Synthesis of Poly (Acrylic Acid) Based Polymers as Quantitative Determined Scale Inhibitor

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Abstract

In present days, the use of water transported from the river as the source material for generating electricity is very common. Generally, this water needs to be purified before it can be used in the process. However, during the water purification process, some calcium ion that existed is not uncommon. The calcium ion will somehow create some dregs when absorbing enormous heat, thus adding polymer to capture the calcium ion is necessary. In this research, we focused mainly on the synthesis of poly (acrylic acid) (PAA) as the material to eliminate the dregs by reducing the Calcium carbonate and Calcium sulfate in the water cooling system. This can be done by the free radical synthesis with emulsion technique. Comparison can be made by the length of Polymer Structure PAA-1, PAA-2, PAA-3 and PAA-4 in the solvent as well as adjustment for the mole ratio of potassium persulfate which is used as the initiator. Then, we can further analyze the structure by using FT-IR technique, resulting in the missing of double bond (C=C) of AA monomer in the 1640-1680 cm-1 wave length interval, and turn to be single bond in the main structure of PAA. This result reflected that the synthesis can truly produce polymer. With that, we can further analyze the ability to eliminate dregs by using titration technique with PAA-1, PAA-2, PAA3 and PAA-4 at the concentration of 20 ppm, with high preventive percentage of 72%, 81%, 100% and 90% accordingly. The test result clearly shows that low concentration can perform better in eliminating dregs. Lastly, the final product of this research can be proved by identifying using the UV-Vis spectroscopy technique.

Keywords: Poly(acrylic acid), Solution Polymerization, Scale Inhibitor

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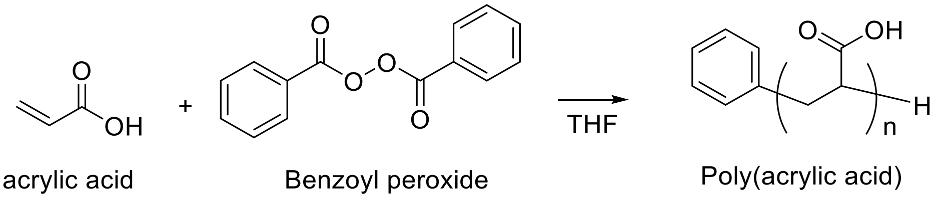
1. Introduction

Circulating cooling water systems for industrial use in the production line has a quality control system. As water from the river is used in the cooling process has a relatively high hardness level. Therefore, there is need for water treatment before use. During the water treatment process a small amount of Ca^{2+} is contained. During water evaporation process, the saturated concentration will cause scale. To solve these problems, the use the polymer with properties to inhibit calcium ions is necessary in order to prevent scale. The addition use of chemicals as an alternative to solve the problem of scale and corrosion in the system is also required. Polymer as chemicals used to create a bond with cations contained in the water, especially Ca^{2+} and Mg^{2+} to produce complexing compounds [1,2] and then removed from the production process by precipitation. Normally the selected polymer to use for water quality control is a group of chemicals Poly(acrylic acid) (PAA) [3,4] which has a chemical structure and a functional group that helps to create a bond with metal ions as well. Acidity and properties to trap scale in order to made crystals of the scale distorted from normal and suspended in the water, so it could not reform to scale again.

In this research is focused on the synthesis and the ability to inhibit scale of Poly(acrylic acid) end capped with phenyl group with different weighing ratio of the monomer to initiator through solution polymerization (Scheme1) and quantitative analysis of remaining polymer in cooling water system.



Scheme.1 The equation of synthesis polymer

2. Experimental

2.1 Polymer preparation

The series of PAAs were synthesized by solution polymerization of Acrylic acid and Benzoyl peroxide with dried THF as solvent. The solution of monomer was stirred under N_2 atmosphere for 10 minutes then refluxed at 70 °C for 3 hrs. The solvent was then removed under reduced pressure and was dried in oven at 70 °C for overnight to obtain the colorless solid polymer.

2.2 Polymer characterization

2.2.1 FTIR analytical

The prepared polymer was mixed with KBr in the ratio of 1:100 and grind to a find powder. The the finely ground mixture was placed into two stainless steel disks and transfer the sandwish disk onto the pistill in the hydraulic press with 4 ton compression for 10 minute and analysed with FTIR spectrometer range of wavelength between 400-4000 cm^{-1}.

2.2.2 UV-visible analytical

The stock solution of PAA 400 ppm was prepared and diluted the concentrations to 10-100 ppm. Measuring the absorbance of polymer solution at wavelength 190-300 nm by UV-Visible Spectrophotometer

2.3 Performance tests of [P(AA-co-AMPS)] as a scale inhibitor

Firstly, the stock solutions of 4000 ppm $CaCl_2$ and 5000 ppm $NaHCO_3$ were prepared as the source of Ca^{2+} ions and HCO^{3-} ions. Then, the blank solution was prepared by using $CaCl_2$ stock solution 12.50 ml and $NaHCO_3$stock solution 12.50 ml then make volume to 250 ml by distilled water in volumetric flask. Next, the standard solution was prepared by using $CaCl_2$ stock solution 12.50 ml and make volume to 250 ml by distilled water in volumetric flask. Lastly, the sample solution was prepared by using stock solution of [P(AA-co-AMPS)] 2500 ppm and diluted to 10-100 ppm and add 12.50 ml of $CaCl_2$ stock solution and $NaHCO_3$ stock solution then make volume to 250 ml by distilled water in volumetric flask. All of portions was placed into shaking water bath at 70 °C shaking speed at 120 rpm for 24 hr, the solution portions were filtered under reduced pressure. The filtrates were titrated with standard EDTA solution and the performance of polymer as $CaCO_3$ inhibitor was calculated using the following equation.

$$\text{Inhibition (\%)} = \frac{\text{EDTA}_{\text{sample}}\text{ (ml)} - \text{EDTA}_{\text{blank}}\text{ (ml)}}{\text{EDTA}_{\text{std.}}\text{ (ml)} - \text{EDTA}_{\text{blank}}\text{ (ml)}} \text{X100} \qquad (1)$$

3. Results and discussion.

3.1 Polymer preparation

All series of PAAs were synthesized via solution polymerization technique using weighing ratios of Acrylic acid to Benzoyl peroxide (Figure 1) which are summarized respectively on Table 1. The Obtained Polymer were tested for the scale inhibition and found that the ratio of synthetic PAA-4 effectively the highest scale inhibition. It has in turn created some aromatic structural in order to extend range of an absorption wavelength of UV-visible and can be quantified the polymer remaining in the cooling water system

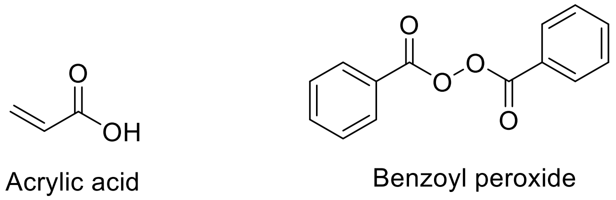


Figure 1 Structure of Monomer

Table.1 The weighing ratio of AA : BPO in each polymer.

No.	Sample	BPO:AA (g)	BPO (g)	AA (g)	M_w (Calculation)	M_w (GPC)
1	PAA-1	1:10	6.871	20.00	438	2,377
2	PAA-2	1:20	3.436	20.00	798	2,503
3	PAA-3	1:30	2.291	20.00	1,158	2,523
4	PAA-4	1:50	1.374	20.00	1,879	2,689
5	PAA-5	1:100	0.687	20.00	3,681	2,831
6	PAA-6	1:150	0.458	20.00	5,482	3,019
7	PAA-7	1:200	0.344	20.00	7,284	3,020

3.2 Polymer characterization

3.2.1 FTIR analytical

The IR spectra of PAAs are showed in Figure 2. The present of absorption at wave number 3400 cm^{-1} (a) are O-H stretching of carboxylic and alcohol group overlaping to the absorption of N-H stretching of the AMPS, C=O stretching of carboxylic and amide groups are presented at wave number 1714.79 cm^{-1} (b). The absent of absorption peak at 1600 cm^{-1}, which is -C=C- bond of the vinyl monomer converted -C-C- into a chain of polymer via the polymerization reaction

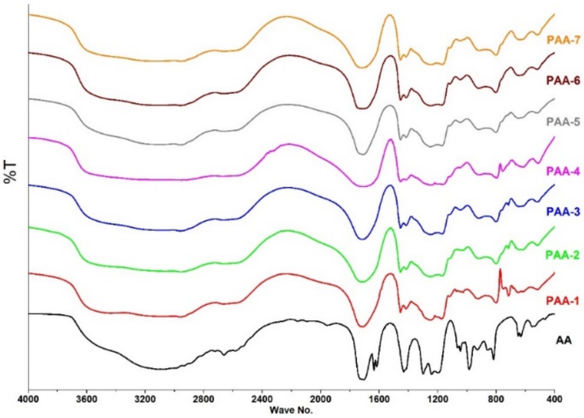


Figure 2 IR spectrum of PAAs

3.2.2 Measuring the UV-Vis absorbance

UV absorption spectra shown in Figure 3, the PAAs have the overlap absorption at wavelength range 195 nm and the line of PAAs, shown two peak of absorptions. By the first wavelength at 195 nm absorption is a carboxyl groups (COOH) of the monomer AA and wavelength at 230 nm is the absorption of aromatic structures of phenyl group.

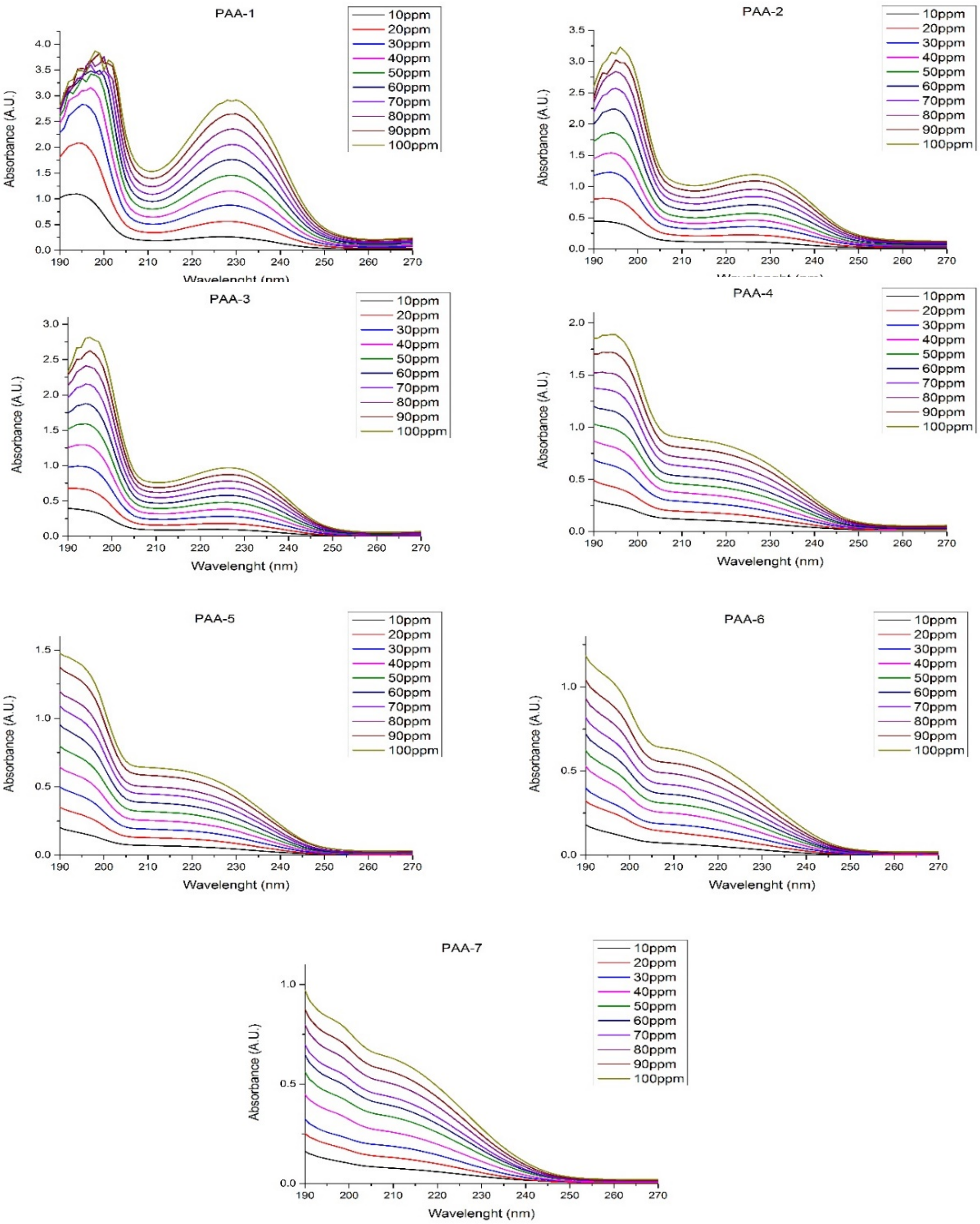


Figure 3 UV-absorbtion of PAAs

Figure 4 the λ_{max} at 230 nm of all series of polymers are used to plot a standard curve in order to quantify the concentration of the remaining of poly(acrylic acid) in the cooling water system. The water samples will be left in the system for measuring the absorbance at 230 nm

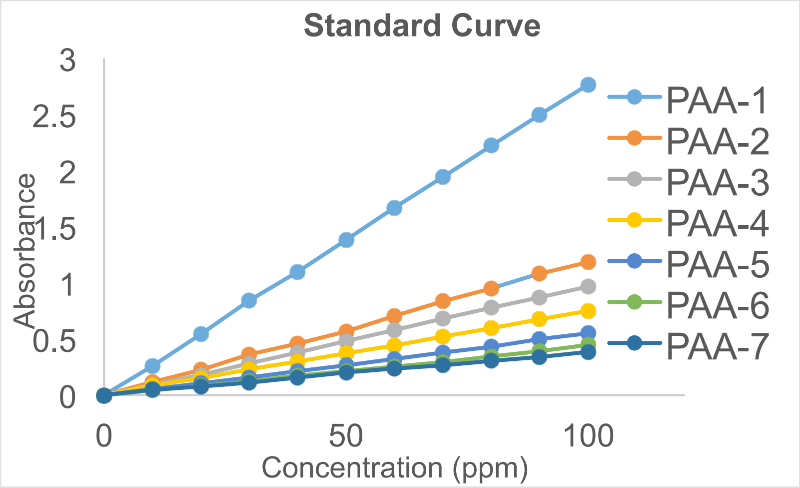


Figure 4 Standard Curve of PAAs

3.2.3 Scale Inhibitor Performance

From the relatively graph between the concentrations of polymers and the percent of scale inhibition which concluded in Figure 2, the data shown that the highest percentage of scale inhibition of polymer under the condition of 200 ppm $CaCl_2$ and 200 ppm $NaHCO_3$ is the polymer with weighing ratio of PAA-4. While effective in inhibiting scale of PAA-1, PAA-2, PAA-3, PAA-5, PAA-7 and PAA-7 was 82.98%, 87.19%, 99.47%, 84.74%, 83.68% and 80.70%, respectively. So ratio of monomer between AA and BPO of PAA-4 was the best ratio for use as scale inhibitor.

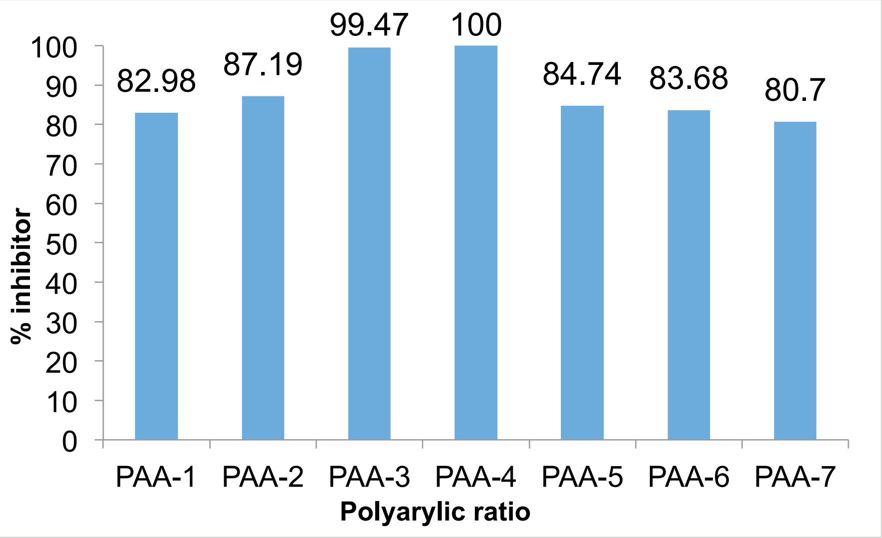


Figure 5 Influence of polymer on $CaCO_3$ inhibition

4. Conclusions.

The PAA-4 shown that it is the highest activity on scale inhibition. Assumptions made that the ratio of copolymer is a suitable match as scale Inhibitor. The short chain polymers (PAA-1, PAA-2 and PAA-3) may be not bonded well to Ca^{2+} ion result to reduce in inhibition performance. In furthermore, the long chain polymer (PAA-5, PAA-6 and PAA-7) are not dissolved well in water then the inhibition efficiency is lower than PAA-4.

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