Silicic Acid Polymerization Catalyzed by Amines and Polyamines

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Polymerization and subsequent gelation of silicic acid in water were catalyzed by amines and polyamines. Particularly effective were poly(allylamine), poly(lysine), and poly(arginine), which promoted spontaneous gelation. The resultant silica gel contained a sizable portion of amines, which altered the surface properties of silica gel.

Polymerization of monomeric or oligomeric silicic acids has been studied in decades. Tarutani reported the dependence of the polymerization rates on pH and inorganic ion concentrations.[1] Organic compounds have been used in various ways to control the silica gel structure: organotin groups were used as protecting groups,[2] polymers as phase separation inducing agents,[3] and alkoxyalkylsilanes as component monomers.[4] Previously we reported that metal ions catalyzed the polymerization of silicic acid, depending on the Lewis acidity of the aqua ions.[5] We are interested in the possibility that organic molecules can catalyze the polymerization of silicic acid leading to a functionalized silica gel with controlled structures. Ultimate goal of our study is to control the structure and properties of silica gel by the use of organic molecules. We report here the polymerization of silicic acid in the presence of amines and polyamines and some properties of the resultant silica gel.

To a clear solution of Na_4SiO_4 (73.5 mg) in 40 mL of borate buffer (pH 8.5), an organic additive was added at 20 °C.[6] The decrease in the concentration of monomeric and oligomeric silicic acid (molybdate reactive silicic acids[1]) was monitored by the molybdosilicate method as a function of time. As shown in Figure 1, addition of 1,3-diaminopropane accelerated the polymerization of silicic acid. Poly(allylamine)[7], poly(lysine), and poly(arginine) showed particularly distinct effects, where gelation occurred spontaneously upon addition of these polyamines to silicic acid solutions. Table 1 summarizes the effects of various organic compounds on the polymerization rate. Silica gel was formed after the solution was aged overnight in the presence of oligoamines and polyamines, while no gelation was observed in the presence of monoamines, amino acids, carboxylic acids, and sugars as well as in the absence of catalyst. The silica gel was collected by filtration, washed thoroughly with water, and characterized by elemental analysis, IR spectroscopy, and powder X-ray diffraction.

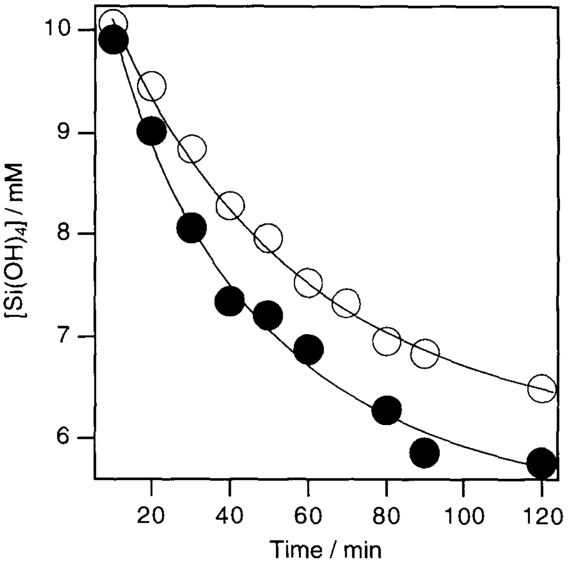

Figure 1. Plot of the concentration of $Si(OH)_4$ against time in the presence of 1,3-diaminopropane (●) and in the absence of diamine (○) in a borate buffer at pH 8.5. $[Si(OH)_4] = 10$ mM, [diamine] = 1 mM. The concentration of $Si(OH)_4$ was calculated from the absorbance at 400 nm of molybdosilicate solutions, in which $[Si(OH)_4]$ is assumed to be proportional to the absorbance.

Table 1. Catalytic effects of various organic compounds on polymerization of silicic acid in a buffer solution at pH 8.5 at 20 °C and the Si–O stretching in the IR spectra of the resultant silica gels

Catalyst	Polymerization rate[a]	Si–O stretching / cm^{-1} of the gel
monoamines[b]	slow	—[f]
1,3-diaminopropane	fast	1078
diethylenetriamine	fast	1079
triethylenetetramine	fast	1073
pentaethylenehexamine	fast	1063
poly(allylamine)	very fast	1039
poly(L-lysine)	very fast	1060
poly(L-arginine)	very fast	1055
amino acids[c]	slow	—[f]
sugars[d]	slow	—[f]
carboxylic acids[e]	slow	—[f]

[a]slow: no acceleration was observed by the molybdosilicate method during 3 h, and no gelation was observed after aging the solution overnight, fast: acceleration was observed by the molybdosilicate method, and gelation occurred after aging overnight, very fast: spontaneous gelation occurred upon addition of catalyst. [b]butylamine and hydroxylamine. [c]L-Lys, L-Lys-L-Lys, and L-Arg-L-Lys. [d]mannose, ribose, glucosamine, and sucrose. [e]dodecanedioic acid, hexadecanedioic acid, and 1,2,4,5-benzenetetracarboxylic acid. [f]No silica gel formed was after aging overnight.

Elemental analysis for nitrogen showed that silica gel prepared with poly(allylamine), poly(L-lysine), and poly(L-arginine) contained 20 wt.%, 24 wt.%, and 32 wt.% of these polyamines, respectively. Thus almost all the polyamines were incorporated in the silica gel during polymerization.[8] Diamine, triamine, tetramine, and hexamine were incorporated less effectively; elemental analysis showed that 30–50% of these amines was incorporated in the resultant silica gel. IR spectroscopic studies also supported the above results (Figure 2). The polyamine–silica gel hybrids showed peaks at 2930, 2949, and 2959 cm^{-1} (the C–H stretching) for poly(allylamine), poly(lysine), and poly(arginine), respectively, which were assigned to the CH_2 group of the polymer.

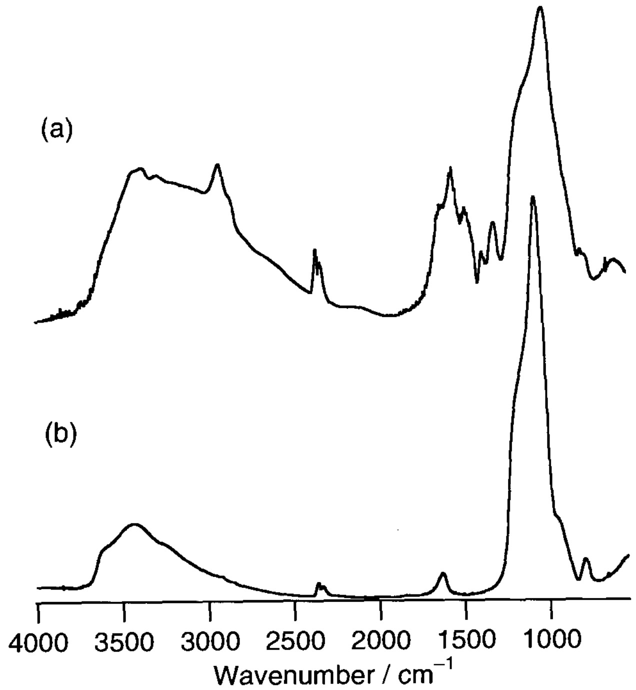

Figure 2. The IR spectra (KBr) of (a) the poly(allylamine)–SiO_2 hybrid, and (b) normal SiO_2 prepared by adding NaCl to the buffer solution of silicic acid.

The amine–silica gel hybrid showed some unique properties different from conventional SiO_2. The Si–O stretching vibration was shifted to a smaller wavenumber: normal SiO_2 prepared from aqueous $Si(OH)_4$ by the addition of NaCl exhibited the Si–O stretching at 1085 cm^{-1} while the amine–SiO_2 hybrids at 1025–1079 cm^{-1} (Table 1). After the heat treatment at 500 °C, this peak was shifted to 1090 cm^{-1}, which is close to that of conventional silica gel. This shift in the Si–O stretching wavenumber appears to be caused by the hydrogen bonding between the NH_2^+ group and the SiO group, which weakens the Si–O bond. The powder X-ray diffraction (Cu-K_α) of the poly(allylamine)–SiO_2 hybrid showed a broad peak at 3.80 Å, while that of the normal SiO_2 at 3.39 Å.

Normal silica gel has a negative ζ potential in neutral water and adsorbs cationic dyes such as rhodamine 6G. However, the amine–silica gel hybrid did not adsorb cationic dyes but adsorbed anionic dyes such as indigo carmine. Therefore the surface electric potential was reversed from negative to positive owing to the amino groups attached to the silica gel. The CD spectrum of the poly(L-lysine)–silica gel hybrid adsorbing indigo carmine dispersed in a KBr disk exhibited a positive Cotton effect at 400 nm (θ = 14 mdeg) and a negative one at 640 nm (θ = –8 mdeg). To check if anisotropy in the solid state produced any artifacts in the CD curve, the CD measurements were repeated with independently prepared samples. The Cotton effect at the low energy (640 nm) was similar to that of a solution of indigo carmine and poly(L-lysine) in water (θ = –13 mdeg at 620 nm). The induced Cotton effects showed that the adsorbed molecule was placed in a chiral environment. Catalytic activities of these silica gels are currently under investigation.

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References and Notes

1 For a review of kinetic studies of silicic acid polymerization, see T. Tarutani, *Anal. Sci.*, **5**, 245 (1989).
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6 Standard concentrations in a typical run; $[Si(OH)_4]$ = 10 mM in a pH 8.5 borate buffer (50 mM) and amines were added so that a molar ratio of N to Si in the initial mixture is 0.2.
7 Nittoboseki, molecular weight 8,500–11,000.
8 If all SiO_2 and polyamines used as starting materials were incorporated in the resultant SiO_2–polyamine hybrid, the calculated wt.% are 16, 29, and 34 wt.% for poly(allylamine), poly(L-lysine), and poly(L-arginine), respectively.