

POLYMERIC AMINES: ROLE IN BIOSILICIFICATION AND POTENTIAL IN NANOTECHNOLOGIES

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ABSTRACT

Condensation of silicic acid was studied in the presence of poly(vinylamine) fractions (238-11000 units). The reaction results in soluble nanoparticles or composite precipitates depending on polymerization degree of the organic polymer and pH. The structure of the nanoparticles in solution was close to a microgel for high-molecular weight polymers or to hyper-branched systems when the extent of polymerization was below 1000. Silicic acid exists in these particles in slightly polymerized form in contrast to silica obtained without polymers. We consider polymer – poly(silicic acid) nanoparticles as a new silica precursor for the design of silica and composite materials. We suspect that a similar method of storing silicic acid in an active state is used in silicifying organisms, at least in diatom algae.

KEY WORDS

Polymeric amines, silicic acid, condensation, diatom algae, nanoparticles.

1. Introduction

Condensation of silicic acid in the presence of organic polymers and oligomers, mainly polybases, has been intensively studied over the last decade [1-6]. Amines were traditionally used in the synthesis of silica and composites [7-10] and increased interest in these systems is connected with the latest achievements of molecular biologists and biochemists in the study of biosilicifying organisms: diatom algae and siliceous sponges. These organisms build their skeletons from micro- and nanostructured silica which makes them attractive for specialists in material science and nanotechnology [11-13].

Study of diatoms led to the discovery of special proteins – silaffins that are associated with biosilica [14, 15]. These proteins contain polyamine side chains with up to 20 nitrogen atoms and the corresponding polyamines were also found in diatoms in the free state. The physiological function of silaffins is not known clearly but they may take part in the intracellular accumulation and transportation of silica precursors as well as the formation of silica valves. One of the intriguing questions

in biosilicification is the chemical form of the pool of silicic acid in cytoplasm. Hypotheses include free $\text{Si}(\text{OH})_4$, organosilicon compounds, small silica particles and polysilicates [16].

Discovery of silaffins resulted in an intensification of the study of reactions in the system $\text{Si}(\text{OH})_4$ – polymeric amine [17-20]. In particular, it was found [21-23] that primary nanoparticles of poly(silicic acid) can be stabilized in solution by complexing with amino- or imidazole-containing polymers. In the case of poly(1-vinylimidazole) the interaction between imidazole units and silanol groups decreases the activity of $\equiv\text{Si}-\text{OH}$ in further condensation [23].

In this study we have obtained poly(vinylamine) (PVA) samples of various polymerization degree (238-11,000) and studied their influence on the condensation of silicic acid. The obtained results reinforce the hypothesis concerning silicon transport vesicles as complexes between organic polymers and oligosilicates [23, 24]. We have obtained and characterized organo-silica nanoparticles based on PVA and suggest they may be potential building-blocks for the design of more complicated nanocomposites.

2. Results

PVA was obtained by the alkaline hydrolysis of poly(vinylformamide) (PVFA) [25]. The PVFA sample had previously been fractionated by precipitation from water into dioxane. Polymerization degree (PD) of PVA fractions were estimated from PD of the corresponding PVFA samples. PD was also measured by static light scattering (SLS) (Table 1) and the obtained values exceed the PD of PVFA precursors, especially for the low-molecular weight fractions. According to dynamic light scattering (DLS) data this is explainable by association of PVA macromolecules. The presence of associates ($d_h > 100$ nm) was observed at pH 5.5-10 too (Figure 1). Potentiometry data (Figure 2) show increase of protonation from 0 at pH 10 to 30% at pH 5.5. ζ -potential remains positive at high pH probably due to sorption of Na^+ ions.

Table 1
SLS and DLS of PVA fractions (in 0.2 M HCl and 0.1 M NaCl)

PD	MW (PD) from SLS	*r _g	*r _h (DLS)
238	22700 (528)	14.6	3.5; 64
1000	113000 (2630)	20.4	5.5; 87
3250	235000 (5470)	25.3	9.0; 134
11000	437000 (10160)	42.2	23.4; 380

*r_g – radius of gyration; r_h – hydrodynamic radius.

Sodium silicate (10 mM) was used as a precursor of Si(OH)₄ in this study. The desired pH was adjusted with 1 M HCl in 30-60 s using predetermined volumes of the acid. We were most interested in three pH values: 10 (fast condensation of silicic acid begins), 7 and 5.5 (the value found in silica deposition vesicles of diatom algae [27]). Condensation of free Si(OH)₄ results in 6-47 nm nanoparticles (Figure 3). A bimodal distribution with additional maxima above 100 nm was found at pH 8 and 9.

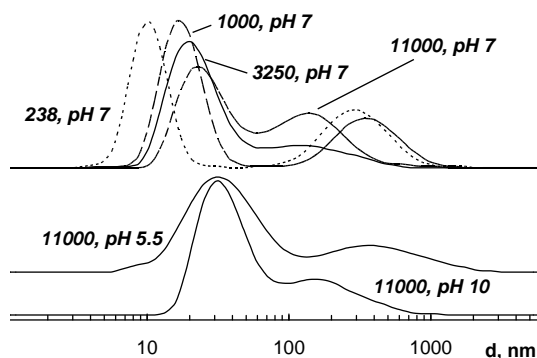


Figure 1. DLS data of 10 mM solutions of PVA fractions of various PD.

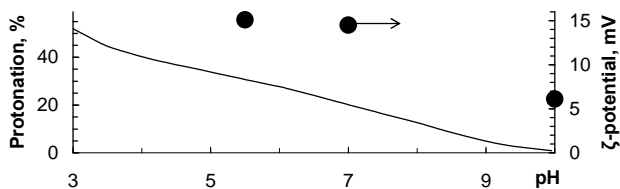


Figure 2. Potentiometry titration data and ζ -potential of PVA-3250 (10 mM, in 0.2 NaCl).

Titration of sodium silicate – PVA solutions with HCl results in precipitates at [Na₂SiO₃]: [PVA] \geq 1.5: 1 and pH 4-9.5. Condensation of Si(OH)₄ in the presence of equimolar amounts of PVA proceeds homogeneously. Condensation of silicic acid is usually monitored by molybdate method [7] which allows the measurement of the concentration of non-condensed species (monomers and dimers). Use of this method in the Si(OH)₄ – PVA system did not show any reliable influence of PVQ polymerization degree on the kinetics of reaction. The equilibrium concentration of silicic acid was 2.8-3 mM after 2 days for all pH values, including blank experiments without PVA (Figure 4). Kinetics of Si(OH)₄ condensation follows a third order reaction during the

initial stage. The corresponding constants (Figure 4) point to acceleration of the reaction in the presence of PVA throughout the entire pH range explored.

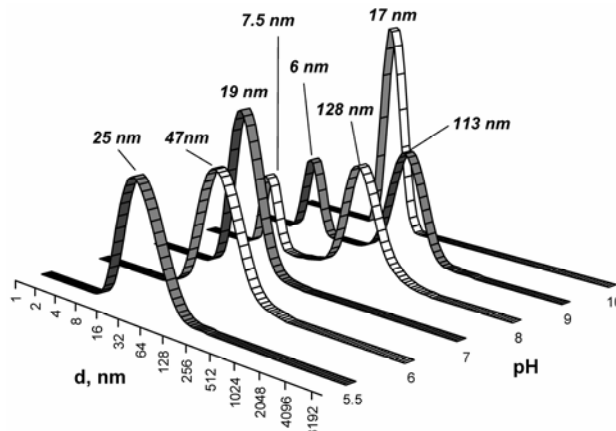


Figure 3. DLS data of the products of silicic acid condensation (10 mM, 5 days) at various pH values.

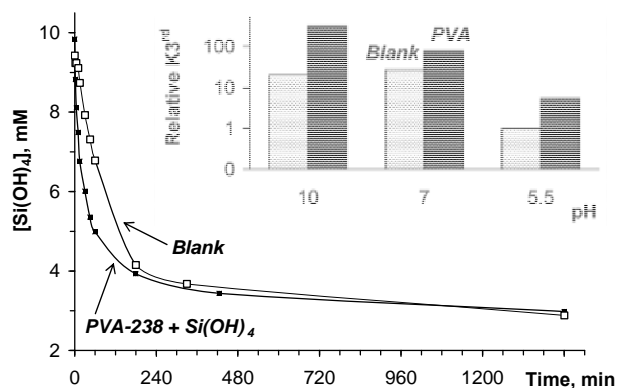


Figure 4. The effect of the PVA on condensation of silicic acid at pH 10 and the k_{3rd} for the Si(OH)₄ at various pH.

All rate constants are relative to the blank at pH 5.5.

[PVA] = [Si(OH)₄] = 10 mM in the initial solutions.

Reaction at pH 10 strongly depends on the polymerization degree of PVA (Figure 5). Low-molecular weight fractions show a gradual increase of size of the particles in solution which finishes with fast aggregation and precipitation after 75 min and 10 days for PVA-238 and PVA-1000 respectively. Even higher-molecular weight fractions give solutions of \approx 60 nm particles stable for more than two weeks.

Condensation at pH 5.5 and 7 did not give precipitates with any PVA fraction. Results of a detailed DLS study (Figure 6) show transitions from a bimodal to unimodal distribution of sizes during the first hours of reaction. The resulting particles are stable for several weeks. Similar data were obtained for other PVA fractions including PVA-3250 and 11000 at pH 10.

