

pH-Responsive Copolymers as Silica Scale Inhibitors

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ABSTRACT

In the present work two synthetic co-polymers, U-PVPyPEGMA-H and Q-PVPyPEGMA-H, with pyridine and polyethylene glycol grafts on a methacrylate backbone, were studied for their potential to influence silicic acid polycondensation in vitro in silicate-supersaturated (500 ppm, 8.3 mM) aqueous solutions. The aim of this study was to evaluate the impact of several experimental parameters on the silicic acid polycondensation process. Working pH plays a significant role on the silicification reaction either in the absence or presence of polymers. In the presence of polymers, pH affects the protonation state of the pyridine N atom, transforming U-PVPyPEGMA, for example, from a silica formation catalyst (at pH=5.0) to a silicic acid stabilizer (at pH = 7.0). Furthermore, the state of N atom on the pyridine ring (non-protonated, protonated, quaternized) strongly affects the silicic acid autocondensation process. Based on our results, a “free” (non-protonated) pyridine ring induces silica inhibition, whereas protonation or quaternization enhances silica formation. Another parameter that was studied was the concentration of the polymers. As the concentration is increased, enhances the silicic acid stabilization activity or the catalytic activity of the polymers. Polymer MW was found to have no major effect on polymer activity either as stabilizers or catalysts.

Key words: silicic acid, inhibition, polyvinylpyridine, polycondensation, pH-responsive polymers

INTRODUCTION

Silicon is an important element of our Planet's crust, which is transferred into water streams through dissolution.¹ Hence, it is usually found as water-soluble silicate or colloidal silica in natural surface waters (sea, rivers, lakes), or underground waters. When such water is used for industrial purposes (eg. industrial cooling), silicate can enter the operating system and can pose a threat to its proper

operation. The main reason is the solubility of amorphous silica, a product of the silicate polycondensation process.²

The solubility of amorphous silica is the main limitation for proper operation of water-dominated production processes. In several areas in the world, the make-up water utilized for industrial applications contains high silica concentrations (50 - 100 parts per million, ppm, commonly expressed as silicon dioxide, SiO₂). Water-soluble silica results from quartz (crystalline SiO₂) dissolution from rock formations into the groundwater, which then is used as make-up water. The risk for formation and deposition of silica scale puts forth serious challenges that pose severe limitations to proper operation of water systems. Water systems operating personnel in power plants, evaporative cooling systems, semiconductor manufacturing, boiler and geothermal systems have to monitor water silica levels (both soluble and colloidal) very carefully on a daily basis. Silica precipitation/deposition frequently is encountered in evaporative cooling systems, where salt concentrations increase through partial evaporation of the cooling water. Silica solubility in water generally is 150 ppm to 180 ppm, depending on water chemistry and temperature. This imposes severe limits on water users, leading either to operation at very low cycles of concentration and consuming enormous amounts of water, or to use of chemical water treatment techniques that prevent silica-scale formation and deposition. Silica and/or silicate deposits are particularly difficult to remove once they form. Potentially hazardous chemical cleaning (based on hydrofluoric acid) or laborious mechanical cleaning usually is required.³

It becomes apparent that the need of well-thought strategies for mitigation of silica scale is a pressing, and still largely unresolved issue. In the past several years we have been working on several chemistry-driven inhibition approaches to combat silica scale. Our previous inhibition chemistry included polyaminoamide dendrimers, polyethyleneimine, polyallylamine hydrochloride, poly(acrylamide-co-diallyldimethylammonium chloride), cationically-modified inulin, combinations of cationic/anionic assemblies, zwitterionic, phosphonate-grafted chitosan macromolecules and neutral polymers, such as polyvinylpyrrolidone and polyethylene glycols.⁴ Our recent focus has been devoted to polymers, that demonstrate pH-dependent behavior.⁵

In this paper, we evaluate the synthetic pH-responsive statistical co-polymers, see Figure 1, unmodified poly(4-vinylpyridine-*stat*-poly(ethyleneglycol)methacrylate) (**U-PVPyPEGMA**) and methyl quaternary poly(4-vinylpyridine-*stat*-poly(ethyleneglycol)methacrylate) (**Q-PVPyPEGMA**) at three pH values, 5.0, 7.0, and 8.5 for their potential to influence silica formation *in vitro* in silicate-supersaturated (500 ppm, 8.3 mM) aqueous solutions. It was documented that the two factors principally affecting silica formation in the presence of **PVPyPEGMA** polymers were solution pH and polymer quaternization, which triggered their action as silicic acid stabilizers or catalysts for silica formation. The **U-PVPyPEGMA** (H and L, unmodified) were synthesized according to published procedures (H and L stand for high and low molecular weights, respectively, see caption of Figure 1).⁶ **Q-PVPyPEGMA** (H and L, quaternized) was prepared by modifying this procedure by alkylating with methyl iodide as a final step. Notations: U = unmodified; Q = quaternized; PVPy = poly(4-vinylpyridine); PEGMA = polyethylene glycol methyl ether methacrylate; For the U polymers, H = high MW 129,030 Daltons, L = Low MW 86,744 Daltons; For the Q polymers, H = high MW 129,125 Daltons, L = Low MW 86,839 Daltons.

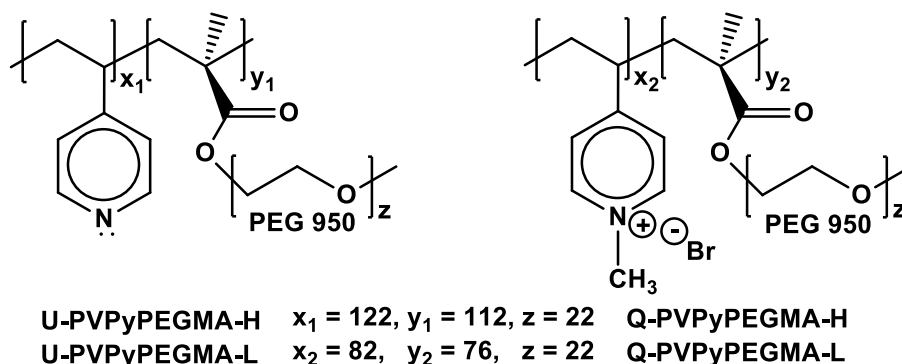


Figure 1: Schematic structures of the copolymer additives used in this work.

EXPERIMENTAL PROCEDURE

Solution preparation

Sodium silicate stock solution

The sodium silicate stock solution used in all experiments containing 500 ppm silicate (expressed as ppm SiO_2 , 8.33 mM) was prepared by dissolving 4.080 g of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in 2 L of DI water. The mixture was stirred for at least a day to ensure complete salt dissolution. A non-glass container must be used to avoid silicate leaching from glass.

Inhibitor stock solutions

Stock solutions of all polymers were prepared by dissolving 0.100 g of the solid inhibitors in 10 mL of DI water (10000 ppm, expressed as actives).

Reagent solutions for the silicomolybdate (molybdenum yellow) method

The following solutions were prepared for the silicomolybdate spectrophotometric detection test: (a) The ammonium molybdate solution (kept in the refrigerator) was prepared by dissolving 10 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 100 mL DI water, to which about 2.5 g of solid NaOH were previously added under stirring, followed by pH adjustment to 7.7–7.8, to avoid precipitation of ammonium molybdate. (b) A 1:1 hydrochloric acid stock solution was prepared by mixing equal quantities of concentrated HCl (37 % w/v) and DI water. (c) The oxalic acid solution was prepared by dissolving 8.75 g of solid hydrated oxalic acid in 100 mL DI water. Glass containers were avoided to exclude any potential silicate leaching.

Silicification protocol (control, in the absence of additives)

A plastic (PET) container was charged with 50 mL of the 500 ppm sodium silicate stock solution (as prepared above). Initial pH was measured 11.8–12.0. The pH was subsequently reduced to 7.00, 5.50 or 8.50 (± 0.1) by addition of HCl (NaOH solution was used for minor pH adjustments, with negligible volume change). The container was then covered with a plastic membrane to avoid CO_2 ingress, and set aside without stirring. It was found that no differences in measurements were noted in stirred or quiescent solutions. Sampling (via a Gilson pipette) was carried out every 2 hours for the first 8 hours or after 24, 48 and 72 hours, after pH adjustment, for quantification of molybdate-reactive silica by the silicomolybdate method (see below).

Silicification protocol (in the presence of additives)

The same protocol was followed as the “control”, with the difference that before pH reduction (to 7.00, 5.50 or 8.50) a suitable volume of the tested additive (from the prepared 10.000 ppm stock solutions) was added to achieve the desirable final additive concentration. The tested additive concentrations were 50, 100, 150, 200, 300, and 400 ppm. After that, the same procedure as the “control” protocol was followed.

Determination of molybdate-reactive silica (silicomolybdate method)

Molybdate-reactive silica (as monosilicic and disilicic acid mixtures), was measured using the well-established silicomolybdate spectrophotometric method (yellow).⁷ In a typical experiment about 4 mL of the working solution was filtered through a 0.45 μm syringe filter, 2 mL of which were diluted up to 25 mL with DI water in a special cylindrical quartz cell of 1 cm path length. 1 mL of the ammonium molybdate stock solution and 0.5 mL of HCl 1:1 (as prepared above) were added to the cell, the mixture is mixed well by shaking and left aside for a 10-minute period. The yellow color is left to develop during that time, at room temperature, as the ammonium molybdate reacts with mono- and disilicic acids as well as any phosphate present and forms yellow-colored complexes. Hydrochloric acid addition ensures a strongly acidic solution, necessary for this reaction to occur quantitatively. It should be noted, as it has been reported before, that during the ten-minute period higher oligomers as well as colloidal silica do not participate in the reaction and do not contribute to the intensity of the yellow color. After that, 1 mL of the oxalic acid stock solution is added and the solution is mixed well followed by a 2 min resting period. Oxalic acid is added to destroy any phosphomolybdate compounds formed in order to avoid any color interference which would lead to incorrect measurements (false positive). The photometer is set to “zero absorbance” using a sample of DI water (“blank”). After the second time period, the sample absorbance is measured at 452 nm, and the results are expressed as “ppm SiO_2 ”. To calculate the

concentration of reactive silica in the original working solution, an appropriate dilution factor (27.5/2) is applied.

RESULTS

Silica stabilization chemistry

Silicic acid polycondensation experiments in the absence (control) or presence of the two synthetic polymers (**U-PVPyPEGMA-H** and **Q-PVPyPEGMA-H**) were carried out at three different pH values, 5.0, 7.0 and 8.5 in 3-day experiments at various concentrations (100-200-400 ppm). The results are shown in Figure 2. Silica formation (in the absence of any additives, control) is strongly pH-dependent. It is only ~ 5.5 % complete at pH 5.0 even after 3 days, indicating a slow process. However, it is much faster at pH values 7.0 and 8.5, with 66.5 % and 67.0 % conversion to amorphous silica, respectively (24-hour measurements). Therefore, silicic acid is fairly stable at pH = 5.0 because all silicic acid molecules are fully protonated, and condensation is minimal. As pH increases to higher values, silicic acid deprotonation starts taking place, thus generating anionic silicate (mono-deprotonated silicic acid), necessary for initiation of the condensation reaction. It was found that the two molecular weights of the polymers tested do not show different effects on silicic acid polycondensation. Hence, discussion of the results to follow will focus on **U-PVPyPEGMA-H** and **Q-PVPyPEGMA-H** (both “high” molecular weight) polymers.

At pH 5.0 (Figure 2, upper) both **U-PVPyPEGMA-H** and **Q-PVPyPEGMA-H** polymers seem to enhance silica formation in a concentration-dependent manner. First, **U-PVPyPEGMA-H** after 24 hours induces the formation of 43 ppm (~9 % at 100 ppm), 98 ppm (~ 21 % at 200 ppm) and 101 ppm (~ 21 % at 400 ppm) colloidal silica below the “control” values, indicating that the presence of **U-PVPyPEGMA-H** catalyzes the polycondensation reaction. **Q-PVPyPEGMA-H** has a similar, but more profound effect, as induces the formation of 95 ppm (~ 20 % at 100 ppm), 129 ppm (~ 27 % at 200 ppm) and 270 ppm (~ 57 % at 400 ppm) colloidal silica below the “control” values, rendering **Q-PVPyPEGMA-H** a more efficient catalyst for silica formation. Overall, it appears that pyridine protonation or quaternization plays a significant role in silica formation, as will be discussed later.

At pH 7.0 (Figure 2, middle) **U-PVPyPEGMA-H** demonstrates a different behavior, as it stabilizes silicic acid. Specifically, it stabilizes 41 ppm (~ 12 % at 100 ppm), 72 ppm (~ 22 % at 200 ppm) and 135 ppm (~ 41 % at 400 ppm) silicic acid above the “control” (24-hour measurements). **Q-PVPyPEGMA-H** also exerts a minor stabilizing effect (23 ppm silicic acid above the control, ~ 7 % stabilization) for both 100 and 200 ppm concentrations, but upon dosage increase to 400 ppm, its action is reverted showing a catalytic effect, inducing the formation of 49 ppm (~ 71 %) colloidal silica below the “control” values.

At pH 8.5 (Figure 2, lower) **U-PVPyPEGMA-H** appears to have no effect at concentrations 100 and 200 ppm, whereas, at 400 ppm it stabilizes only 34 ppm silicic acid (~ 10 %) above the control. **Q-PVPyPEGMA-H** on the other hand, exerts a mild catalytic effect at concentrations 100 and 200 ppm, inducing the formation of ~ 20 ppm (~ 12 %) colloidal silica below the control value. When present at 400 ppm concentration, it induces formation of additional 67 ppm (~ 41 %) colloidal silica.