Inhibitory Effects of Multicomponent, Phosphonate-Grafted, Zwitterionic Chitosan Biomacromolecules on Silicic Acid Condensation

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This article reports the inhibitory effects of phosphonated chitosan (PCH, synthesized from chitosan (CHS) by a Mannich-type reaction) on the in vitro silicic acid condensation. In particular, the ability of PCH to retard silicic acid condensation in aqueous supersaturated solutions at circumneutral pH is studied. Furthermore, the effect of anionic carboxymethyl inulin (CMI) polyelectrolyte on the inhibitory activity of PCH is systematically studied. It was discovered that when PCH is added in dosages up to 150 ppm, it can inhibit silicic acid condensation, thereby maintaining soluble silicic acid up to 300 ppm (for 8 h, from a 500 ppm initial stock solution). The addition of CMI to working solutions that already contain PCH can further enhance the inhibitory action of PCH. A combination of 150 ppm PCH and 100 ppm CMI maintains 400 ppm soluble silicic acid for 8 h. PCH and CMI combinations also affect colloidal silica particle morphology.

Introduction

The diatom is an ideal protist biosystem for investigation of the mechanism of silicon transport, which is an integral part of the biosilicification process.[1−5] The latter leads to the construction of intricate silica structures that resemble lacework-like patterns of breathtaking beauty and are utilized by nature as structural biomaterials.[6−9] Putting this into perspective, the gross biogenic silica production in surface waters was estimated to be ~240 ± 40 Tmol of Si per annum. This means that marine biological systems process an astonishing 6.7 Gt of silicon annually.[10] Environmental concentrations of dissolved silicon in the ocean are rather low (~70 μM),[10] so diatoms must employ an efficient silicon transport system.[11] Silicon (as orthosilicic acid or silicate) must be transported extracellularly and intracellularly into the silica deposition vesicle (SDV), where silica morphogenesis occurs.[12−15] Cells maintain pools of dissolved silicon (in poorly defined chemical form) in relatively high concentrations. Intracellularly, local concentration gradients might be present, which allows an increase in silicate concentration at the site of deposition, most likely at the edges of the expanding SDV. Silicon is taken up during only a specific time in the cell cycle (just prior to cell wall synthesis), and the kinetic parameters for silicon transport were found to vary during the uptake period.[16,17]

The above significant observations point to the necessity of maintaining a relatively high silicic acid concentration (above its maximum solubility) for a period of time and on an as-needed basis before its condensation and uptake for the construction of the cell wall. Nanopatterned silica formation may be a precisely chosen pathway in nature that leads to preferred structural motifs; however, this is not the case in several engineering applications, such as water chemical technology.[18] In supersaturated silica-laden process waters, silicic acid polymerizes via a condensation polymerization mechanism at appropriate pH regions.[19] After Ostwald ripening,[20] the resulting amorphous silica precipitate is transformed into a hard and tenacious scale deposit on critical industrial equipment, such as heat exchangers, transfer pipes, and so on. Silica removal by dissolution is a challenge[21,22] and thus limits the usual control approaches to maintaining undersaturation (leading to water wastage) or pretreatment (with high capital/equipment costs).

Herein, we report a strategy for retarding silicic acid condensation in supersaturated aqueous solutions by using nontoxic, "green", zwitterionic phosphonomethylayed chitosan (PCH, Figure 1) and its combination with "green," anionic carboxymethyl inulin[23] (CMI, Figure 1).

This approach is based on the following principles: (a) A water-soluble sodium silicate ($Na_2SiO_3 \cdot 5H_2O$) is utilized as the silica synthon (in contrast with TEOS used in several in vitro studies). (b) A modified chitosan polymer in which phosphonate groups have been chemically introduced by design is utilized.[24] PCH is a polymer that possesses both cationic ($-NH_3^+$, $-NH_2^+R$, and $-NH^+R_2$) and anionic charge ($-PO_3H_{(2-x)}^{x-}$, $x = 0$, 1, or 2), in contrast with purely cationic chitosan. (c) The pH of silicic acid condensation is circumneutral. (d) The initial silicic acid concentration in our experiments is 500 ppm (expressed as ppm SiO_2), corresponding to ~8.33 mM. We have purposely selected the aforementioned silicic acid concentration to resemble actual silicate levels in the cell and to represent a worst-case scenario in process waters. We note that although the intracellular silica pool can be as high as 450−700 nM/cell[25] the actual level seems to range from less than 1 to about 20 mM (equivalent to a solution of ~1% w/v SiO_2), as recalculated from the silica content and the biovolume for more than 70 species that have been compared for their silica content.[26] (e) The present focus is additive-induced retardation/inhibition of the condensation of soluble silicic acid and also the examination of the morphological features of precipitated silica nanoparticles that form after (unavoidable) silica deposition occurs. We mention that the inhibitory action of PCH is not 100% effective; therefore, silicic acid condensation eventually takes place and produces amorphous silica.

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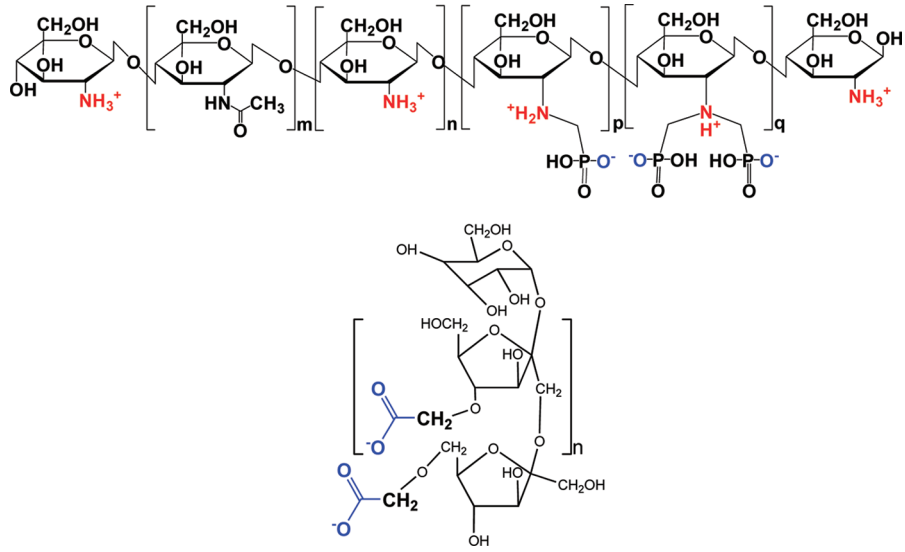

Figure 1. Schematic structure of the zwitterionic phosphonomethylated chitosan backbone (upper, $m = 0.16$, $n = 0.37$, $p = 0.24$, $q = 0.14$) and anionic carboxymethyl inulin (lower).

Experimental Section

Instruments. IR spectra were recorded on an FT-IR Perkin-Elmer FT 1760 instrument. The measurements of soluble silicate were made with an HACH 890 spectrophotometer (Hach, Loveland, CO). SEM images were collected on a scanning electron microscope LEO VP-35 FEM.

Reagents and Materials. Sodium silicate ($Na_2SiO_3 \cdot 5H_2O$), ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), and oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) were from EM Science (Merck). Sodium hydroxide (NaOH) was from Merck, and hydrochloric acid (37%) was from Riedel de Haen. Acrodisc filters (0.45 μm) were from Pall-Gelman. In-house, deionized water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts. PCH was synthesized according to published procedures.[24] Molecular weight determination for PCH was performed by viscosity analysis of a PCH aqueous solution. The solvent system used was 0.3/0.2 M AcOH/AcONa. The values for the Mark−Houwink equation K and a constants were 1.81×10^{-2} and 0.93, respectively. Viscosity measurements were made on an Ubbelohde viscometer (Schott Geräte TYP 52520/II). The average molecular weight was found to be ~254 KDa. The LC_{50} of PCH was 280 ± 30 mg/L (Zebra fish), which is similar to that of chitosan (300 ± 18 mg/L), indicating that phosphonomethylation does not enhance toxicity. The average MW of CMI was ~2.5 KDa. CMI has been investigated in a series of acute toxicity (oral rat, >2000 mg/kg b.w.), subacute toxicity (28 days, rat 1000 mg/kg b.w.), mutagenicity (Ames test, in vitro cytogenetics, no effect), and dermal sensitization studies (guinea pigs, no effect) to evaluate its toxicological profile.[27] Carboxymethylation of inulin on a laboratory scale can be achieved in aqueous alkaline medium with monochloroacetic acid as the reagent.[23] Carboxymethyl inulin was from Solutia.

Preparation of Supersaturated Sodium Silicate Stock Solutions. A solution containing 500 ppm sodium silicate (expressed as ppm SiO_2) was prepared by dissolving 4.4 g of $Na_2SiO_3 \cdot 5H_2O$ in 2.5 L of nanopure water. The pH of the above solution was 11.50. Stock solutions of the additives (PCH and CMI) in water were 1% (10 000 ppm). The PCH solution had a pH of 7.65 and the CMI solution had a pH of 7.03. The following solutions were prepared for the silicate spectrophotometric detection test: (a) Ammonium molybdate (10 g) was dissolved in 100 mL of water, and its pH was adjusted between 7 and 8 with NaOH to avoid precipitation of ammonium molybdate. This solution was kept in an airtight PET container in the refrigerator. (b) HCl 1:1 was prepared by mixing one volume of 37% HCl with an equal volume of water. (c) Oxalic acid (8.75 g) was dissolved in 100 mL of water. All solutions were kept in PET containers (glass containers must be avoided to minimize SiO_2 dissolution and silicate leaching in the test solutions).

Silicic Acid Condensation Protocol (Control). To a plastic container that contained a Teflon-covered magnetic stir bar was added 100 mL of the 500 ppm (expressed as ppm SiO_2) sodium silicate stock solution. The pH of this solution was initially ~11.5 and was adjusted to 7.00 ± 0.1 by the addition of HCl (and NaOH, if needed, for accurate pH adjustment). The pH was not readjusted during the course of the experiments. We found that it always remained in the range of 7.0–7.3 within the first 8 h. Then, the container was covered with a plastic membrane to minimize exposure to laboratory conditions and was set aside under quiescent conditions. (Stirring does not alter results.) The solutions were checked for soluble silicic acid by the silicomolybdate method:[28] every hour for the first 8 h (short-term experiments) or after 24, 48, and 72 h (long-term experiments) time intervals after the pH adjustment to 7.00 ($t = 0$).

Inhibition of Silicic Acid Condensation Protocol. To plastic containers charged with Teflon-covered magnetic stir bars were added 100 mL portions of the 500 ppm (as SiO_2) sodium silicate stock solution. In each container, different volumes of polymer (10 000 ppm stock solution) were added to achieve the desirable additive concentration. For example, for a 50 ppm inhibitor concentration, 0.5 mL of the (10 000 ppm) inhibitor stock solution was added. After that, a procedure that was the same as the control test was followed. All volume alterations beyond the initial 100 mL were taken into account in the final calculations.

Results

The chemically modified chitosan biopolymer PCH was tested for its ability to inhibit the condensation of silicic acid and to influence silica formation in short-term experiments (8 h duration) at 150 ppm (Figure 2). Silicic acid condensation appears to be virtually independent of the additive dosage within the first 8 h. (See the Supporting Information.) Silicic acid (as measured by the silicomolybdate method[28]) reaches a value of ~300 ppm, which is an additional ~100 ppm silicate stabilization compared with the control. PCH was also tested in 24−48−72 h (long-term) tests and was found to be effective at dosages of >60 ppm. (e.g., at 60 ppm PCH, $[SiO_2]_{soln} = 226$ ppm (24 h); see the Supporting Information. $[SiO_2]_{soln}$ increases almost linearly as [PCH] increases to 200 ppm but then levels off.)

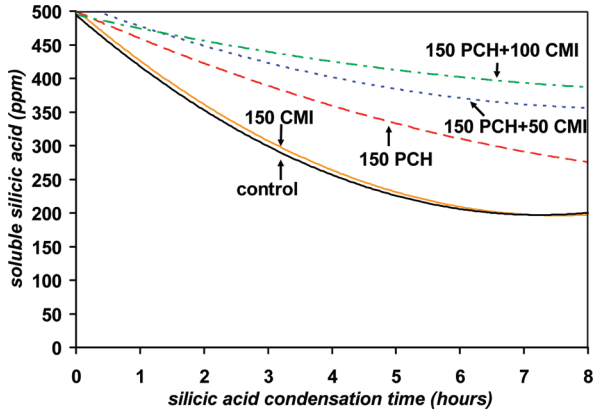

Figure 2. Inhibition of silicic acid condensation in the presence of zwitterionic PCH and combinations with anionic CMI. Soluble silicic acid is expressed as ppm SiO_2.

Combinations of PCH/CMI added to silicic acid supersaturated solutions cause a substantial delay of silicic acid condensation (8 h experiments), which suggests that CMI causes alterations in the solution structure of PCH and perhaps creates supramolecular assemblies through electrostatic ($-NH_3^+\cdots{}^-OOC-$) interactions. Specifically, a 150/50 ppm PCH/CMI combination inhibits condensation, thus resulting in ~100 and ~160 ppm additional silicic acid levels compared with similar solutions that contain only PCH and the control, respectively. A CMI level increase to 100 ppm leads to further stabilization (~380 ppm soluble silicate). A further CMI level increase has no effect. When CMI was tested as an inhibitor, it showed no activity beyond that of the control. (See Figure 2.)

PCH/CMI combinations were also tested in 24−48−72 h (long-term) tests. A much less profound overall inhibiting effect was observed, with the most effective combination being 150/50 ppm PCH/CMI, which yielded $[SiO_2]_{soln}$ = 241 ppm (24 h). (See the Supporting Information.) Therefore, the effect of CMI in augmenting the inhibitory action of PCH appears to be short term (8 h), and it slowly deteriorates over time (>24 h). We note that when anionic CMI is used as the sole inhibitor (no PCH added) there is no effect on long-term silicic acid condensation. (See the Supporting Information.) This is in accord with previous results obtained in our laboratory (not published) that showed that anionic polyelectrolytes do not affect silicic acid condensation at low (<150 ppm) dosages. The above experiments were repeated in the presence of 0.5 M NaCl. Similar results were obtained but with systematically lower soluble silicic acid (20−50 ppm).

PCH apparently retards silica formation, but its inhibiting effect slowly deteriorates over time. We studied precipitated silica to evaluate the PCH or PCH/CMI template effect. Significantly, PCH is eventually entrapped in the silica amorphous matrix, as demonstrated by FT-IR spectroscopy of silica precipitates from working solutions. This is supported by the examination of the main band of amorphous silica at ~1100 cm^{-1}, which is assigned to the Si−O vibration. The silica−PCH composite shows this main band but with a fine structure (Figure 3), which results from superposition of the Si−O band and the wide band from PCH assigned to the P═O and P−O vibrations, which are also centered around 1100 cm^{-1}.

In addition, two bands at ~1650 and 1580 cm^{-1} from the ν(C═O) asymmetric stretch of the PCH amide functionalities were identified. Encapsulation of cationic organic molecules within the silica matrix is not uncommon and has been previously documented in vitro and in vivo.[29−32]

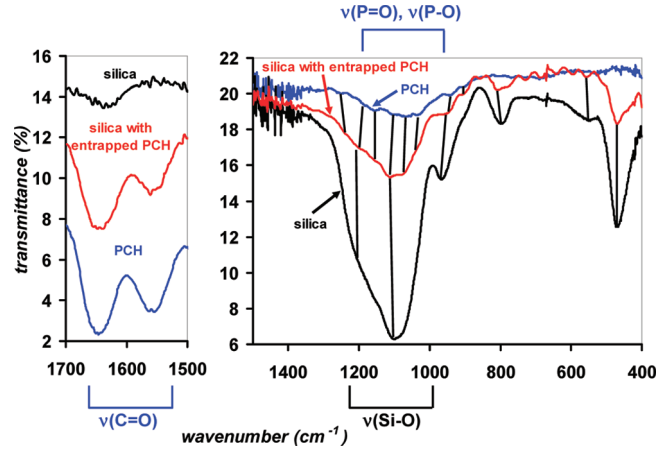

Figure 3. PCH entrapment within the colloidal silica matrix, as demonstrated by FT-IR spectroscopy. Bands due to the antisymmetric $\nu_{C=O}$ vibrations appear at the 1500−1700 cm^{-1} region (left). Bands due to the Si−O and Si−O−Si vibrations appear in the 900−1300 cm^{-1} region (right). The red (middle) spectrum corresponds to silica precipitates that form from working solutions containing PCH. This spectrum is a superposition of the spectra from pure PCH and pure silica. The lines are included to aid the reader.

Silica particle morphology was investigated by SEM (Figure 4) to assess the possible effect of additives on produced silica particle morphology. Silica particles appear after ~6 h of condensation reaction. In the presence of PCH (Figure 4, row 1) the gradual silica particle growth is obvious. Particles are distorted spheres, and their size appears to be ~100 nm after 8 h, growing to ~300−500 nm after 72 h and finally transforming into large aggregates (~2 μm) composed of smaller particles after 4 weeks.

PCH/CMI (150/50 ppm) combinations cause the formation of visibly more discrete silica particles after 8 h (Figure 4, row 2). After 72 h and 4 weeks, the growth of SiO_2 particles is gradual with no large aggregates forming. However, PCH/CMI (150/50 ppm) combinations direct the precipitation of large SiO_2 particles (~2 μm) after 8 h (Figure 4, row 3). After 72 h, particle aggregation continues and well-shaped spherical particles (~0.5 μm) appear. Finally, upon prolonged particle growth (4 weeks), flower-shaped structures are formed (Figure 4, 3c). On the basis of the above results, CMI plays a profound role not only in silicate solubility enhancement (albeit only within 8 h) but also in SiO_2 particle morphogenesis. Although SiO_2 precipitates are inhibited, their particle size appears to be larger. This may be related to the slower silica particle formation and growth in the presence of PCH/CMI.

Discussion

The purpose of this work is to identify and exploit novel synthetic polymer architectures as inhibitors of silicic acid condensation in short-term (<8 h) and long-term experiments (>8 h). PCH, a zwitterionic polymer that contains grafted aminomethylenephosphonate moieties, was shown to delay amorphous silica formation substantially. In synergy with PCH, CMI, an anionic polyelectrolyte (but an inactive silicic acid condensation inhibitor), further mitigates the inhibitory action of PCH. We note, however, that PCH (alone or with CMI) is unable to maintain all initial silicic acid in solution (500 ppm). Silica precipitates are inevitably formed for several reasons: (a) PCH polymer folding may create local high concentrations of cationic charge, therefore inducing silicic acid condensation. (b) PCH entrapment within the silica matrix depletes the

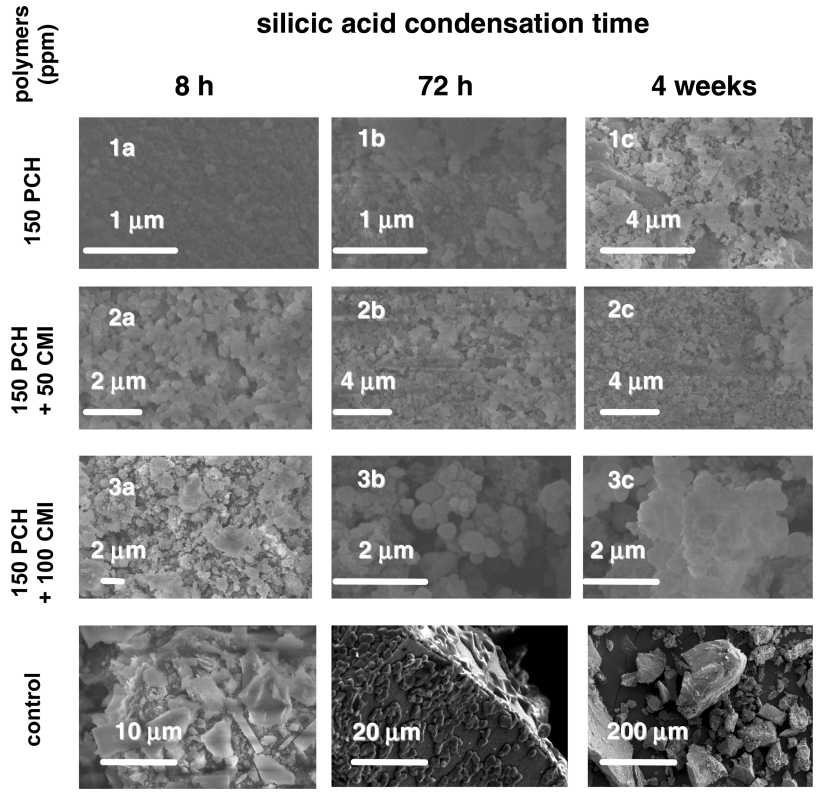

Figure 4. Morphological, time-dependent evolution of silica precipitates in the presence of PCH and PCH/CMI combinations (in ppm).

working solution from the inhibitor. (c) Silicic acid is in more than 10^4-fold excess. The above-described chemistry points to a delicate interplay between polymer(s) charge(s) and in vitro silicic acid polymerization. This could be conceptually linked, at least from a biomimetic/model chemistry point of view, to silicon pool maintainance within the diatom cell, during which relatively high silicic acid levels must be maintained for a period of time.[33] However, thus far, molecules (either polymers or small molecules) that could have such a role in the diatom have not been identified, and any biomimetic/model approach linked to the maintenance of high silicon pools in the diatom contains a high degree of speculation.

The precise mechanism of PCH-mediated, silicic acid condensation disruption is not well understood, but important observations can be put forth. These are based on data reported by us[34−39] and other groups.[40−49] It is well established that polymers that contain some degree of cationic charge (either purely cationic or zwitterionic) interact with silicic acid (or silicate anions) through cooperative interactions, such as hydrogen bonds (or electrostatic interactions, depending on pH, which in turn determines the degree of silicic acid deprotonation, polyamine protonation, or both). These polymer−silicate (or silicic acid) interactions are certainly the source of silicate stabilization in solution. The absence of such interactions, either by using neutral or anionic additives or by blocking cationic ammonium groups by neutralization (by externally added anionic molecules), results in a dramatic drop in silicic acid levels. In the case of PCH, it is worth noting that its parent polymer, chitosan, has been reported by Chang et al. to catalyze silicic acid condensation and to enhance agglomeration of produced colloidal silica particles.[29] Chang et al. did not report any silicic acid measurements, but it is reasonable to assume that they will be low. Their results are in concert with those reported for diatom-extracted silaffins and other synthetic cationic polymers.[30−49] When chitosan is modified into PCH (by grafting phosphonate anionic groups), a zwitterionic polymer is the product. In PCH, there are still protonated amine groups (necessary to interact with anionic silicate or neutral silicic acid), but their propensity to catalyze silicic acid condensation and silica particle agglomeration is compromised. Therefore, PCH is considered to be a silica inhibitor rather than a silicic acid condensation catalyst.

Data published on inhibitory effects of polymers on silica formation are rather limited. Besides our recently published research,[34−39] there are papers that describe the chemistry of some inhibitors. For example, phosphinopolycarboxylic acid (PPCA) causes the stabilization of 325 ppm soluble silicate, albeit at a very high dosage (1000 ppm).[50] Amjad et al. have tested a number of polymers for silica inhibition with an emphasis on reverse osmosis systems.[51] They discovered that a proprietary polymer at a polymer/silica ratio of 1:12 can maintain ~500 ppm of soluble silica in a pilot scale RO system for ~5 h. The conditions of the study were 600 ppm initial silica, 200 ppm Ca, and 120 ppm Mg at 40 °C and pH 7.

A mixture containing MoO_4^{2-}, ethylenetriamine-penta-(methylenephosphonic acid) and a modified polyacrylate copolymer was found to be effective in preventing the formation and deposition of silica-containing deposits.[52] A carboxylate/sulfonate/balanced terpolymer was tested in the field.[53] This multipolymer contains balanced hydrophilic/hydrophobic functional groups that enhance adsorption of the dispersant on colloidal silica and magnesium silicate composite scales when the temperature is raised. In addition, the multipolymer contains sulfonate and carboxylate groups that impart tolerance to soluble iron and superior dispersancy. The presence of the hydrophilic groups serve to induce steric repulsion between silica particles that have polymer chains adsorbed onto them. At 12.5 ppm, hypersperse SI 300, a polyanionic/neutral polymer, maintained soluble silica up to 370 ppm in RO systems.[54]

Recently, Perry et al. have used poly(1-vinylimidazole) mass fractions to inhibit silicic acid condensation.[55] The Si source was sodium silicate. It was reported that very high concentrations of poly(1-vinylimidazole) (5.3 mM) can stabilize ~5 mM silicic acid (or ~300 ppm SiO_2) at pH 7. On the basis of our results, PCH at much lower concentration, 5.91×10^{-4} mM (150 ppm), can stabilize ~5 mM silicic acid (or ~300 ppm SiO_2) at pH 7. A direct comparison between the inhibitory activities of these polymers is not possible because of the lack of data on the time dependence of silicic acid stabilization by poly(1-vinylimidazole).

Breakthrough discoveries in the field of biosilicification include the fact that zwitterionic proteins, sillafins, and LCPAs play a catalytic role and indeed accelerate silicic acid condensation (either in vivo or in vitro).[12−15] On the basis of the results described herein, it appears that PCH can delay silicic acid condensation for a period of time but ultimately cannot stop silica formation. Also, it appears that PCH plays a dual role in amorphous silica synthesis. It retards silicic acid condensation and concurrently acts as a template for modified silica particle morphologies. An intriguing question would be whether silaffins and LCPAs (known to act as silica templates) can enhance silicic acid solubility. Such studies would certainly shed some light onto this effect, but to our knowledge, none have appeared in the literature.

Conclusions

The principal findings of this work are summarized below: (1) PCH is an inhibitor of silicic acid condensation at 40−200 ppm dosage levels in 8 h condensation reactions. (2) PCH cannot quantitatively inhibit polymerization of silicic acid (at an initial level of 500 ppm). It can merely retard the condensation reaction. (3) There is no measurable effect of anionic CMI on polymerization of silicic acid. (4) CMI exerts no adverse effects at any dosage on the inhibitory activity of PCH. (5) Entrapment of PCH into the silica colloidal matrix occurs, leading to the formation of SiO_2−PCH precipitates. This was demonstrated by FT-IR spectroscopy.

Biosilicification is an intricately complicated process whose precise mechanism is still only partially delineated despite several enlightening studies.[34−49,56−63] Furthermore, the effects of a plethora of nature-derived or synthetic polymers and small molecules on biomimetic silica formation have been documented, aiming at delineating the intricacies of (bio)synthesizing silica, a seemingly simple material. The elucidation of the mechanisms that govern biosilica formation and the role that biopolymers play in silica-producing organisms may have significant implications in industrially important scientific fields beyond biology, such as nanoparticle technology.[56−66] Controlling the size and shape (other than spherical) of additive-mediated silica particles in a designed fashion is still an unattained goal, but progress is constantly being made.[40,67] Such research has implications beyond SiO_2-related research. Bioinspired research has been reported for TiO_2- and GeO_2-related chemistry. [56,64,68−74]

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Supporting Information Available. Full experimental details of silicate supersaturation protocols, toxicity studies, instrumentation, and materials. Also, additional results (long-term studies, optical images of precipitated silica, and data analyses). This material is available free of charge via the Internet at http://pubs.acs.org.

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