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Silicic acid condensation under the influence of water-soluble polymers: from biology to new materials

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Silicon is among the most abundant elements on the Earth. It occurs in many minerals and plays an important role in several biochemical processes. Some living organisms use silicon dioxide as a substrate for building elements of their bodies. Unicellular diatom algae build frustules from silicon dioxide. The skeleton of siliceous sponges is a silica–protein composite. Similarly, rice hulls which protect seeds, contain silica as an important component. The living organisms assimilate silicon from the environment in the form of silicic acid. However, the biochemical mechanisms involved in the transformation of silicic acid to solid siliceous materials are still poorly understood. Evidently, condensation of silicic acid in the living organisms proceeds under control of biopolymers and it is important to know how various types of polymers influence the condensation. Bio-inspired chemistry involving the interaction between polymeric silicic acid and functional polymers results in interesting composite materials, including nanoparticles and bulk materials. This review contains a brief description of the mechanism of silicic acid condensation in aqueous medium and also includes a discussion on various precursors of silicic acid. The main focus of the review is on the influence of polymers bearing nitrogen and oxygen-containing functional groups on silicic acid condensation starting from monomer to three-dimensional polymer. Influence of molecular weight of the organic polymer on the condensation and structure of the resulting product is also elaborated. The biological importance of the obtained data and strategies for novel applications of the synthesized composite materials are described in the concluding section of the review. The biomimetic condensation processes open up new vistas for development of novel materials and applications in the biomedical and process industries.

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Introduction

Silicon is among the most abundant elements on the Earth, it occurs in many minerals and plays an important role in biochemical processes. Some living organisms use silicon dioxide as a structural material in their bodies.[1] Diatom algae are unicellular organisms which provide more than 20% of photosynthetic oxygen and contribute to a corresponding amount of primary organic production.[2] The diatom cell lives in a "glass house"[3] – siliceous frustule built from silicon dioxide in a form similar to molten quartz glass (Fig. 1A). Sponges belong to a class of ancient and interesting invertebrates which play an important role in ecosystems as filtering organisms. They also serve as a residence for an enormous number of symbionts. Sponge bodies are inexhaustible source of biologically active compounds.[4] Siliceous sponges represent more than 90% of sponges[5] and their skeleton is based on siliceous spicules – composite needle-like constructions (Fig. 1B). Rice (*Oryza sativa*) is a staple crop consumed predominantly by the Asian population. It has been found that the xylem sap in these plants are rich in silicic acid. The role of silicon in augmenting disease resistance,[6] chlorophyll a content and growth[7] of rice plants has been demonstrated by different research groups. Silica deposits have been found in the cell walls of rice plants and it has been postulated that these silica deposits enhance the stability of the cell wall structure during mitotic cell division.[8] Similarly, silicon deposits have also been identified in the stomata of rice plants and it is believed that these deposits tend to reduce water loss through transpiration.[9] The nano-dimensional silica particles in rice are believed to be formed using hemi-cellulose callose as a template.[10] Biogenic silica and composites are a great challenge to material science specialists because these materials are highly ordered at various levels and a lot of them, *e.g.* diatom frustules consists of a material similar to melting quartz glass[11] which artificial analogs are produced at temperatures above 1000 °C only. Siliceous organisms put many questions to biologists and biochemists: how living organisms capture silicon from the environment? How they store and transport silicon in their bodies? How they build highly ordered constructions from silicon dioxide without high temperatures and hazardous chemicals?

Silicon is present in natural water mainly in the form of monomeric silicic acid. Evidently, transformation of $Si(OH)_4$ to solid SiO_2 or siliceous composites proceeds through condensation in the presence of some organic substances, probably biopolymers. The nature and action mechanism of these substances is yet not thoroughly deciphered. The main approach to discovering novel biosilicification agents involves isolation and separation of organic substances from biosilica, structure identification, study of silicification activity using *in vitro* models, monitoring the transformation of the molecule of interest in the organism and finally formulation of the hypothesis on the mechanism of biosilicification. This strategy had resulted in the discovery of

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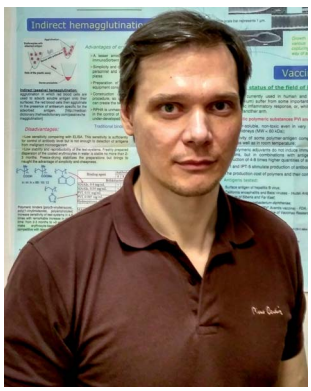

Stanislav Zelinskiy was graduated from the Department of Chemistry, Irkutsk State University, Russia in 1998. He received his Ph.D. in Catalysis from the Irkutsk State University in 2002. He is a researcher in Limnological Institute SB RAS, Irkutsk, Russia. He is author of 25 scientific articles and 5 patents. His scientific interests include synthesis, structure and reactivity of organic compounds; metal-complex catalysis; synthesis of fluorescent dyes and labels.

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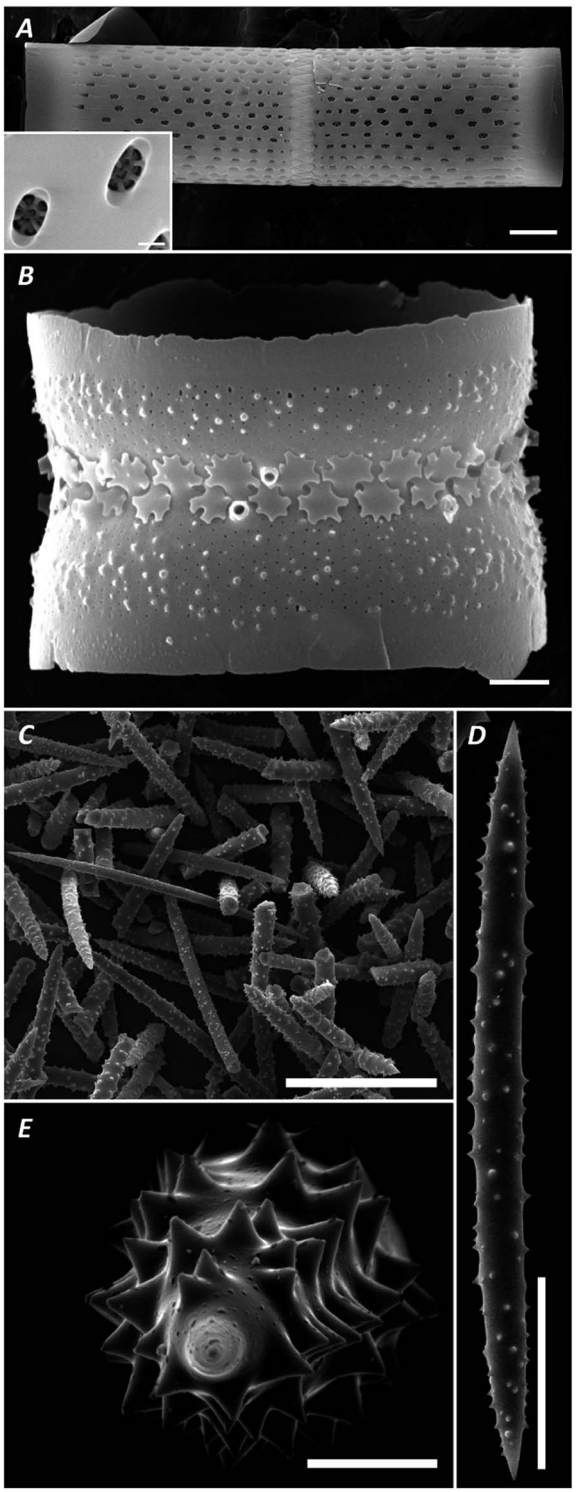


Fig. 1 Siliceous valves of diatoms *Aulacoseira baicalensis* (K. I. Meyer) Simonsen (A), *Stephanodiscus meyeri* Genkal & Popovskaya (B) and spicules of sponge *Lubomirskia baicalensis* (Pallas, 1773) (B). Scale bar represents 5 (A, E), 0.5 (A, insertion), 1 (B), 100 (C) and 50 (D) μm.

silaffins – proteins with phosphate and polyamine post-translation modifications[12,13] and silicateins – proteins capable of catalyzing hydrolysis of Si–O–C bonds.[14] The growing interest in biosilicification during the last few decades has resulted in concerted research efforts devoted to aqueous phase silicic acid condensation in the presence of organic polymers bearing functional groups similar to groups in the hypothesized natural silicification agents. Such studies have at least two objectives – to understand biological processes with simpler and available models and to obtain new bioinspired material, including nanoparticles and bulk composites with the intricate and complex morphologies commonly encountered in the biological systems.

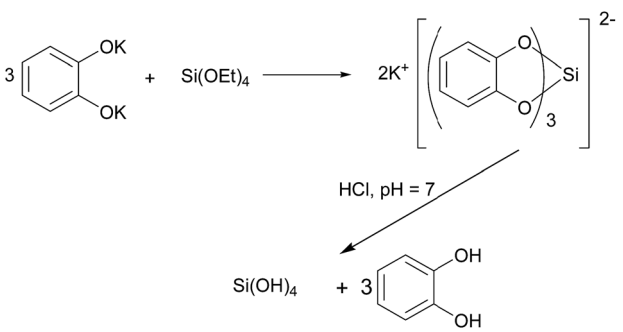
This review summarizes information about $Si(OH)_4$ condensation in aqueous medium in the presence of oligomeric or polymeric molecules capable of interacting with monomeric or polymeric silicic acid. Biological importance and possible applications of these materials are also discussed. Siliceous materials are intensively studied in various fields and we limit this review with water-based systems where free silicic acid is evidently present and plays an important role.

Precursors of silicic acid

Silicic acid is not stable in the free state and hence it is produced *in situ* from various precursors. The most simple and cheap precursors are inorganic silicates like sodium, potassium silicates and liquid glasses of variable composition, *e.g.* $Na_2O \cdot xSiO_2$.[15] Silicic acid is a very weak acid ($pK_a = 9.7–9.9$)[16,17] and addition of acid to a solution of inorganic silicates results in formation of $Si(OH)_4$. The other convenient way to obtain silicic acid from inorganic silicates is through the action of cation-exchange resin in H-form. This procedure facilitates the formation of $Si(OH)_4$ solution free from inorganic salts. Siliceous sols were prepared by acidification of sodium silicate solution with HCl (pH = 1–2) following with action of a cation-exchange resin which removes Na^+ ions.[18] The obtained solutions were not analyzed and it seems that monomeric silicic acid is the main component of these solutions because $Si(OH)_4$ is stable in acidic area.[19]

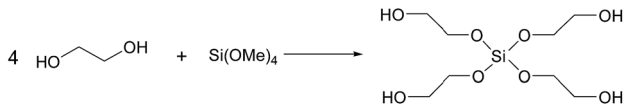
There are also several organic derivatives of silicic acid which are easily hydrolyzable in aqueous medium. Tetramethyl orthosilicate $Si(OMe)_4$ (**TMOS**) interacts with water and gives rise to silicic acid and methanol in approximately ten seconds. TMOS is usually added to 1–2 mM HCl solution which prevents $Si(OH)_4$ from condensation during hydrolysis.[20,21]

Silicon catecholate salts are obtained by the reaction between 1,2-dihydroxybenzene (catechol) salt and tetraethyl orthosilicate (**TEOS**).[22] These compounds are readily hydrolysable at neutral pH values as shown below:



The first study on silicon catecholate salt hydrolysis[23] showed that the concentration of the complex reduces from 50 mM to 20–28 mM during the first 2 min of the reaction and these levels remained virtually unaltered even after 24 h. These data however are in contradiction with the results[24] reported for potassium silicon catecholate salt (**K2-SiKat**) which showed a decrease of K2-SiKat concentration from 30 mM to 0.1–0.7 mM immediately after the pH was adjusted to 7.

Tetrakis(2-hydroxyethyl)orthosilicate (**THEOS**) was obtained by the reaction between TMOS and ethylene glycol[25] as follows:



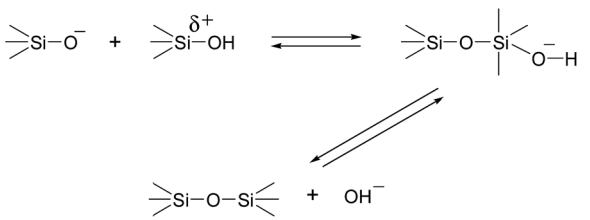
This is a water soluble compound which on hydrolysis gives rise to silicic acid. THEOS was recommended as the precursor for synthesis of unshrinkable silica gels in aqueous medium.[26] There is however, no information about the hydrolysis rate for THEOS and hence participation of partially hydrolyzed forms in the condensation reaction cannot be excluded.

Inorganic silicates produce silicic acid immediately after neutralization with acid and the only byproduct formed is inorganic salt, *e.g.* NaCl. Hence these compounds are most suitable for study of mechanism of silicic acid condensation and for simulating biochemical reactions. On the other hand, the fast hydrolysis rate and alkaline nature of the silicates complicates experiments and can result in irreproducibility. Organic precursors do not have these disadvantages and can be applied for design of siliceous materials. But the stepwise hydrolysis and formation of organic byproducts decrease the utility of these compounds to serve as precursors of $Si(OH)_4$.

Silicic acid condensation in aqueous medium

Condensation of silicic acid has been extensively studied for many decades and it is described in several books and reviews.[19,27–31] We describe here the main peculiarities of the reaction in aqueous medium.

Silicate ions SiO_4^{4-} are stable at high pH values but at pH 13 formation of oligosilicate particles containing several silicon atoms was observed.[32] The condensation proceeds as a nucleophilic substitution reaction (S_N2) between ~Si–OH and ~Si–O^- moieties through a pentacoordinated transition state:[27,33–37]



This reaction requires ionized silanol and neutral ~Si–OH groups. The first ionization constant of $Si(OH)_4$ (pK_{a1}) is 9–10[16,17,38–45] and the subsequent pK_a values are estimated as 11.7–13.4.[17,38–45] While discussing quantitative values concerning silicic acid, we must remember that $Si(OH)_4$ is highly unstable and exists at low pH or in very diluted solutions only. In other cases, various condensed forms appear in several seconds which poses a challenge to the investigators. So, we have some intervals in the measured values. Condensation of silicic acid is a reversible process and the minimal concentration of monomeric $Si(OH)_4$ in equilibrium with solid silica or condensed soluble siliceous particles is estimated as 2–3 mM.[19]

Assuming pK_{a1} as 10, one can calculate the dependence of the concentration of unionized $Si(OH)_4$ species on pH (Fig. 2A). The ~Si–OH moieties occur at relatively high pH and according to our observations, 100 mM aqueous solutions of sodium silicate contain >50% of oligosilicates after several weeks of storage. A decrease in pH to 9.5–10.5 results in formation of considerable amounts of $Si(OH)_4$ and $Si(OH)_3O^-$ molecules which leads to fast condensation of the silicic acid monomers. Further decrease of pH to 7 and below results in almost completely unionized silicic acid and the condensation rate drops.

The other participant of the condensation reaction is oligosilicate molecules or poly(silicic acid) (**PSA**): dimers, trimers and larger particles. PSA contains more acidic groups than monomeric $Si(OH)_4$. The pK_0 for ionization of a first ~Si–OH group on the surface of PSA particles is estimated as 6.8.[19,46] Thus, after formation of PSA particles we have ~ Si–O^- moieties even at neutral and acidic conditions (Fig. 2B). This results in two peculiarities of silicic acid condensation:

(a) Condensation at pH 7 and below proceeds with an incubation period which is necessary for formation of primary PSA particles.[19,47]

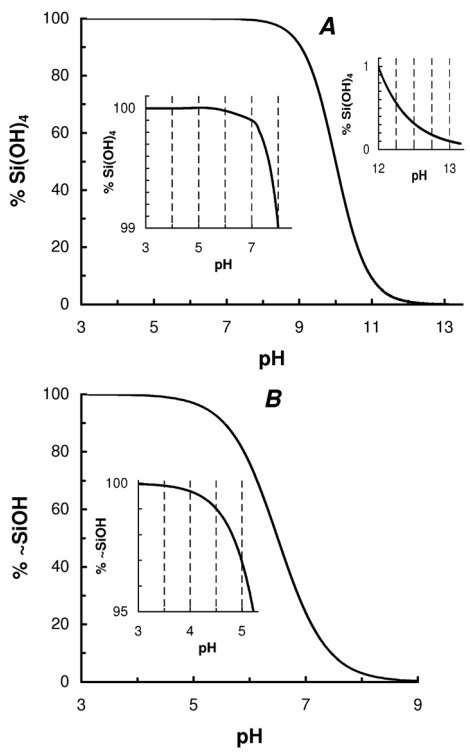


Fig. 2 Effect of pH on the percentages of $Si(OH)_4$ and –SiOH moieties.

(b) The condensation rate depends not only on pH but also on prehistory of the solution, *e.g.* if monomeric silicic acid is maintained at pH 5, it will be stable for some time, but if the solution is stored at pH 9 for several minutes prior to incubation at pH 5, PSA particles will appear and we will observe condensation on the surface of these particles. This unique characteristic opens up a wide range of possibilities for design of siliceous materials. However, it also poses difficulties in data reproducibility.

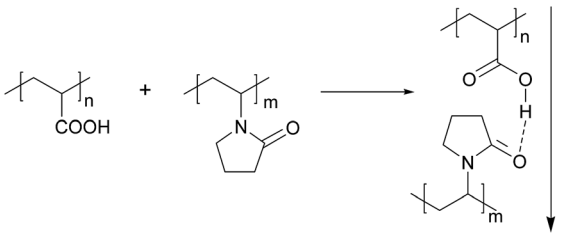
Thus, the first stage of silicic acid condensation results in formation of soluble PSA particles accompanied by a decrease of $Si(OH)_4$ concentration to 2–3 mM. Further fate of these particles depends mainly on pH and total silicon concentration. There are two possibilities for transformation of the primary PSA particles: aggregation and Ostwald ripening.[19,27] Aggregation is observed at pH < 7 because primary particles are almost uncharged in this condition and therefore can interact with each other giving rise to 3D gel structures at concentration greater than 50–100 mM.[48] Ostwald ripening[49,50] is a process of growing large particles at the expense of small particles and this is more characteristic at pH > 7 where PSA particles bear negative charge that prevents aggregation through electrostatic repulsion.

Study of the silicic acid condensation in aqueous medium requires methods for precisely measuring the concentration of monomeric silicic acid. The widely used procedure for quantification of silicic acid involves the reaction of silicic acid with molybdate in acidic medium resulting in the formation of yellow molybdosilicate complexes, the absorbance of which can be measured using a spectrophotometer.[51–53] Sensitivity of the method increases when the yellow complex is reduced to blue products with *N*-methylaminophenol (metol).[54,55] The procedure is optimized to allow only monomers and dimers of silicic acid to react with the molybdate reagent.[24,31,56] The molybdate method is not applicable in the presence of phosphates, *e.g.* when a phosphate buffer is used. An alternate method to measure monomeric silicic acid and its various condensed forms is through ^{29}Si NMR spectrometry.[48] Unfortunately, the natural content of this isotope (4.7%) does not permit the study of fast reactions at relatively low concentrations (tens of mmol). Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is also must be mentioned as a convenient and quick method which allows to distinguish monomer and oligomer siliceous species using absorbance in the wavenumber region 1250–850 cm^{-1}.[57]

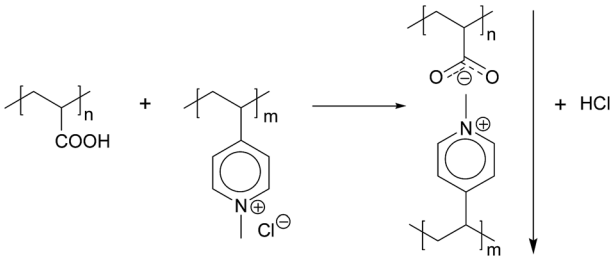
Influence of organic polymers on condensation of monomeric silicic acid

A scan of literature reveals many reports that have described silicic acid condensation in the presence of organic polymers. These have been summarized in Table 1. Study of $Si(OH)_4$ condensation using the molybdate method demonstrated the influence of some polymers on kinetics of the reaction. Acceleration[58,59,63,64,73,82,96,99,108,112,136,158,159] and inhibition[24,72,83–85,102,124,133–135,137] of the reaction monitored as consumption of $Si(OH)_4$ has been reported. As mentioned earlier, the condensation of monomeric silicic acid near neutral pH values proceeds mainly through its reaction with PSA particles. Polymers can influence the process by interaction with $Si(OH)_4$ or with PSA molecules. The interaction between PSA and functional organic polymers proceeds similar to the interpolymer reactions between two organic polymers. These reactions have several peculiarities.[168]

(a) The interaction is caused by relatively weak bonds which cannot result in new compounds in the case of monomeric analogs. For example, a weak poly(acrylic acid) can interact with a very weak base poly(1-vinylpyrrolidone) in water solution giving rise to insoluble compound of 1 : 1 stoichiometry:[169]



(b) The interpolymeric reactions are favorable from an entropy point of view comparing with a reaction between small molecules and unusual reactions are possible with polymers, *e.g.* displacement of strong acid with weak acid:



(c) The cooperative character of the interpolymeric reactions appears in the presence of a minimal critical length of the interacting sequences after which the interaction becomes almost irreversible. The value of critical length depends on the nature of the interacting groups and possible supramolecular effects. For instance, substitution of poly(acrylic acid) with poly(methacrylic acid) in the reaction with polyethylene glycol (PEG) decreases the critical length from $\approx$100 to $\approx$20 because of the stabilizing effect arising due to the hydrophobic interactions of the methyl groups from the methacrylic acid moiety.[170]

(d) The stoichiometry of the interacting polymeric chains is also important, especially in the case of rigid chain polymers and PSA particles which are strengthened due to cross-linking through Si–O–Si bonds.

Thus, organic polymers which bear basic groups can interact with PSA by two ways:

1. Ionic bonds in the case of relatively strong polymeric bases or polymeric cations:

Table 1 Influence of water soluble polymers on silicic acid condensation

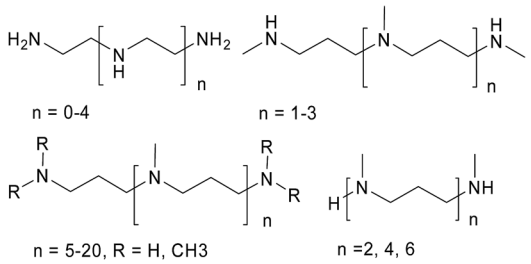
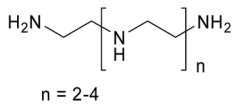
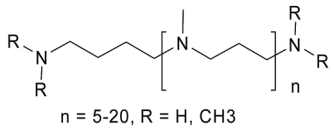
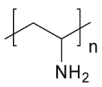
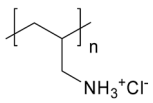
#	Polymer	Precursor	Brief description of the result	Ref.
1	Ethylene (CH_2CH_2) and propylene ($CH_2CH_2CH_2$) based polyamines: 	K_2-SiKat	Polyamines accelerate silicic acid condensation. Siliceous precipitate consist of 200–400 nm in diameter spheres, propylene based polyamines give hollow spheres	58 and 59
2	Triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine: 	Na_2SiO_3	Spherical particles of 200–300 nm size were obtained at pH 7 (phosphate buffer). Addition of the enzymes (proteases) to the systems resulted in their encapsulation	60
3	Long-chain polyamines from diatoms 	TMOS	Spherical composite particles were obtained. Particle size increased up to 900 nm when phosphate buffer was applied	61 and 62
4	Poly(vinyl amine) 	Na_2SiO_3	Polymer accelerates condensation at pH 5.5–10 giving rise to soluble composite nanoparticles or composite precipitates depending on polymer : Si ratio. Long chain polymeric fraction (polymerization degree 11 000) gives core–shell particles consisting of one macromolecule and several 3–6 nm silica particles in the core	63 and 64
5	Poly(allyl amine) (PAAm) 	TMOS	Composite nanoparticles were found in the solution during condensation. Changing of citrate buffer with phosphate results in increase of diameter of soluble particles (from 5 to 120 nm) and size of spherical particles in precipitate (from 170 to more than 2500 nm). Condensation at pH 6 resulted in smoother surface of the particles than at pH 7.	65–70
6			Amorphous silica fiber-like structures 100 nm in diameter were obtained under externally applied shear (stirring the reaction mixture and (b) flowing Through a 1/8 in. Tube)	
7			Addition of cationic surfactant *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide decrease size of the obtained insoluble particles from 3000 to 45–80 nm	71
			The polymer did not influence considerably on the rate of $Si(OH)_4$ condensation at pH 5.5–6 but can interact with silica nanoparticles, especially in the presence of phosphate buffer	72

Table 1 (*Contd.*)

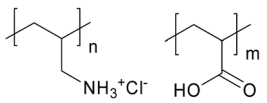
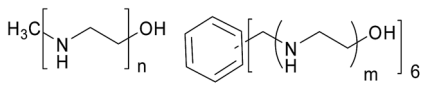
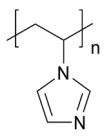
#	Polymer	Precursor	Brief description of the result	Ref.
8		Na_2SiO_3	Reaction at pH 8.5 resulted in accelerating of condensation and gel formation. The obtained product contains 20% of PAAm	73
9		K_2-SiKat pH 6.8	Polymer does not influence on the condensation at pH 6.8 in undersaturated solutions of silicic acid (<2–3 mM) and accelerates dissolution of preliminary condensed siliceous particles	74
10		THEOS	In the presence of phosphate buffer, composite spheres of 300–3000 nm in diameter were obtained.	75
11		Na_2SiO_3	60–80 nm particles were precipitated at pH 7 (without buffer). Reaction in the presence of model drug (ibuprofen) resulted in drug-loaded particles	76
12		TMOS	Polymer produced aggregates with trisodium citrate and after silicification monodisperse 40–100 nm composite particles with a high zeta potential (around +20 mV) were obtained	77
13		Na_2SiO_3	Turbidimetry study of silica precipitation under the action of polymer depending on pH and concentration	78
14	Various polyamines and amine-containing substances	Na_2SiO_3	Precipitates were obtained at pH 5–9. Adding of various enzymes to the reaction mixture allowed to obtain immobilized products	79
15	Poly(allylamine hydrochloride), Poly(acrylic acid) 	Na_2SiO_3	Interpolymeric complex from organic polymers was silicified with $Si(OH)_4$, pH 3 or 8. The technology allows 3D printing with submicrometer resolution	80
16	Linear poly(ethyleneimine)  n = 5050 m = 200	Na_2SiO_3	Composite materials of various morphologies were obtained at pH 9.4. Polymer content was about 25%. Composites can reduce metal ions ($NaAuCl_4$ and Na_2PtCl_4) giving rise to 2–3 nm metal clusters tightly located on the silica without elimination even after sonication.	81
17	Poly (1-vinylimidazole) 	K_2-SiKat	The initial rate of condensation increase under the action of polymer at pH 6.8, the maximum increase was observed for 106 kDa fraction. The acceleration is explained with partial protonation of the polymer. Composite precipitate consists of aggregated submicrometer particles. Polymer : silica ratio in precipitates drops from 3.16 to 0.31 when the reaction time changed from 4 h to 7 days	82

Table 1 (*Contd.*)

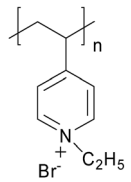
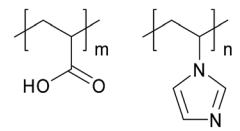
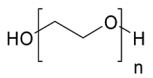
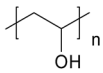
#	Polymer	Precursor	Brief description of the result	Ref.
18		Na_2SiO_3	Polymer inhibits silicic acid condensation after oligomeric PSA is formed. Polymer fractions of MM $\geq$ 100 kDa give stable solutions of composite nanoparticles while shorter chains create composite precipitates. Increase of silicon : imidazole ratio > 1.5 results in precipitates for all polymer fractions	83–85
19	Poly(N-ethyl-4-vinylpyridinium bromide) 	Sol of PSA Na_2SiO_3	Insoluble polymer–PSA complexes were formed at pH 7–9 and soluble complexes were observed at pH 3. Using of silicic acid instead of PSA results in higher content of silicon in soluble complexes	86 and 87
20	Copolymers of 1-vinylimidazole and acrylic acid  n= 18-92%	Na_2SiO_3	Inhibitory action of organic polymers on the condensation was found for copolymers containing more than 44% of imidazole units. This effect is connected with deactivating of silanol groups of primary silica nanoparticles in complexing with copolymers. Condensation of silicic acid in the presence of copolymers results in formation of stable soluble nanoparticles of 20–30 nm in radius. These nanoparticles are negatively charged and their interaction with positively charged composite particles based on poly(vinyl amine) results in fibrous composite material	64 and 85
21	Polyethylene glycol (PEG) 	Na_2SiO_3	Mesoporous silica were prepared using PEG as a templating agent. The material was applied as desiccant for dehumidification of cooling systems	88
22	Poly (vinyl alcohol) 	Na_2SiO_3	Polymer was added to solutions obtained by acidification of sodium silicate solution with HCl (pH = 1–2) following with action of a cation-exchange resin. Transparent and flexible hybrid films were obtained after gelation at 45 °C	18

Table 1 (*Contd.*)

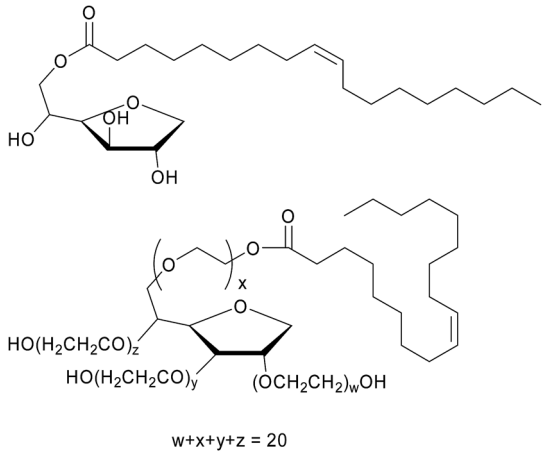
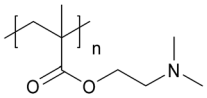
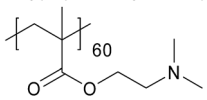
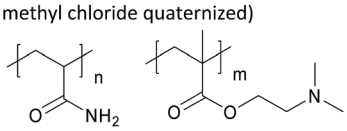
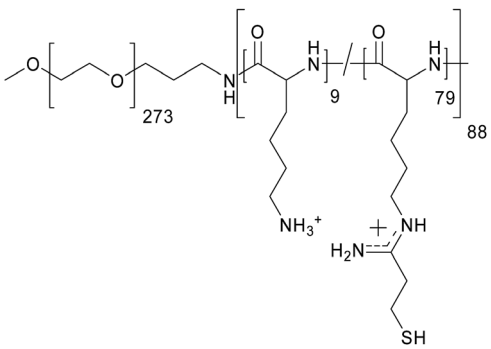
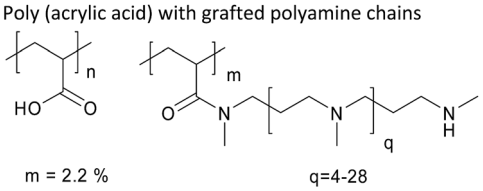
#	Polymer	Precursor	Brief description of the result	Ref.
23	Span-80 and Tween-80  w+x+y+z = 20	Water glass	Mesoporous silica microspheres for delivering poorly water-soluble drugs were prepared by silicic acid condensation in oil emulsion	89
24	Poly(2-(dimethylamino) ethyl methacrylate) 	Sol PSA	Insoluble polymer–PSA complexes were formed at pH 7–9 and soluble complexes (R_g = 24 nm) were observed at pH 3. The solubility was observed up to 50% of polymeric units interacted with PSA by ionic bonds	90–92
25	Poly(2-(dimethylamino)ethyl methacrylate) 	Na_2SiO_3	Particles of 30–800 nm in diameter were obtained when pH changed from 6.6 to 8.1	93
26	Poly(acrylamide-co-2-(dimethylamino) ethyl methacrylate, methyl chloride quaternized) 	TMOS	Composite porous particles of 50 nm diameter with positive ζ-potential at pH 7 were obtained	94
27	PEG-block-polycation copolymer 	Na_2SiO_3	Polymer polyplex with siRNA was obtained and silicified pH 7.4 (HEPES buffer). The obtained 100–140 nm particles were used for siRNA delivery	95
28	Poly (acrylic acid) with grafted polyamine chains  m = 2.2 % q=4-28	Na_2SiO_3	The polymer accelerate condensation at pH 5.5 gives rise to soluble composite nanoparticles (170–190 nm in diameter). According to TEM data, polymer and silica are uniformly distributed in these particles. Sedimentation-induced concentration (50 000*g*) results in precipitate with reduced amount of polymer (<4%)	96

Table 1 (*Contd.*)

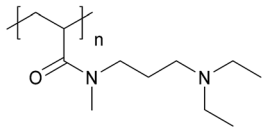
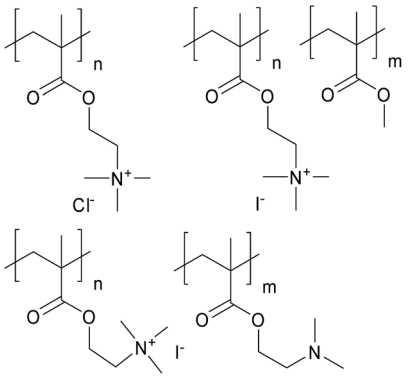
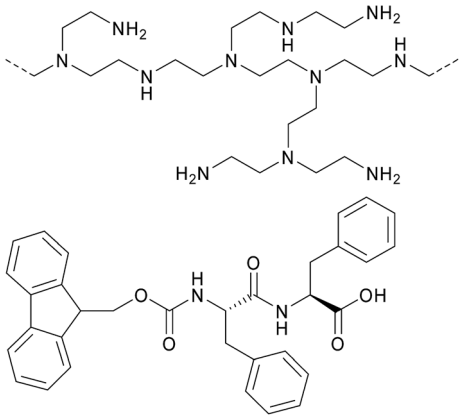
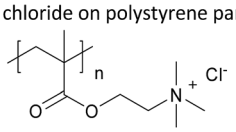
#	Polymer	Precursor	Brief description of the result	Ref.
29	Polystyrene latexes modified with $\sim NH_2$ and $\sim COO^-$ groups	Na_2SiO_3	100–200 nm core–shell particles were obtained at pH 9.7. Hollow particles were obtained with calcination. Slow drying of the particles on a surface resulted in highly organized hexagonal lattices.	97
30	poly(N-(3-(diethylamino)propyl)-N-methylacrylamide) 	Na_2SiO_3	The thermo- and pH-responsive polymer works as a matrix for various siliceous composite structures, including 200–300 nm solid spherical raspberry-like particles and hollow hemispherical particles of more than 1000 nm diameter	98
31	Quaternized 2-(dimethylamino)ethylmethacrylate (DMAEMA) homopolymer and block copolymers of DMAEMA with methyl methacrylate (MMA) 	Na_2SiO_3	The polymers accelerate condensation at pH 7.2 giving precipitates from aggregated $\approx$100 nm particles. ^{29}Si MAS NMR spectra show increase in condensation degree with increase of quaternization degree	99
32	Branched polyethyleneimine Fmoc-diphenylalanine peptide 	Na_2SiO_3	Self-organization of the organic components followed by silicification resulted in 800 μm beads which can encapsulate enzyme (epoxide hydrolase SpEH)	100
33	Polymer of 2-(methacryloyloxy)ethyltrimethylammonium chloride on polystyrene particles employed as a template 	Na_2SiO_3	Hollow siliceous particles (1–2 μm) were prepared starting from polystyrene beads. These particles were used in UV blocking applications, such as cosmetics and finishing materials for buildings	101

Table 1 (*Contd.*)

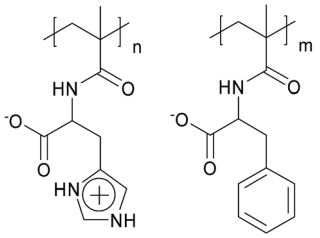
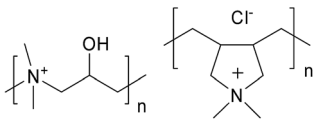
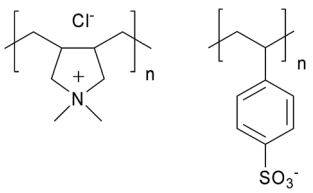
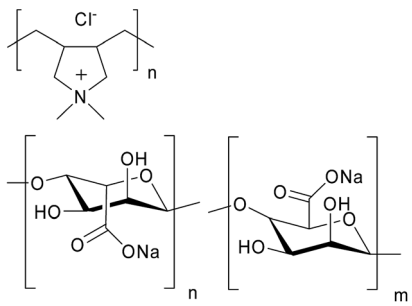
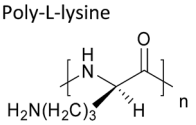
#	Polymer	Precursor	Brief description of the result	Ref.
34	poly-N-methacryloyl- L-histidine (poly-MHist) and poly(N-acryloyl-L-phenylalanine) (poly-PHE) 	Na_2SiO_3	Poly-MHist inhibits initial condensation and it is most efficient at pH 7 (where the polymeric chains are neutral) than at pH 5.5 and 8.5. The inhibition effect was not observed after 8 h. The polymer is not found in solid products. Poly-PHE does not influence of the silicic acid condensation	102
35	Epicholorhydrin-dimethylamine copolymer and poly(diallyldimethylammonium chloride) 	Na_2SiO_3	Treatment of soil (sand) particles with polymeric cation following with silicification improved the engineering properties of soils	103
36	Poly(diallyldimethylammonium chloride) sodium polystyrene sulfonate 	TMOS	Yeast cells were treated with polymeric cation and anion followed by encapsulation with silicic acid. The cell viability after 30 days increased >2 times comparing with native cells	104
37	Poly(diallyldimethylammonium chloride) and sodium alginate 	Na_2SiO_3	*Dunaliella tertiolecta* cells were encapsulated into hybrid organo-inorganic beads. Photosynthetic activity remained for at least 400 days	105
38	Poly-L-lysine 	TMOS	200–400 nm particles were obtained at pH 7 in the presence of phosphate buffer. Poly(allyl amine) addition results in formation of disk-like 100–200 nm structures	69 and 106
39			Precipitation was observed at pH 6.8, 7.5 and 9.2 Tris buffer solutions. Addition of alcohol or carbohydrates resulted in decrease of diameter of spherical products from 540 to 80 nm	107
40			200–1100 nm bimodal distributed particles were obtained at pH 6 and 7 in the presence of phosphate buffer. Particle surface was smoother at pH 6 than at pH 7	66

Table 1 (*Contd.*)

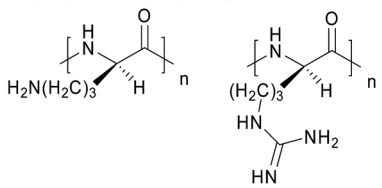
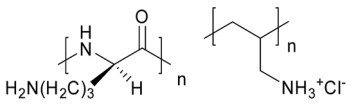
#	Polymer	Precursor	Brief description of the result	Ref.
41			The polymer accelerated condensation in phosphate buffer at pH 7.5 and 11.2. Polymer containing 222 amino acid residues gives hexagonal silica platelet (0.5 and 5 μm) and polymer of 20 units gives spherical 200 nm particles	108
42			Hexagonal structures (500–1000 nm) were observed with non-perturbed solutions and passing the solution throw a tube results in petal-like and fiber-like structures	109
43		K_2-SiKat	Initial condensation rate at pH 6.8 (non-buffered solutions) increased with increase of the oligomer length (2–5 units) and does not change in the case of polymer. Oligomers give 85–140 nm composite particles and polymer – 460 nm	24
44			Polymer does not influence the condensation at pH 6.8 in undersaturated solutions of silicic acid (<2–3 mM) and accelerates dissolution of preliminary condensed siliceous particles.	74
45		THEOS	Spherical (200–400 nm) and hexagonal (400–1000 nm) composite particles were obtained at pH 6.8 (phosphate buffer)	75
46		Na_2SiO_3	Silica was obtained by condensation at pH 5 in pore channels of polycarbonate membranes using preimmobilized poly-L-lysine	110
47	Poly-L-lysine and poly-D-lysine	TMOS, waterglass	Condensation at pH 7 (phosphate buffer) resulted in hexagonal composite particles (500–2000 nm) due to polymer self-organization. Spherical particles were also observed with poly-D-lysine	111
48	Poly-l-lysine and poly-l-arginine 	Waterglass	Poly-L-lysine accelerated condensation at pH 7.2 (Tris–HCl buffer), increase in the polymer chain length increased the acceleration. Both polymers give composite precipitates containing 50–100 nm particles at pH 7.2 and 9.2, while precipitation was not observed at pH 4.9	112
49	Poly(lysine), poly(allylamine) 	TMOS	Particles with non-uniform surface were obtained at pH 3.5 (citrate buffer)	113

Table 1 (*Contd.*)

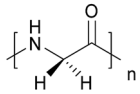
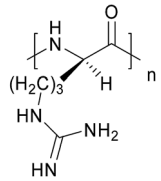
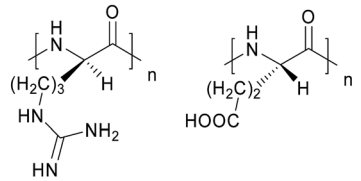
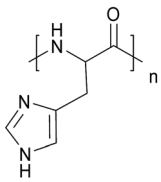
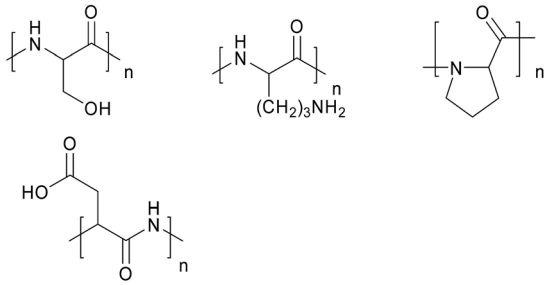
#	Polymer	Precursor	Brief description of the result	Ref.
50	Glycine oligomers 	K_2-SiKat	Initial condensation rate was slightly decreased at pH 6.8 (without buffer)	24
51	Poly-L-arginine 	TMOS, waterglass	The polymer precipitates silica at pH 7 (phosphate and phosphate-citrate buffers) in the form of 300–500 or <100 nm spheres in the case of polymers with MW 13 kDa and 55.3 kDa respectively	114
52		Na_2SiO_3	Polyarginine formed polyplexes with plasmid DNA and silicic acid was added at pH 7.3 (HEPES buffer) giving rise to Si-coated nanoparticles (114–126 nm in diameter). These particles were used for transfection	115
53	poly(L-arginine) poly(D-glutamic acid) 	Na_2SiO_3	Multilayered particles were prepared starting from polymers, histone mimetic H3K4(Me3) tail peptide and GFP plasmid DNA or GFP mRNA. This complex was used for silicic acid condensation (pH 7.4, Tris buffer) and poly-L-arginine was placed on the siliceous surface. The resulted 170 nm particles were used for transfection	116
54	Poly-L-histidine 	TMOS	Precipitate of aggregated 50 and 150–200 nm spheres was obtained at pH 7 (phosphate buffer)	117
55		K_2-SiKat	The polymer accelerates silicic acid condensation at pH 6.8 (without buffer). Composite net-like precipitates contain polymer	82
56	Homopeptides of serine, lysine, proline and aspartic acid 	Waterglass	Peptides exhibit a stronger catalytic effect on silicic acid condensation than amino acids. Poly-lysine and poly-proline lead to the precipitation of solid phases containing both silica and peptides. The precipitates are formed of agglomerated quasi-spherical particles (diameter <100 nm). Gels prepared in the presence of p-Pro exhibit a rather flat surface, whereas those precipitated in the presence of p-Lys exhibit a more uneven surface	118

Table 1 (*Contd.*)

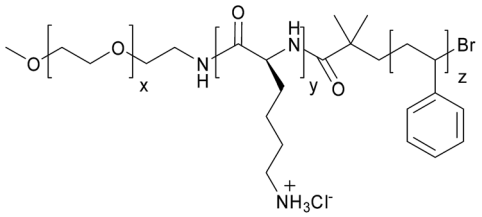
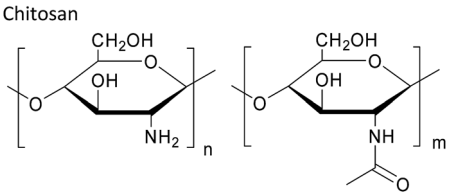
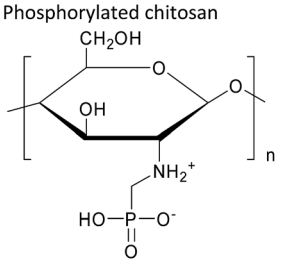
#	Polymer	Precursor	Brief description of the result	Ref.
57	Poly(ethylene glycol)-b-poly(L-lysine)-b-poly-(styrene) (PEG-PLL-PS) triblock copolymer 	TMOS	Condensation at pH 7.5 (phosphate buffer) resulted in Janus hollow silica spheres with hydrophobic PS chains tethered to the inner surface and PEG attached to the outer surface	119
58	β-Casein	Na_2SiO_3	17 nm particles of protein coated with silica were obtained at pH 5.9 (citrate buffer)	120
59	Chitosan 	TMOS	Spherical composites (1000 nm aggregates from 15 and 50–200 nm particles) were obtained at pH 5.8 in the presence of phosphate ions	121
60		Na_2SiO_3	Manganese peroxidase was immobilized into 100 nm composite particles which protected it from ultrasonic destruction	122
61		Na_2SiO_3	Thermally stable microcapsules as food additives were prepared from soybean oil (core) and composite shell from chitosan and precondensed silicic acid	123
62	Phosphorylated chitosan 	Na_2SiO_3	Inhibition of the condensation was observed at pH 7 and 8.33. Composite particles of various sizes were obtained: 100 nm (6 h), 300–500 nm (72 h), aggregates >2000 nm (4 weeks)	124

Table 1 (*Contd.*)

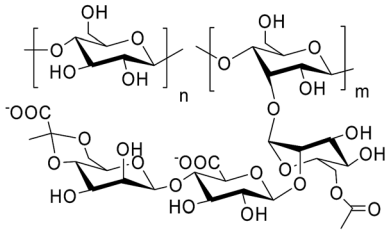
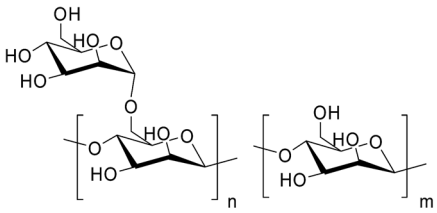
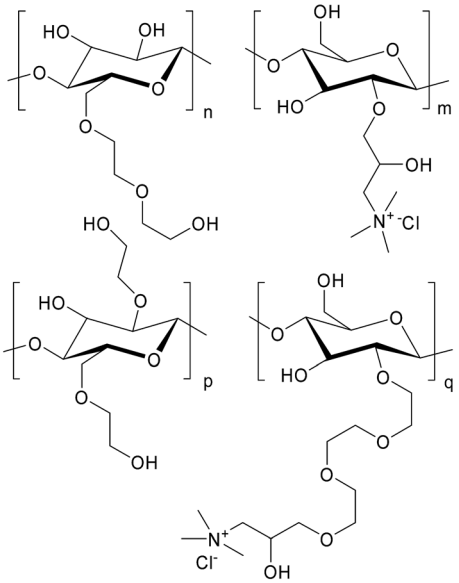
#	Polymer	Precursor	Brief description of the result	Ref.
	Xanthan (1), locust bean gum (2) and Cationic derivative of hydrohyethylcellulose (cat-HEC) (3):  (1)  (2)			
63	 (3)	THEOS	A composite gel was obtained and used to immobilize enzymes	125 and 126

Table 1 (*Contd.*)

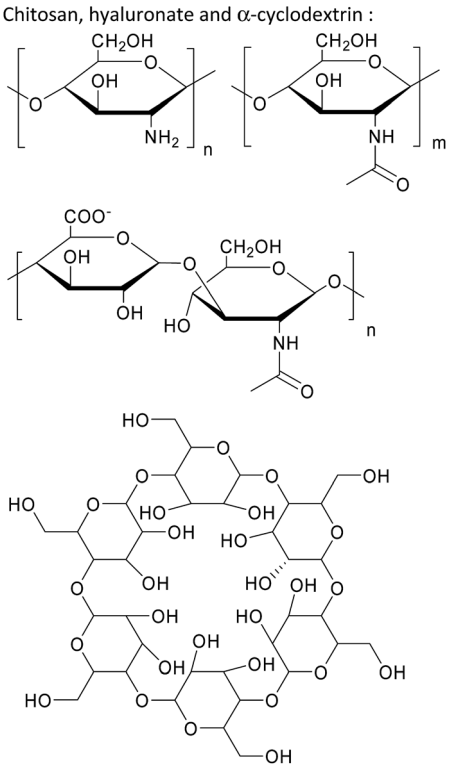
#	Polymer	Precursor	Brief description of the result	Ref.
64	Chitosan, hyaluronate and α-cyclodextrin : 	THEOS	Hydrogels were obtained at pH 5.5–6	127

Table 1 (*Contd.*)

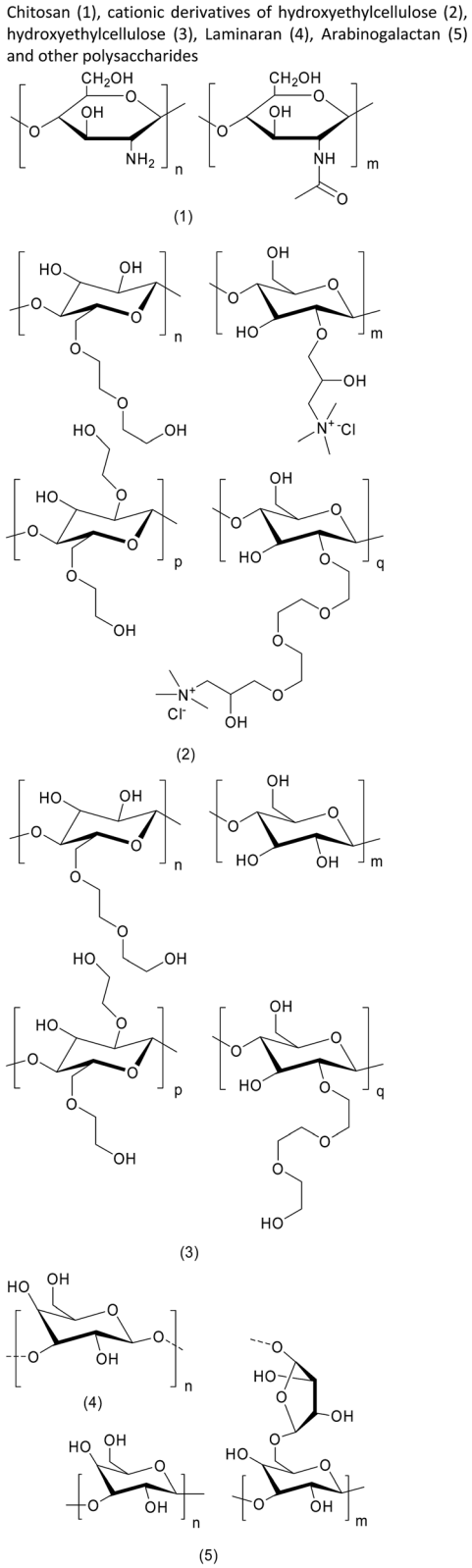
#	Polymer	Precursor	Brief description of the result	Ref.
65	Chitosan (1), cationic derivatives of hydroxyethylcellulose (2), hydroxyethylcellulose (3), Laminaran (4), Arabinogalactan (5) and other polysaccharides 	THEOS	Formation of composite gels is described	128 and 129

Table 1 (*Contd.*)

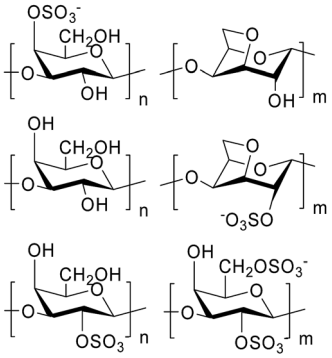
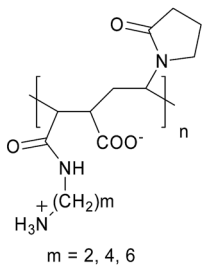
#	Polymer	Precursor	Brief description of the result	Ref.
66	Carrageenans κ- , ι- , and λ- 	THEOS	Polymers promoted the mineralization, acting as a template for the inorganic component. The increase of silicate concentration led to a rise in the stiffness and brittleness of the material, whereas the polysaccharide addition made it softer and more elastic. κ-Carrageenans brought about shrinkage of hybrid materials that led to water separation, while ι- and λ-carrageenans did not induce the syneresis. κ- and ι-carrageenans experienced a thermoreversible phase transition in the hybrid materials owing to the helix–coil transition	130
67	Maleic acid - 1-vinylpyrrolidone copolymer modified with diamines  m = 2, 4, 6	TMOS	The copolymers slightly decrease condensation rate at pH 5.5–6 (acetate buffer) and interact with primary PSA particles giving rise to composites	72
68	Polyethyleneimine, polyethylene glycol, chitosan, phosphonomethylated chitosan	Na_2SiO_3	Stabilization of soluble silicic acid with these polymers is discussed	131

Table 1 (*Contd.*)

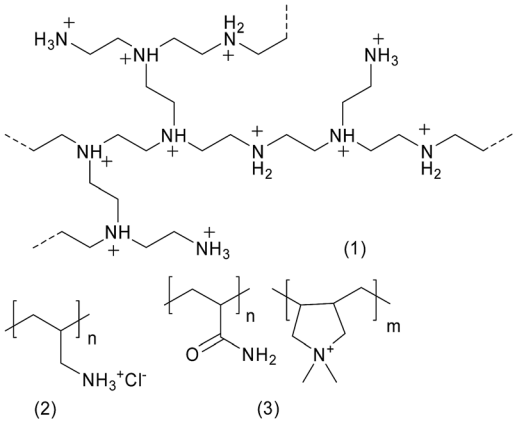
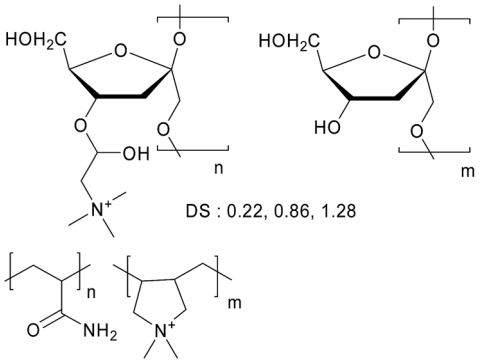
#	Polymer	Precursor	Brief description of the result	Ref.
69	Polyethyleneimine (1), poly(allylamine hydrochloride) (2), poly(acrylamide-*co*-diallyldimethylammonium chloride) (3). 	Na_2SiO_3	Cationic polymers enhance silicate solubility	132
70	Cationic inulin and poly(acrylamide-*co*-diallyldimethylammonium chloride)  DS : 0.22, 0.86, 1.28	Na_2SiO_3	Polymers inhibit silicic acid condensation at pH 7 and cationic charge density correlates with inhibitory activity	133

Table 1 (*Contd.*)

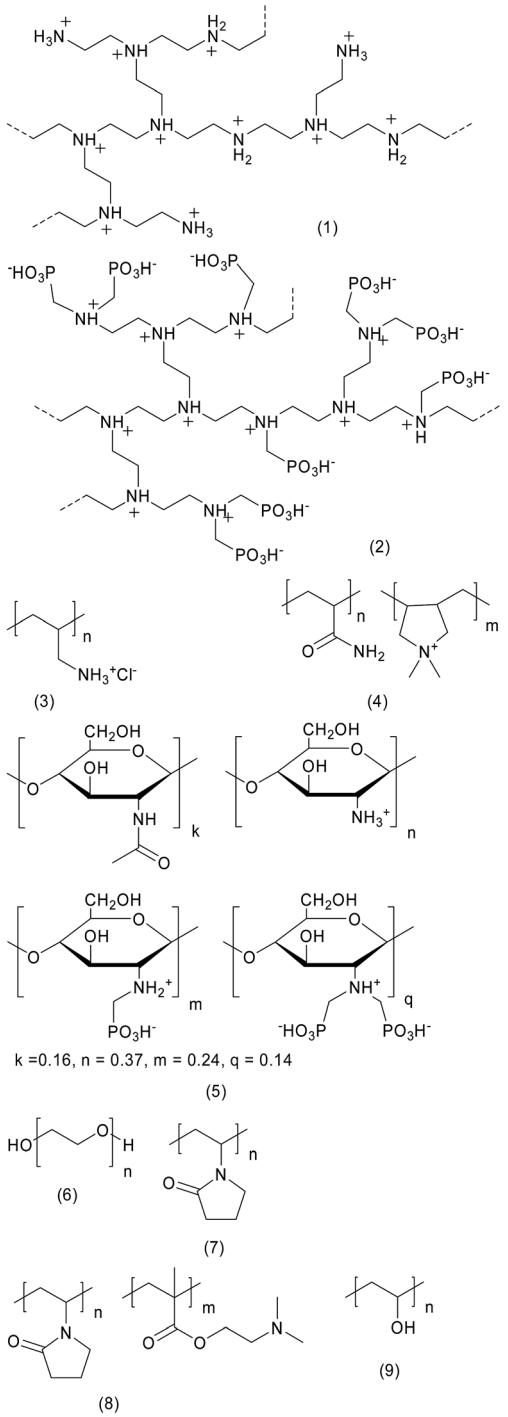
#	Polymer	Precursor	Brief description of the result	Ref.
71	Polyethyleneimine (1); phosphonomethylated polyethyleneimine (2); polyallylamine (3); poly(acrylamide-co-diallyl-dimethylammonium chloride) (4); phosphonomethylated Chitosan (5); polyethylene glycol; phosphonium-grafted polyethylene glycol (6); polyvinylpyrrolidone (7); poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate) (8); polyvinyl alcohol (9)  k =0.16, n = 0.37, m = 0.24, q = 0.14	Na_2SiO_3	Synergistic combinations of cationic and anionic polymers create *in situ* supramolecular assemblies that can inhibit the condensation of silicic acid. Condensation in the presence of PEG (1.55–20 kDa, pH 7, without buffer) gives rise to spherical particles with maximum diameter near 1000 nm with 6 and 10 kDa samples	134 and 135

Table 1 (*Contd.*)

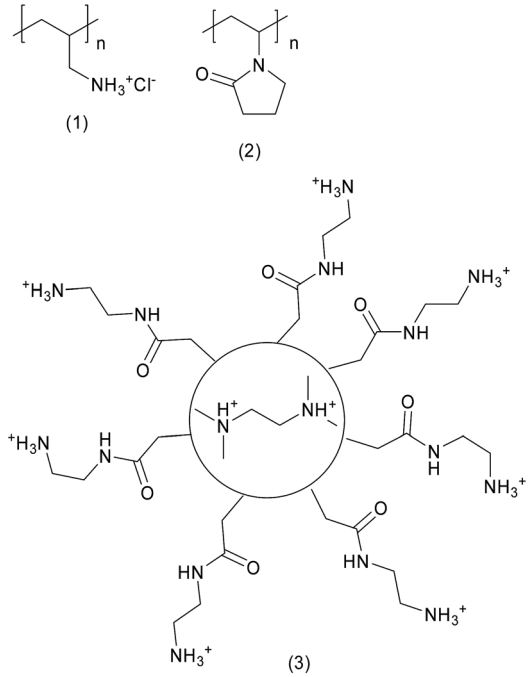
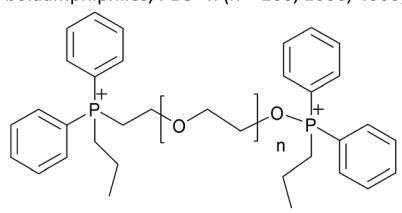
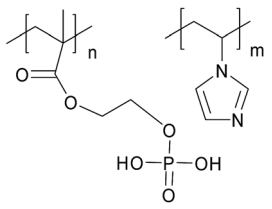
#	Polymer	Precursor	Brief description of the result	Ref.
72	Poly(allylamine hydrochloride) (1), poly(vinylpyrrolidone) (2), poly(aminoamide) dendrimer of generation 1 (3) and poly(ethyleneimine) (4) 	Na_2SiO_3	The additives accelerate silicic acid polycondensation at pH 5.4 and 7 (without buffer), except for poly(1-vinylpyrrolidone), which shows a minor inhibitory effect	136
73	phosphonium-grafted dicationic ethylene oxide bolaamphiphiles, PEG^{+}-n (n = 200, 1000, 4000) 	Na_2SiO_3	PEGP + -200 showed no influence on condensation at pH 7. In the case of PEGP + -1000, and PEGP + -4000, it was found that the inhibitory activity is additive dosage-dependent, demonstrating that there is a clear increase in stabilization ability upon phosphonium PEG dosage increase. The condensation results in spherical particles near 1000 nm	137
74	Poly(2-methacryloyloxyethyl-co-1-vinylimidazole): 	Na_2SiO_3	Condensation of silicic acid in the presence of the copolymer results in composite particles containing aggregated or non-aggregated copolymer coils with embedded silica	138

Table 1 (*Contd.*)

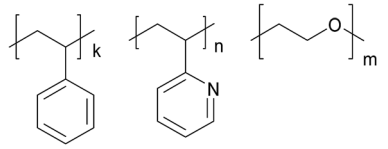
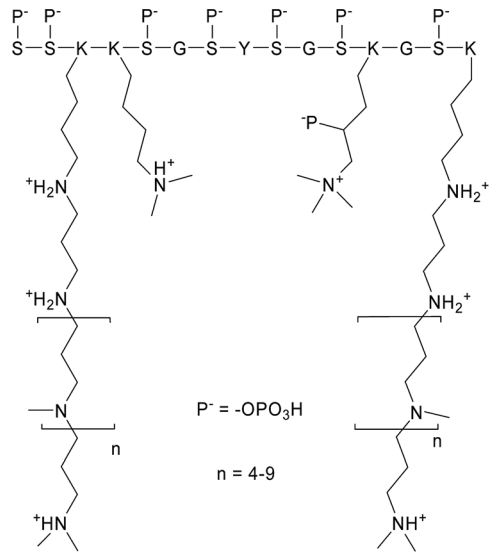
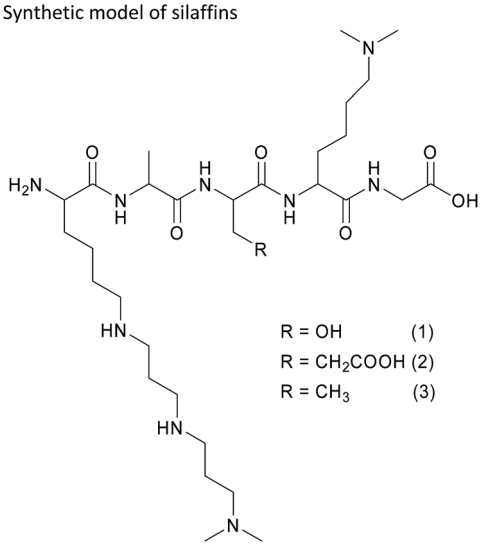
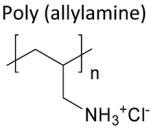
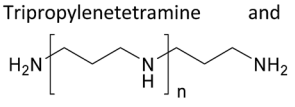
#	Polymer	Precursor	Brief description of the result	Ref.
75	poly (styrene-*b*-2-vinyl pyridine-*b*-ethylene oxide) 	TMOS	Silicic acid condensation at pH 4 around polymer micelles results in hollow nanoparticles, the average values of the outer diameter, thickness of the shell, and void diameter are 20, 6, and 11 nm, respectively	139
76	Silaffins  $P^- = -OPO_3H$ n = 4-9	TMOS	Native silaffins induce formation of various siliceous structures, from spherical particles to porous mass at pH 5.5 (acetate buffer). Dephosphorylated silaffins produce insoluble silica in the presence of phosphate ions only	13 and 140–142
77	Synthetic model of silaffins  R = OH (1) $R = CH_2COOH$ (2) $R = CH_3$ (3)	TMOS	Condensation at pH 6.8 (phosphate buffer) resulted in: 1 – silica spheres (hundreds nanometers) and amorphous silica; 2. – few silica spheres but rather grainy silica structures; 3. – silica spheres (hundreds of nanometers)	143
78	Poly (allylamine) 	TMOS	Stable solution of 40–70 nm composite particles was obtained after condensation at pH 6.8 (Tris buffer). Phosphate ions induced formation of spherical particles or hexagonal structures when phosphate was added to the composite nanoparticles	144
79	Tripropylenetetramine and pentapropylenehexamine  n = 2, 4	TMOS	A network of fused silica nanoparticles (diameter around 400 nm) is observed at pH 7 (phosphate-citrate buffer)	145

Table 1 (*Contd.*)

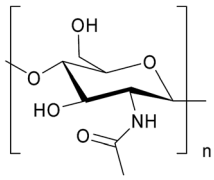
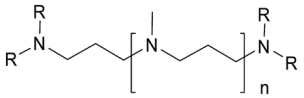
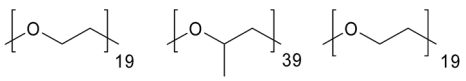
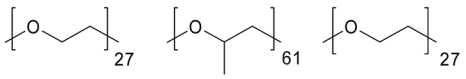
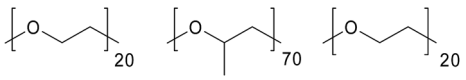
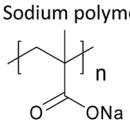
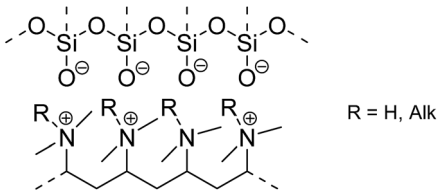
#	Polymer	Precursor	Brief description of the result	Ref.
80	Poly-N-acetyl-D-glucosamine (chitin) 	Na_2SiO_3	Chitin does not influence silicic acid condensation at pH 5.5 (without buffer) but chitin fibers can be silicified	146
81	Type I collagen	K_2-SiKat waterglass	Low concentrations of a silicate solution promotes fibril formation at pH 7.4 (Tris buffer). The collagen effect on silicic acid condensation was low	147
82	Silicatein	Na_2SiO_3	*E. coli* was transformed with the silicatein gene. *E. coli* expressed the silicatein protein which was deposited on the cell surface of the bacteria where it mediates the formation of poly(silicate) after further incubation with monomeric silicic acid	148
83	Polyamines and native silacidins isolated from diatom *Thalassiosira pseudonana*  n = 5-20, R = H, CH_3	TMOS	Polyamines do not initiate silica precipitation at pH 5.5 (acetate buffer) but in the presence of acidic peptide silacidin 200–1500 nm spherical particles were obtained	149
84	Peptides corresponded to sequences from silaffins: SKKSGSYSGSKGSKRRIL – R5 (from silaffin-1A_1) SSKKSGSYSGYSTKKSGSRRIL – R2 (from silaffin-1A_2) SSKKSGSYYSYGTKKSGSYSGYST – R1 (from silaffin-1B)	TMOS, Na_2SiO_3	Turbidity was found during silicic acid condensation in the presence of the peptides at pH 7–7.55 (phosphate and phosphate-citrate buffers) SEM showed 100–300 nm composite particles	69,107 and 150–152
85	SSKKSGSYSGSKGSKRRIL (R5 peptide) and n-AEAEAKAKA EAEAKAKSSKKSGSYSGSKGSKRRIL-c - EAK-R5 - chimera consisting of an hydrophobic-polar protein and a silaffin peptide and demonstrated self assembly into hydrogels	TMOS	R5 and EAK-5 initiate silicification at pH 8 (phosphate buffer) giving rise to hydrogels. Particle size was 80–160 and 300–600 nm for EAK-R5 and 320–700 nm for R5	153
86	Native sericin (protein from cocoons of the silkworm *Bombyx mori*). Polyserine (MW 3000–10 000)	K_2-SiKat	The results demonstrate that in aqueous systems, the effect of hydroxyl-containing additives is negligible, although as the molar ratio of the Si/OH groups decreases, the effect of these molecules becomes more apparent (some acceleration of the condensation)	154
87	Chimeras from protein of *Nephila clavipes* spider silk and R5 peptide	TMOS K_2-SiKat	Mineralization in the presence of R5 peptide alone gives silica particles with a size distribution of 0.5–10 μm in diameter, reactions in the presence of the new fusion proteins generate nanocomposite materials containing silica particles with a narrower size distribution of 0.5–2 μm in diameter. The composite morphology and structure could be regulated by controlling processing conditions to produce films and fibers	155

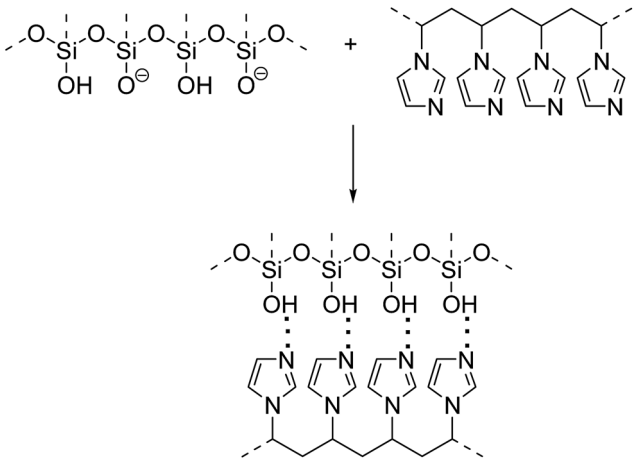
Table 1 (*Contd.*)

#	Polymer	Precursor	Brief description of the result	Ref.
88	Self-assembled α-helical fibers from two α-helical peptides designed to coassemble into a heterodimer. The resulting matured fibers are 50–100 nm thick and tens of micrometers long	Waterglass	Surface of the fibers is positively charged at pH 7.5 which allows the use of the fibers as matrix for silica formation. Proteolysis removes peptides giving the cleanest preparations of silica nanotubes	156
89	R5 peptide and phage peptide clones: SSKKSGSYSGSKGSRRIL – R5 APPGHHHWHIHH – Si3-3 MSASSYASFSWS – Si3-4 KPSHHHHHTGAN – Si3-8 MSPHPHPRHHHT – Si4-1 MSPHHMHHSHGH – Si4-3 LPHHHHLHTKLP – Si4-7 APHHHHPHHLSR – Si4-8 RGRRRRLSCRLL – Si4-10 TVASNSGLRPAS – Ge4-1	TMOS	R5 peptide gives silica spheres with diameter 500–1000 nm; phage peptide clones form silica nanoparticles with diameter 200–400 nm	157
90	Extracts from horsetail *Equisetum telmateia*	K_2-SiKat	Acceleration of the initial condensation rate at pH 7 in the absence of multiply charged cations, formation of primary 2 nm siliceous particles.	158 and 159
91	Gelatin	Waterglass	Silicate of gelatin forms as a flaky, white and opaque precipitate, when the solution of silicic acid is gradually added to a solution of gelatin in excess. The precipitate is insoluble in water, and is not decomposed by washing. Silicate of gelatin prepared in the manner described, contains 100 silicic acid to about 92 gelatin units	160–162
92	Gelatin and alginic acid	Na_2SiO_3	Gelatin activates silica formation at pH = 5, alginic acid does not interfere with silica condensation controls silica morphology through the assembly the gelatin–silica aggregates at the microscale	163
93	Poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) (EO19-PO39-EO19) 	Na_2SiO_3	Meso–macroporous siliceous materials were prepared using the emulsion template process. Ibuprofen was immobilized on the material as a model drug	164
94	Poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) (EO27-PO61-EO27) 	Na_2SiO_3	The polymer was used as emulsifier in aqueous medium for octadecane encapsulation into siliceous spherical particles at pH 2.95–3.05	165
95	Poly(ethyleneoxide)–poly(propyleneoxide)–poly(ethyleneoxide) EO20-PO70-EO20 	Na_2SiO_3	The polymer was used as emulsifier in aqueous medium for synthesis of siliceous mesocellular foams using hexane as pore-forming agent	166
96	Sodium polymethacrylate 	Na_2SiO_3	A mixed solution was dried and dip-coated into 2 M NH_4HCO_3 solution giving rise to macroporous film	167



This kind of interaction increases the amount of silanol anions which are active in reaction with unionized monomeric silicic acid and acceleration of $Si(OH)_4$ condensation is observed in neutral and acidic conditions.[99,112,118,158,171,172]

2. Polymers with weak basic groups interact with PSA particles by forming hydrogen bonds. Multiplicity of these interactions enhances binding and decrease in the number of silanol anions as seen in the silicic acid condensation in the presence of poly(1-vinylimidazole) shown below:



The decrease in ~Si–O$^-$ concentration results in a decrease in the condensation rate.[84,85,102] The same effect is probably dominant in the case of poly(*N*-methacryloyl-L-histidine),[102] poly(1-vinylpyrrolidone)[136] and PEG.[134,135,137]

There is a series of reports which contradict these schemes.[131,137,173,174] For instance, inhibition of $Si(OH)_4$ condensation is observed for a wide range of polymeric cations and amines. The reason for this contradiction is possibly due to the different procedures employed for measurement of monomeric silicic acid concentration. K. Demadis *et al.*[173] have used the silicomolybdate method provided by the HACH Company[175] which allows the measurement of a "soluble" ("reactive") silica, *i.e.* short oligomers of unknown length apart from the monomer and dimer molecules. In other reports,[124,132–134,176,177] the molybdate procedure employed also has variations from the recommended protocol for measuring monomeric and dimeric forms of silicic acid exclusively.[56] Thus, it appears that the visible inhibition of $Si(OH)_4$ condensation with polycations can be explained by the stabilization of oligomeric forms of PSA through their complexation with polymers that prevents further aggregation of these oligomers.[178] On the other hand, when a blue molybdenum procedure, elaborated to measure only monomer and dimer of silicic acid is employed,[136] the same team reported acceleration of the condensation with polymeric bases. These findings imply the importance of the quantification method employed.

The formation of organic polymer – short PSA oligomer complexes also explain dissolution of silica in the presence of polymers capable of interacting with charged silicate species.[74,134,179] According to our view, the same concepts are involved in the inhibition action of adipic acid/amine-terminated polyethers D230/diethylenetriamine copolymer.[180] This polymer contains many groups capable of forming hydrogen bonds. Moreover, the addition of polyepoxysuccinic acid increases the inhibition, possibly due to neutralization of amine groups in the copolymer. We must also mention that study of the kinetics of $Si(OH)_4$ condensation requires a strict observance of all protocols, including $Si(OH)_4$ preparation from a precursor. For example, in ref. 24 the authors showed that long neutralization of sodium silicate (during 10 min) can result in formation of primary PSA oligomers and the system becomes more complex with presence of entities other than the desired silicic acid–polymer.

Most reports devoted to the kinetics of $Si(OH)_4$ condensation in the presence of water-soluble polymers demonstrate the influence of polymers on the condensation rate only and the equilibrium $Si(OH)_4$ concentration was 2–3 mM in the siliceous solutions without additives. These values were also observed as when the condensation proceeded with precipitation of silica–polymer composite. We observed[181] a decrease of the equilibrium concentration when silicic acid was condensed in the presence of poly(vinyl amine) (PVA) gel containing Zn^{2+} ions. This gel was able to capture 20% of silicon from 0.1 mM solution which was attributed to the formation of highly stable PVA–PSA complex with participation of zinc ions.

Interaction of polymeric silicic acid with organic polymers in solution

Condensation of silicic acid in the presence of polymers capable of interacting with PSA results in solutions containing composite nanoparticles or various insoluble products. As mentioned in the earlier sections, PSA–polymer complexes are similar to interpolymer complexes of organic polymers. Interaction between two polymers bearing hydrophilic groups gives rise to so-called stoichiometric or non-stoichiometric complexes.[182–184] In the first case, all reactive groups, *e.g.* ~COOH and ~NH_2 react with each other and all hydrophilic groups become blocked from interaction with water medium which often results in water insolubility. The non-stoichiometric complexes are obtained when one of the components is in deficiency or when some peculiarities of the main polymeric chains do not allow stoichiometric interaction. The free polymeric segments provide solubility of these complexes. Polyampholytes often gives soluble interpolymeric complexes because only one group (basic or acidic) can interact with another polymer. Both variants are observed in PSA–polymer complexes but siliceous systems differ from organic interpolymer complexes because condensation and/or dissociation reactions can proceed during interaction with organic polymer. Thus, $Si(OH)_4$ condensation in the presence of organic polymer includes several parallel processes:

1. Silicic acid condensation and growth of siliceous oligomers.

2. Interaction of the siliceous oligomers with organic polymer when the oligomer size will be sufficient for this interaction.

3. Further transformations of the polymer–PSA complex, including sintering of the silica nanoparticles and conformational changes of the organic macromolecules.

Several main factors influence interaction between growing siliceous particles and organic polymers in aqueous medium.

Nature of the polymeric functional groups, pH and ionic strength

As mentioned earlier, the ability of the organic polymer to interact with PSA by means of hydrogen and/or ionic bonds depends on the basicity of functional groups. Certainly, pH, ionic strength and temperature must influence this reaction by changing the critical length of the interacting sequences. This effect was observed with polymeric amines.[64,90] Greater protonation of the amine groups at pH 7 compared with pH 9–10 resulted in enhancement of polymer–PSA interactions, larger compaction of the composite nanoparticles in the solution and increase in the precipitation probability. Control of pH in the reaction medium is often achieved using a buffer. In this case, we must take into account that phosphate, citrate and other multivalent anions influence the silicic acid condensation in the presence of polymeric amines resulting in precipitation of composites.[65,71] The ability of citrate ion to give aggregates with poly(allylamine) was utilized[77] to synthesize monodisperse 40–100 nm composite particles.

Length and flexibility of the polymer chain

Growth of siliceous particles during silicic acid condensation proceeds at the same time with interaction with organic polymer and depending on the polymer length at least two situations are possible:

1. Polymer chain is long and flexible enough to capture siliceous particle into polymeric coil (Fig. 3A). This results in encapsulation of siliceous particles in organic macromolecules giving rise to soluble composite nanoparticles similar to non-stoichiometric complexes between organic polymers. This behavior was observed for amine containing polymers,[112] polymers with imidazole moieties[82–84] and polyampholytes.[85] Irrespective of the nature of the functional group and ability of the polymer to accelerate or to inhibit $Si(OH)_4$ condensation, composite soluble nanoparticles can be obtained if the polymer units can interact with ~Si–OH or ~Si–O^- and the chain is sufficiently long and flexible. Clusters of 50–180 nm particles built up from regularly sized particles 7–8 nm in diameter were formed from silicic acid condensation in the presence of horsetail extract (*Equisetum telmateia*).[158] Insoluble cellulose macromolecules can also stabilize 4 nm diameter silica particles.[185]

2. When the polymer chain is relatively short, a single polymer coil can not consume a siliceous particle and various aggregates are formed (Fig. 3B–D). Depending on the nature of the polymer and the reaction conditions, we can obtain large multiparticle aggregates solubilized with free segments of the polymeric chains (Fig. 3B) or insoluble material with siliceous particles serving as cross-linker for the organic polymer (Fig. 3C). In the latter case, further fusion of the siliceous particles is possible when organic polymer is deficient (Fig. 3D).

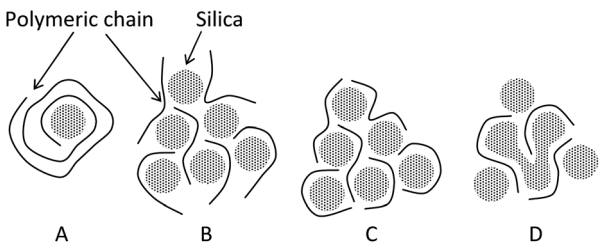


Fig. 3 Schematic representation of different silica–polymer composites. A – long polymeric chain stabilizes siliceous particle; B–D – relatively short polymeric chains which give multiparticle aggregates, soluble (B) or insoluble (C and D).

Polymer : Si ratio

Interaction between growing PSA nanoparticles and macromolecular chains often results in stable soluble nanoparticles[63,64,85,90–93,95,96,115,116,120,131,132] or in a product consisting of uniform spherical composite particles.[24,61,62,65–71,75–77,98,99,106–108,111,112,114,117,121,124,134,135,137,139,143,149,153,155,157] These variants exist in the case of relatively low silicon content in the system, when all PSA nanoparticles can find chains of organic polymer. Further increase in the silicic acid content results in formation of insoluble non-uniform products[64,83] because of cross-linking by means of silicic acid which was condensed independent of the polymer control.

Biosilicification: how living cell can control silica formation?

Discovery of silaffins[12,13,140–142] – proteins with post-translational phosphate and polyamine modifications (Table 1, # 73) intensified research focused on investigating silicic acid condensation in the presence of polymeric bases and ampholytes. Silaffins are associated with siliceous frustules of diatoms and the hypothesis of biogenic silica growth around matrix of silaffins was formulated.[140,141,143] Unfortunately, silaffins can be isolated from diatom frustules in microgram quantities only which is not sufficient for study of their properties including their influence on silicic acid condensation. Hence, synthetic organic polymers can serve as a good model of silaffins. On the other hand, introduction of organic polymers into nonaqueous sol–gel systems is a well-known strategy to obtain interesting composite materials.[27,186–188] Thus $Si(OH)_4$ condensation regulated by water soluble polymers is expected to result in new bioinspired materials.

On analyzing the reported data on silicic acid–polymer systems (Table 1), we found two peculiarities which distinguish synthetic products from diatom frustules (Fig. 1A and B). The

precipitates obtained during silicic acid condensation in the presence of organic polymer do not have regular organization at the level of several microns. The usual spherical morphology of these products are often found associated as a continuous structure. The observations of organized structures in some reports[144,189] can be attributed as a sampling artifact because the samples for microscopy were prepared by air-drying of wet precipitates. We showed[85] that air-drying of composite precipitates can result in self-organization of the particles into highly ordered structures in which the morphology is very distinct from the initial particles precipitated from solution. Self-association under slow drying gives highly organized hexagonal lattices from monodisperse 100–200 nm siliceous particles.[97] Composite precipitates obtained using an organic polymer contain the polymer in significant amount (≥10%) but the siliceous frustules of diatoms contain <5% of organic compounds,[190,191] and this organic material are not only from silaffins. Moreover, thorough cleaning of diatom frustules decreases carbon content below 0.2%.[190]

PSA nanoparticles or oligomers stabilized with biopolymers are the most probable form of silicon in diatoms and similar silicifying organisms.[24,64,144] So, a mechanism of conversion of these composite nanoparticles to almost clear silica must exist. This mechanism must be genetically controlled with the object to provide a large diversity of species-specific frustules. A possible mechanism for such control from the cell is desiccation under the action of aquaporines.[11] This hypothesis includes transport of aquaporines to specified places on the membrane of silica deposition vesicle (SDV) by means of cytoskeleton. SDV contains the precursor of silica (composite nanoparticles) and the aquaporines function as specific pores which pump water out of SDV. Removal of water results in increase of silica precursor concentration which then initiates condensation of soluble composite nanoparticles to solid silica. The question that arises here is: can this desiccation-induced condensation produce silica without large content of organic substances? We have done a model experiment with polyampholyte containing polyamine side-chains.[96] Desiccation was simulated by centrifugation at 50 000*g* which concentrated the composite organo-silica particles at the bottom of the centrifuge tube. We found formation of precipitate from 100–200 nm sintered particles. The precipitate contained 4% of organic polymer which is closer to biosilica than usual composites obtained from silicic acid and organic polymers. Thus, we hypothesize that silaffins function as stabilizing agents of PSA in diatoms and during desiccation-induced condensation a major part of organic polymer is eliminated from the solid material. A possible scheme of the biosilica synthesis is presented on Fig. 4.

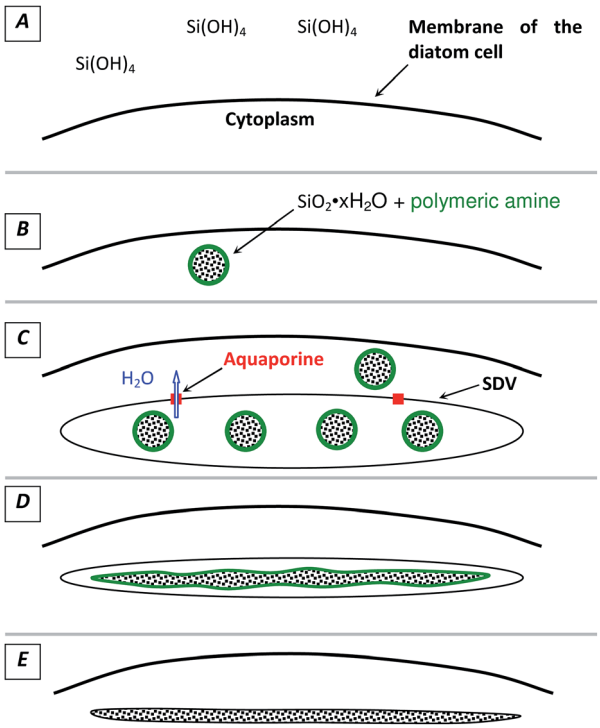


Fig. 4 Scheme of biosilica synthesis in a diatom cell. A – a cell before $Si(OH)_4$ capture from the environment; B – siliceous nanoparticles stabilized with polymeric shell; C – the siliceous particles are in SDV (Silica Deposition Vesicle) and aquaporines pump water out of SDV; D and E – concentrating-induced condensation and elimination of organic polymer giving rise to solid silica.

Application areas of the new knowledge in silicic acid condensation

Study of silicic acid condensation in the presence of water-soluble polymers is related to processes in solution and to formation of solid substances. Both areas provide valuable information for practical applications.

The ability of organic polymers to stabilize PSA in an easily hydrolysable form is the basis of water treatment applications. Polymers of silicic acids are the cause of detrimental precipitates in industrial and domestic water flow systems. The addition of various polymers capable of interacting with PSA prevents the precipitation.[131,134,192–194]

The soluble composite nanoparticles could be considered as new biomimetic precursors for the synthesis of more complex siliceous structures. These nanoparticles bear negative or positive charge depending on the nature of the organic polymer and can interact with oppositely charged objects. For instance, poly(allyl amine)-based composite nanoparticles formed hexagonal structures when phosphate ions were added to the solution.[144] Positively charged nanoparticles obtained by $Si(OH)_4$ condensation in the presence of poly(vinyl amine) reacted with negative composite nanoparticles obtained with poly(1-vinylimidazole-*co*-acrylic acid) giving rise to a fibrous material containing 40–50% of SiO_2.[64]

The ability of PSA particles to interact with polymeric amines was employed[85,195] to create silicified materials by means of direct ink writing with 3D-printers. These studies are based on bioinspired concepts using matrix-assisted condensation of silicic acid.

A major application of silicification in aqueous medium is the encapsulation of biologically active substances,[76,95,115,116,120,196] including drug delivery.[197] The

siliceous shell is usually formed around a complex of polymeric cation and encapsulated moiety, *e.g.* nucleic acid in transfection applications. The obtained particles with sizes typically below 200 nm serve as delivery agents, and can release the drug or internalize into the cell following the destruction of the siliceous shell. Silicic acid condensation in the presence of positively charged surfaces opens new vistas for silicification of relatively large objects such as living cells[104,105,148] which retain viability longer than native cells. Islet cell encapsulation in a siliceous layer has been found to be beneficial to extend the survival of the cells. Enzyme encapsulation in siliceous shells is another promising strategy to design highly effective catalysts. Enzymes in free state are homogenous catalysts with disadvantages of low life time, poor stability and large difficulties in separation from the reaction products. Silicic acid condensation in the presence of polymeric bases and enzymes gives rise to particles containing the enzyme[80,100,122] which retains its catalytic activity. The siliceous layers protect the enzyme from undesirable factors and helps to separate the catalyst from the reaction medium through sedimentation. This approach is protected with an extensive patent.[79] Particles obtained from silicic acid and polymeric bases can also capture other substances, *e.g.* soybean oil.[123]

Silicic acid condensation around cationic spherical matrix is a convenient way to obtain hollow particles of various sizes, from hundreds of nanometers to micrometers. The hollow siliceous particles can be applied as containers in drug delivery, as plastic fillers and in design of complex microdevices. Assembly of these particles can commence from organic beads obtained by emulsion polymerization of styrene following with amination of the beads, silicic acid condensation around beads and calcination to remove the organic polymer (Fig. 5A).[97,101] A solid matrix in the form of porous membrane was applied for synthesis of silica microtubes.[110] The alternative one-step approach to obtain hollow particles involves silicic acid condensation around self-organized low molecular polyamines (Fig. 5B).[58] The latter method avoids the calcination stage and hence facilitates recycling of the matrix. A similar approach was applied for assembly of core–shell and hollow particles from zein (a major storage protein from corn *Zea mays*).[198]

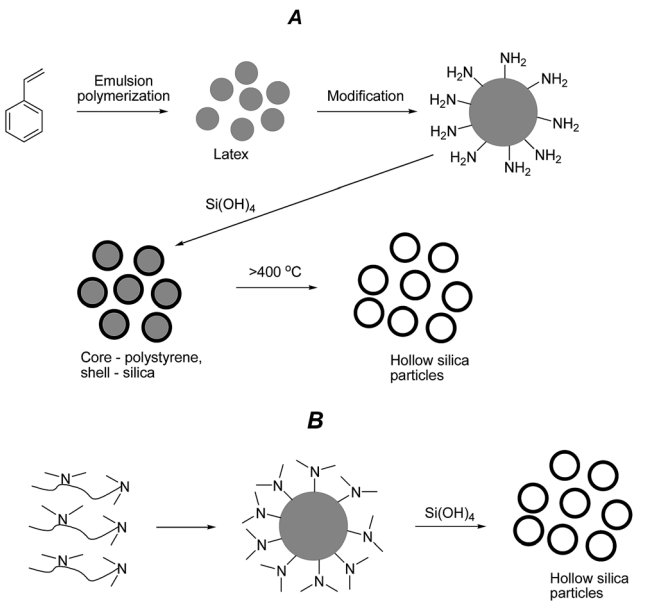


Fig. 5 Schemes of latex-templated synthesis of hollow siliceous particles (A) and silicification on self-organized nano-droplet from low-molecular polyamines (B).

Composite submicrometer particles obtained in aqueous medium can be loaded with a fluorescent dye and applied as liquid flow tracers.[97]

The main part of siliceous composite materials is prepared from organic precursors of silicic acid. Sodium silicate is attractive because it is a cheap and ecology-friendly substance comparing to alkoxysilanes. Mesoporous forms of silica based on an amine surfactant as the structure-directing porogen were prepared and used as reinforcing and toughening agents for epoxy polymers.[199] The material obtained from sodium silicate showed smaller framework pore sizes (4–5 nm) comparing with TEOS-based silica (6–21 nm) and provided exceptional strength and toughness.

Introduction of organic polymers, *e.g.* poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer into siliceous gel on the condensation stage results in highly ordered mesoporous structures and pore sizes in the range from 7.5 to 10 nm.[200]

Silicic acid and its oligomers act as cross-linking agents during polymerization of acrylic acid or acrylamide.[201] The obtained material can be applied as environmentally-friendly superabsorbent because the crosslinking bonds ≡Si–O–(O=)C– are hydrolysable and the sorbent dissolves after several days after application.

Porous materials were obtained by condensation in the presence of PEG[88,164] or similar surfactants and emulsifiers such as Span-80 and Tween-80.[89] Condensation in the presence of water-insoluble substance, *e.g.* octadecane, results in the substance encapsulation with a smooth and compact silica surface[165] and in the case of hexane siliceous mesocellular foams were obtained.[166] Organo-silica composites can be applied for synthesis of highly ordered carbon materials by dissolution of silica in hydrofluoric acid. This approach allowed to obtain highly nitrogen doped mesoscopic carbons which show high electrocatalytic activity.[202,203]

Conclusion: future prospects in $Si(OH)_4$–polymer systems

Silicic acid condensation in the presence of water-soluble polymers is a dynamically developing area and several important points come to the fore:

(a) Development of methods to study silicic acid condensation in solution where the traditional molybdate method must be re-examined and standardized with the objective to ensure that the obtained data correspond to monomeric and dimeric forms of $Si(OH)_4$. This is possible with the use of ^{29}Si NMR spectrometry and isotope-enriched silicic acid. A promising and

widely-spread method which allows to distinguish various forms of condensed $Si(OH)_4$ is attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, including multiple reflection approach. This method requires a special study devoted to the band assignment in water medium in comparison with ^{29}Si NMR data. Soluble nanoparticles formed under silicic acid condensation are difficult systems for study. Light scattering methods are often not sensitive enough for siliceous phase while electron microscopy is complicated and associated with aggregation during sample preparation. So, new approaches are needed in this area, including unusual techniques such as laser ablation combined with aerosol spectrometry.[64]

(b) Simulation of biosilicification where the reaction in aqueous medium is an adequate model to study behavior of silicic acid in living organisms. The accumulated knowledge allows to approach synthesis of artificial silica with structures similar to biogenic silica. On the other hand, mimicking the silica biosynthesis must include simulation of the cell structures participating in this process on a micrometer level, *e.g.* membranes bearing active domains, because the transition from partially condensed silicic acid coordinated with organic polymer to organized solid silica structures is an important but poorly understood process. The *in vitro* experiments do not exclude study of living cells like diatoms, sponges, cell cultures of higher organisms. Further progress in this area is expected from coupling of modern equipment with specially designed tracers including fluorescent or spin probes, *e.g.* tagged silicic acid.

(c) New materials for encapsulation of biologically active compounds into silica or composite particles that opens new possibilities for drug delivery and design of prolonged action preparations. Self-organized water soluble nanoparticles are an attractive option that has emerged from the investigations on silicic acid condensation processes. These particles combine rigidity of siliceous structure with variable functionality of organic polymer. Reversible drying of this nanoparticles is a large challenge for chemists because the presence of active silanol groups provokes aggregation and condensation under usual freeze drying. Elaboration of the novel drying techniques will result in new drug formulations and can solve the problem of the cold chain with preparations containing protein or nucleic acid.

(d) New organic polymers can be developed as further progress in construction of siliceous nanocomposites requires new functional polymers with easily tunable structure, including functionality and the chain length. We can expect involvement of "smart" polymers showing thermo- and pH-sensitivity for the design of "smart" composites.

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