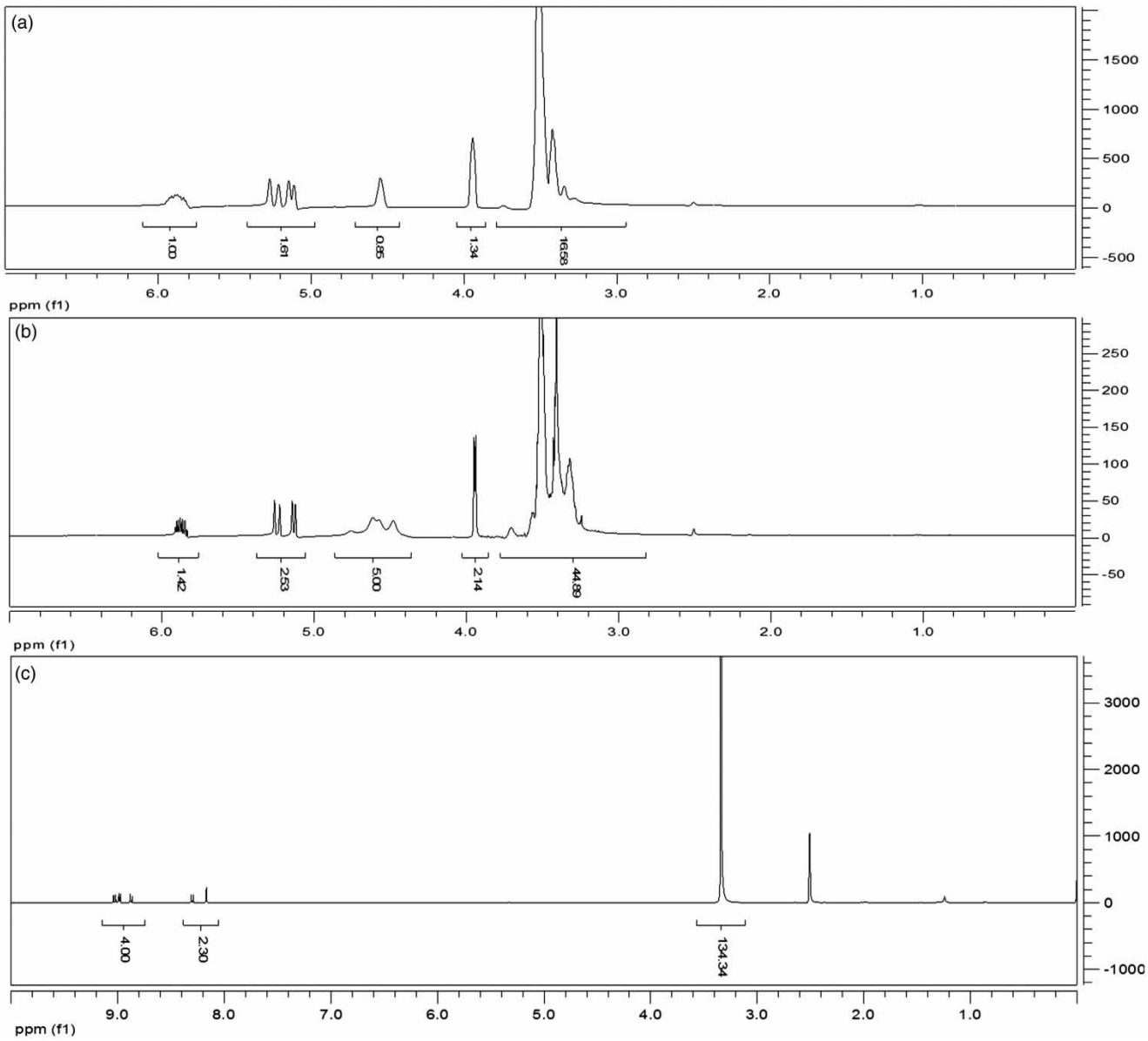

Figure 3 | ^{1}H NMR spectra of APEG (a), APEG-PG-(OH)5 (b) and MA/APEG-PG-(OH)5/PA (c).

R = 0.9991). This positive linear relationship can be used to measure MA/APEG-PG-(OH)5/PA concentration accurately. The dosage change of MA/APEG-PG-(OH)5/PA is pointed out by the fluorescence spectra of MA/APEG-PG-(OH)5/PA. The detection limit of MA/APEG-PG-(OH)5/PA is 0.39 mg/L according to the detection limit formula: $Dr = 3\sigma/k$, where σ is 11 times determination of blank solution's standard deviation and k is slope of calibration curve (Gao *et al.* 2011).

Analysis of the inhibition efficiencies for calcium carbonate scale

Influence of MA/APEG-PG-(OH)n/PA dosage and *n* value

The ability to control calcium carbonate deposits of *MA/APEG-PG-(OH)n/PA* was shown in Figure 6(a). We found that MA/APEG-PG-(OH)n/PA have the similar

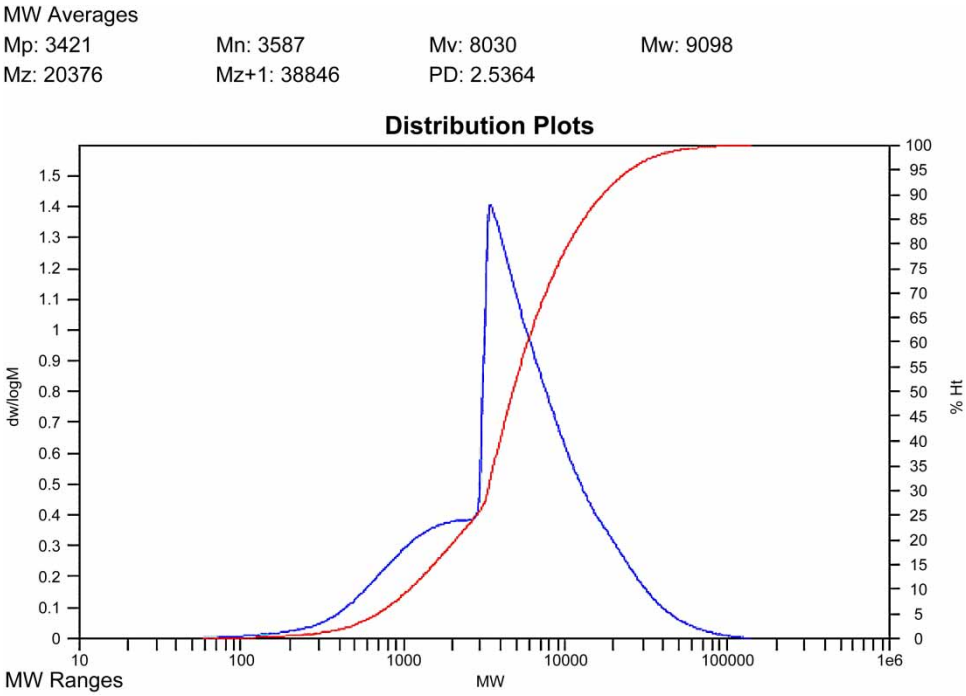

Figure 4 | Retention curve profiles of MA/APEG-PG-(OH)5/PA.

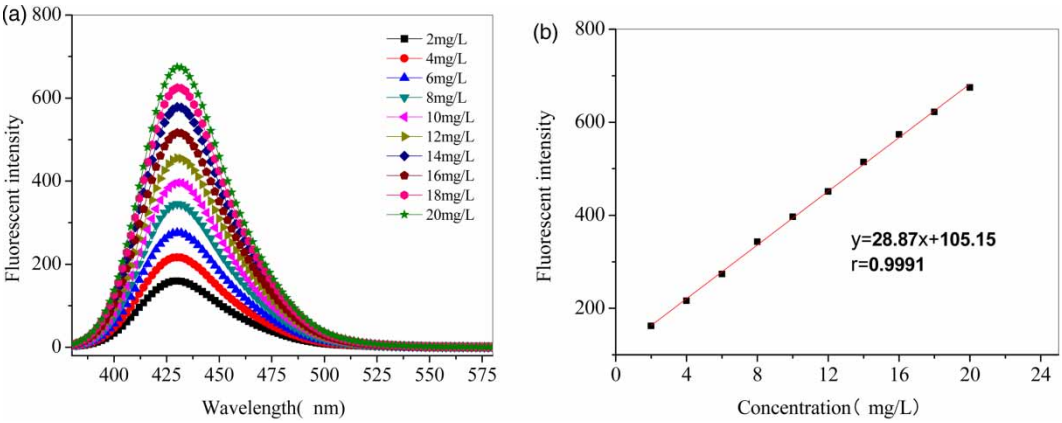

Figure 5 | Fluorescence emission spectra of MA/APEG-PG-(OH)5/PA solutions (a). Linearity of the fluorescence intensity with the concentration of MA/APEG-PG-(OH)5/PA (b).

tendency of the dosage on the performance behavior, for example at the dosage of 2–4 mg/L, the polymers show poor calcium carbonate inhibition; in a certain range, scale inhibition effect increases with increasing the copolymer concentration; and when dosage exceeds the threshold, the effect is no longer increase. It has been reported on polymeric threshold inhibitors in earlier studies. It should be noted that the number of the hydroxyl groups also has a great influence on the scale inhibition effect. Compared to the copolymer of MA/APEG-PG-(OH)n/PA (n = 3,7,9,11), MA/APEG-PG-(OH)5/PA displays superior ability to inhibit the precipitation of calcium carbonate, with approximately 91% inhibition at a level of 8 mg/L. Threshold dosage of MA/APEG-PG-(OH)5/PA is much lower than MA/APEG-PG-(OH)n/PA (n = 3,7,9,11).

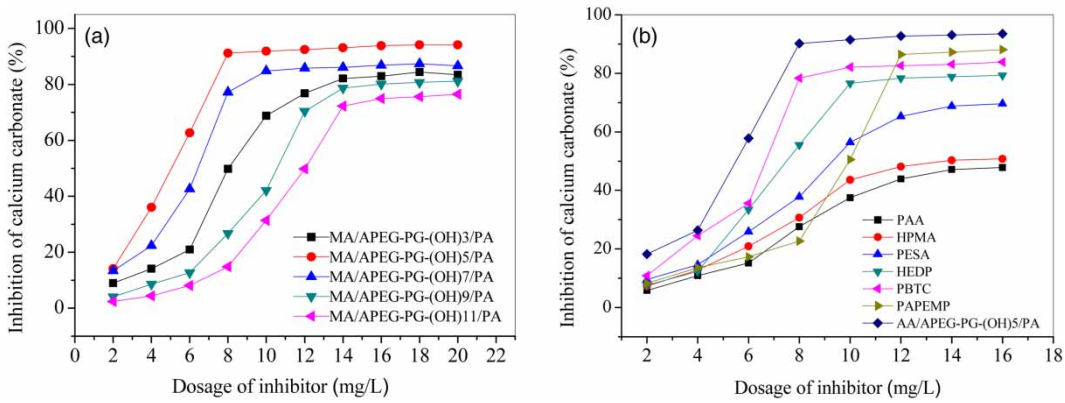

Figure 6 | (a) Inhibition rate on calcium carbonate precipitation in the presence of varying dosages of MA/APEG-PG-(OH)n/PA (n = 3,5,7,9,11); (b) calcium carbonate inhibition of scale inhibitors.

Comparisons of inhibition efficiency

During the last two decades, investigations on polymeric inhibitors to prevent or retard calcium carbonate scales have caught much attention of academic and industrial researchers (Xyla *et al.* 1992; Kotachi *et al.* 2006). Common inhibitors evaluated include PAA, N-(2-hydroxypropyl) methacrylamide (HPMA), polyepoxysuccinic acid (PESA), 2-phosphonobutane-1,2,4,-tricarboxylic acid (PBTC), etidronic acid (HEDP), and polyamino polyether methylene phosphonic acid (PAPEMP), etc., containing acrylic acid or maleic acid and other monomers with different functionalities (i.e. $-CONH_2$, $-COOR$, SO_3H).

In this work, we also studied the influence of these inhibitors on the prevention of calcium carbonate scales as shown in Figure 6(b). It was suggested that the inhibitor composition has an interesting impact on inhibitor effectiveness. As effective inhibitors on calcium carbonate deposits, phosphonates such as HEDP, PBTC and PAPEMP, exhibited significant ability to control calcium-carbonate scales, and their inhibition on calcium carbonate is superior to that of the other investigated nonphosphorus inhibitors including PAA, HPMA and PESA. However, it can be seen from Figure 6(b) that the copolymer of MA/APEG-PG-(OH)5/PA displayed the best ability to control calcium carbonate deposits among all inhibitors investigated.

It is also worth mentioning that PAA and HPMA inhibitors, containing carboxyl groups and possessing molecular structure similar to MA/APEG-PG-(OH)5/PA inhibitor, can hardly control calcium carbonate deposits even at a high dosage. This fact suggests that the side-chain polyethylene glycol (PEG) segments of APEG-PG-(OH)5 and carboxyl groups of AA might play an important role during the control of calcium carbonate scales.

Characterization of $CaCO_3$ scales

In order to investigate calcium carbonate crystals, the XRD was measured in Figure 7. The XRD patterns in Figure 7(a) showed that calcite was the main crystal form in $CaCO_3$ precipitation without scale inhibitor. The diffraction peak strength of the calcite crystal deposited in the blank sample without scale inhibitor was the strongest at 29.24° (the characteristic crystal face 104 of the calcite), which confirmed that the 104 face was the major growth surface without scale inhibitor. In addition, the diffraction peaks at 23.12°, 36.00°, 39.22°, 43.06°,47.52° and 48.38° corresponded to the calcite crystal faces 102, 100, 113, 202, 018 and 118, respectively. However, when the novel copolymer inhibitor was added (in Figure 7(b)–7(f)), the characteristic diffraction peaks of calcite observed in Figure 7(a) were reduced significantly in Figure 7(b)–7(f), which illustrated that the growth of the crystal faces 104, 113, 202 and 118 was completely inhibited by the scale inhibitor. Instead, the diffraction peak at 24.90°, 27.10°, 32.74°, 43.88° and 50.08° (the characteristic crystal face 110, 112, 114, 300 and 118 of vaterite) were observed. This indicated that the scale inhibitor could not only greatly inhibit the crystal growth of calcite but also transform a large amount of calcite phase to the vaterite phase. In a typical aqueous

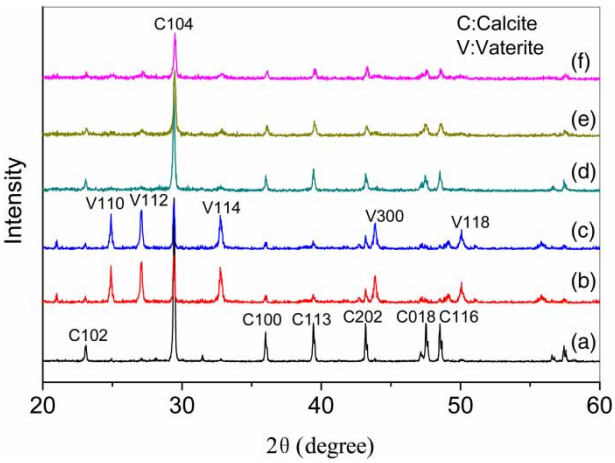

Figure 7 | XRD image of the $CaCO_3$ crystal formed in the absence of MA/APEG-PG-(OH)5/PA (a) and with the presence of different amounts of MA/APEG-PG-(OH)5/PA (b)–(f) ((b) 2 mg/L; (c) 5 mg/L; (d) 10 mg/L; (e) 20 mg/L; (f) 30 mg/L).

system, vaterite is the first phase of calcium carbonate and then changed to a more stable phase (aragonite or calcite) over time (Wei *et al.* 2007). Therefore, the polymer not only can chelate with Ca^{2+}, but also modify the formation of $CaCO_3$. As shown in Figure 7(b)–7(f), With the increase of the addition amount of MA/APEG-PG-(OH)5/PA, the diffraction peaks of calcite and vaterite were decreased. The crystallinity of $CaCO_3$ scales decreased significantly. That is to say, MA/APEG-PG-(OH)5/PA can transform a large amount of calcite phase and vaterite phase to amorphous with the added amount increasing. Amorphous calcium carbonate had loose accumulation, which was difficult to contact with surface equipment firmly, and can be easily washed away by water. In conclusion, the loss of heat transfer can be minimized and scale inhibition can be obtained.

In order to investigate the effect of the scale inhibitor on the growth and morphology changes of $CaCO_3$ crystals, the $CaCO_3$ scales formed in the absence and presence of the scale inhibitor were characterized by SEM analysis. The scanning micrographs of $CaCO_3$ crystals are shown in Figure 8. Compared with the images, both the size and shape of the calcium carbonate precipitation were different due to the addition of an antiscalant. As shown in Figure 8(a), the $CaCO_3$ crystals in the blank sample had regular rhombohedron shape with average particle size of about 5–20 μm. They also had a glossy surface and compact structure. This indicated that the $CaCO_3$ crystals in the blank sample without scale inhibitor were mainly composed of calcite, which was the most thermodynamically stable form of $CaCO_3$ crystal.

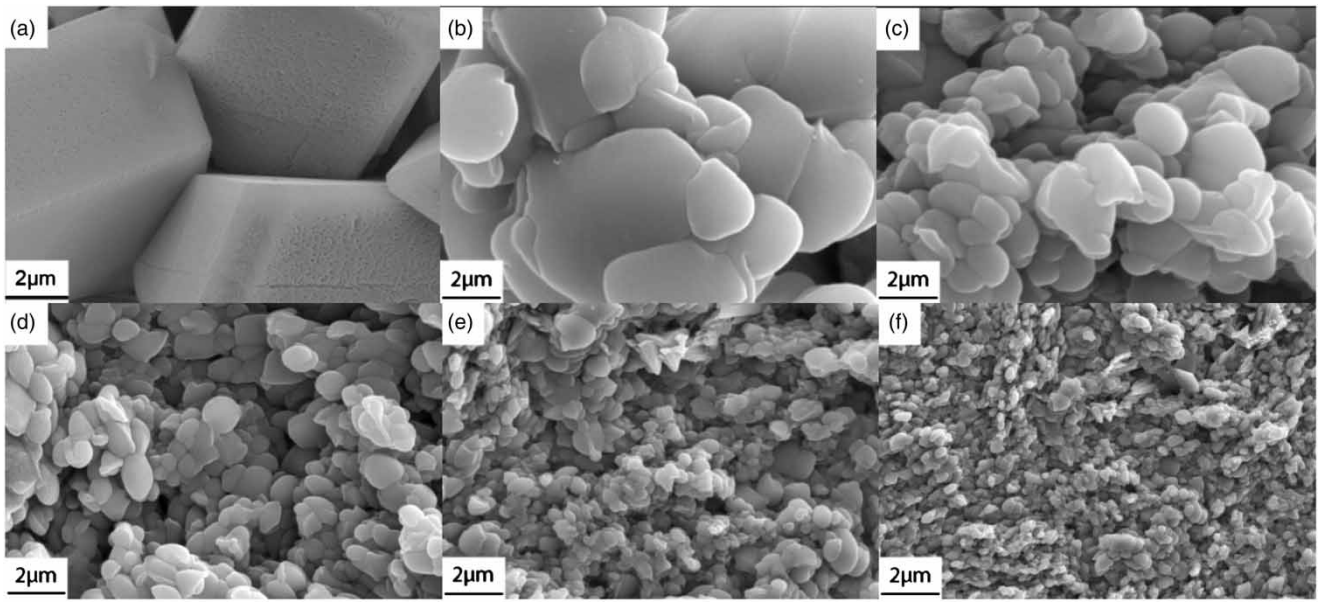

Figure 8 | SEM image of the $CaCO_3$ crystal formed in the absence of MA/APEG-PG-(OH)5/PA (a) and with the presence of different amounts of MA/APEG-PG-(OH)5/PA (b)–(f) ((b) 2 mg/L; (c) 5 mg/L; (d) 10 mg/L; (e) 20 mg/L; (f) 30 mg/L).

When the scale inhibitor was added into the sample, the $CaCO_3$ crystal loses its sharp edges, and the morphology has been modified from rhombohedron forms to the smaller fragments with relatively loose accumulation. Furthermore, the greater the amount of scale inhibitor added, the stronger the influence is on calcium carbonate crystal morphology. Calcium carbonate particles become smaller and smaller as shown in Figure 8(b)–8(f). When the MA/APEG-PG-(OH)5/PA concentration increased to 30 mg/L, the irregular spherical $CaCO_3$ particles' diameter are all in nanoscale (100–300 nm).

The major components of the scale inhibitor were AA and APEG-PG-(OH)n. During $CaCO_3$ crystal growth, the APEG-PG-(OH)n group could affect the scale inhibition efficiency by occupying the active sites on the surface of $CaCO_3$ crystals and changing the extent of chemical bonding with the surface.

In addition, the APEG-PG-(OH)n group and $-COO^-$ group had a high chelating ability toward calcium ions to form stable chelation compounds. These would interfere with the nucleation and growth of $CaCO_3$ crystals so that the crystals became irregular. The distortion in the $CaCO_3$ crystals increased their internal stress, which would lead to crystal fractures and inhibition of deposition of microcrystals. Previous studies suggested that vaterite could be more thermodynamically stable than calcite at certain temperatures or in the presence of some inhibitors (Kralj *et al.* 1997). Thus, it was illustrated that the vaterite possessed higher thermodynamic stability than calcite in the presence of the scale inhibitor. Because vaterite have a higher solubility product and free energy than calcite, the scale was easy to dissolve and can be washed away by water.

CONCLUSIONS

As a green scale inhibitor, the copolymer of MA/APEG-PG-(OH)n/PA was synthesized and exhibited excellent calcium carbonate inhibition. MA/APEG-PG-(OH)5/PA displays superior ability to inhibit the precipitation of calcium carbonate, with approximately 91% inhibition at a level of 8 mg/L. Threshold dosage of MA/APEG-PG-(OH)5/PA is much lower than MA/APEG-PG-(OH)n/PA (n = 3,7,9,11). The result also shows that MA/APEG-PG-(OH)5/PA has better scale inhibition than common inhibitors.

A good relationship between MA/APEG-PG-(OH)5/PA fluorescent intensity and its dosage ensures that MA/APEG-PG-(OH)5/PA is a valuable indicator for cooling water system performance.

XRD and SEM analysis showed that the copolymer of MA/APEG-PG-(OH)5/PA had a great impact on the morphology and size of the calcium carbonate crystal. MA/APEG-PG-(OH)5/PA can transform a large amount of calcite phase and vaterite phase to amorphous with the added amount increase.

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REFERENCES

Alimi, F., Tlili, M., Gabrielli, C., Georges, M. & Ben Amor, M. 2006 Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate. *Water Research* **40**, 941–1950.

Amjad, Z. & Koutsoukos, P. G. 2014 Evaluation of maleic acid based polymers as scale inhibitors and dispersants for industrial water applications. *Desalination* **335**, 55–63.

Chaussemier, M., Pourmohtasham, E., Gelus, D., Pécoul, N., Perrot, H., Lédion, J., Cheap-Charpentier, H. & Horner, O., 2015 State of art of natural inhibitors of calcium carbonate scaling. *Desalination* **356**, 47–55.

Du, K., Zhou, Y. & Wang, Y. 2009 Fluorescent-tagged no phosphate and nitrogen free calcium phosphate scale inhibitor for cooling water systems. *Journal of Applied Polymer Science* **113**, 1966–1974.

Fu, C., Zhou, Y., Liu, G., Huang, J., Sun, W. & Wu, W. 2011 Inhibition of $Ca_3(PO_4)_2$, $CaCO_3$, and $CaSO_4$ precipitation for

Industrial Recycling Water. *Industrial & Engineering Chemistry Research* **50**, 10393–10399.

Gao, L. J., Feng, J. Y., Jin, B., Zhang, Q. N., Liu, T. Q., Lun, Y. Q. & Wu, Z. J. 2011 Carbazole and hydroxyl groups-tagged poly (aspartic acid) scale inhibitor for cooling water systems. *Chemistry Letters* **40**, 1392–1394.

Gatti, R. & Lotti, C. 2011 Development and validation of a pre-column reversed phase liquid chromatographic method with fluorescence detection for the determination of primary phenethylamines in dietary supplements and phytoextracts. *Journal of Chromatography A* **1218**, 4468–4473.

Hasson, D., Shemer, H. & Sher, A. 2011 State of the art of friendly 'green' scale control inhibitors: a review article. *Industrial & Engineering Chemistry Research* **50**, 7601–7607.

Kotachi, A., Miura, T. & Imai, H. 2006 Polymorph control of calcium carbonate films in a poly(acrylic acid)–chitosan system. *Crystal Growth & Design* **6**, 1636–1641.

Kralj, D., Brečević, L. & Kontrec, J. 1997 Vaterite growth and dissolution in aqueous solution III. Kinetics of transformation. *Journal of Crystal Growth* **177**, 248–257.

Wang, C., Zhu, D. Y. & Wang, X. K. 2010 Low-phosphorus maleic acid and sodium *p*-styrenesulfonate copolymer as calcium carbonate scale inhibitor. *Journal of Applied Polymer Science* **115**, 2149–2155.

Wang, L. C., Cui, K., Wang, L. B., Li, H. X., Li, S. F., Zhang, Q. L. & Liu, H. B. 2016 The effect of ethylene oxide groups in alkyl ethoxy carboxylates on its scale inhibition performance. *Desalination* **379**, 75–84.

Wei, H., Shen, Q., Wang, H. H., Gao, Y. Y., Zhao, Y., Xu, D. F. & Wang, D. J. 2007 Influence of segmented copolymers on the crystallization and aggregation of calcium carbonate. *Journal of Crystal Growth* **303**, 537–545.

Xyla, A. G., Mikroyannidis, J. & Koutsoukos, P. G. 1992 The inhibition of calcium carbonate precipitation in aqueous media by organophosphorous compounds. *Journal of Colloid and Interface Science* **153**, 537–551.

Zhang, H., Luo, X., Lin, X., Tang, P., Lu, X., Yang, M. & Tang, Y. 2016 Biodegradable carboxymethyl inulin as a scale inhibitor for calcite crystal growth: molecular level understanding. *Desalination* **381**, 1–7.

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