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Silicic Acid Polymerization Catalyzed by Amines and Polyamines

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Amines, particularly polyamines, catalyzed the polycondensation of silicic acid in water. The resultant gel contained these polyamines with a N/Si molar ratio of up to 0.5. IR and powder X-ray studies showed that silica gel and polyamines are hybridized at a molecular level through hydrogen bonding. The gel adsorbed anionic dyes from water, whereas normal silica gel adsorbs cationic dyes. Induced CD was observed for the indigo carmine adsorbed on silica gel–poly(L-lysine) hybrid, showing that the hybrid provides a chiral environment to the adsorbate.

Uses of an organic catalyst for inorganic synthesis and an inorganic catalyst for organic synthesis are frequently seen in a number of chemical processes such as bioceramics formation, chemical evolution, and zeolite synthesis. As one of these approaches to novel material synthesis, we are interested in the silica gel synthesis catalyzed by an organic catalyst. Because silica gel is an important material as adsorbent and catalyst support, synthesis of functionalized silica gel by use of organic catalysts should be interesting for practical applications. Several approaches have been taken to achieve functionalization of silica gel with the aid of organic compounds, such as molecular imprinting,[1—3] functionalization of silica gel surface,[4] use of deoxyalkylsilicic acid as a monomer,[5] and use of organic polymer as a phase separation inducing agent.[6] However, little attention has been paid to silica gel synthesis over catalyst, particularly over an organic catalyst.[7] Tarutani[8] reported that the rate of silicic acid polymerization depends on the pH and on the presence of inorganic ions.[9] We screened organic catalysts for silicic acid polymerization and found that amines and polyamines catalyzed the polymerization and subsequent gelation, resulting in amine–silica gel hybrids.

Results and Discussion

Preparation of Silica Gels and Kinetic Studies: An aqueous solution of silicic acid (10 mM, 1 M = 1 mol dm^{-3}) was prepared by dissolving sodium orthosilicate hydrate in a 50 mM borate solution buffered at pH 8.5. In the absence of catalyst, the solution undergoes gelation slowly. Two characteristic rates, the rate of silicic acid polymerization and the rate of gelation, were monitored in the presence of a range of organic molecules to evaluate the catalytic activity of organic molecules. Firstly, the concentrations of monomeric and oligomeric silicic acid were determined spectrophotometrically via a molybdosilicate method. With this method, only monomeric and oligomeric silicic acid (molybdate–reactive silicic acid) can be detected. In the control experiment without any catalyst, the half-life of aqueous silicic acid (10 mM) at 20 °C in a pH 8.5 borate buffer was 60 min. In the presence of some amines, the rate was accelerated. As a representative example, the decrease in the concentration of molybdate–reactive silicic acid is demonstrated in Fig. 1. In the presence of 1,3-diaminopropane, the consumption of silicic acid was a bit faster than the control experiment. In the presence of poly(allylamine hydrochloride), gelation occurred spontaneously and the silicic acid concentration reached equilibrium within 20 min (Fig. 1). In Table 1 are listed the half-lives of molybdate–reactive silicic acid in the presence of various organic molecules.

After aging a solution of silicic acid and a catalyst, the solution became turbid and precipitation of a gel occurred.

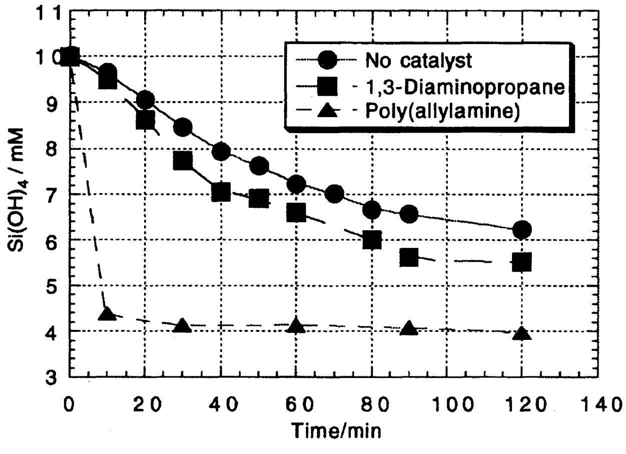

Fig. 1. Plot of the concentration of Si(OH)$_4$ against time in the presence of 1,3-diaminopropane (■) or poly(allylamine hydrochloride) (▲), and in the absence of amines (●) in a borate buffer at pH 8.5. [Si(OH)$_4$] = 10 mM, [diamine] = 1 mM, poly(allylamine hydrochloride) 0.187 mg mL^{-1}. SiO$_2$, 600 ppm, N/Si molar ratio = 0.2 in the initial mixture. The concentration of Si(OH)$_4$ was calculated from the absorbance at 400 nm of molybdosilicate solutions, in which [Si(OH)$_4$] is proved to be proportional to the absorbance.

Table 1. Catalytic Effects of Various Organic Compounds on Polymerization of Silicic Acid in a Borate Buffer Solution (H_3BO_3–KCl, 50 mM) at pH 8.5 at 20 °C
Initial Concentrations were $[Si(OH)_4] = 10$ mM, [catalyst] = 1 mM.[a]

Catalyst	Half-life of molybdate–reactive silicic acid (min)	Time required for gelation (min)
Poly(allylamine hydrochloride)	<1	<1
Poly(L-lysine hydrobromide)	<1	<1
Poly(L-arginine hydrochloride)	<1	<1
Pentaethylenehexamine	—[f]	ca. 30
Triethylenetetramine	—[f]	ca. 30
Diethylenetriamine	35	ca. 120
1,3-Diaminopropane	40	ca. 720
1,4,7,10-Tetraazacyclododecane (Cyclen)	40	<4320
Amino acids[b]	60	>4320
Sugars[c]	60	>4320
Carboxylic acids[d]	60	>4320
Monoamines[e]	60	>4320
No catalyst	60	>4320

a) For polyamines, the concentration of the polyamines in the reaction mixture was $2/n$ mM, where n is the degree of polymerization. b) L-Lysine methyl ester, L-Lys–L-Lys, and L-Lys–L-Arg. c) D(+)-Mannose, sucrose, D-ribose, and D(+)-glucosamine. d) 1,12-Dodecanedicarboxylic acid, 1,16-hexadecanedicarboxylic acid, 4,4′-bi(benzoic acid), iminodiacetic acid, acetylenedicarboxylic acid, *trans*-1,4-cyclohexanedicarboxylic acid, phthalic acid, 1, 2,4,5-benzenetetracarboxylic acid, α,α-dimethylmalonic acid, 2,5-pyrroledicarboxylic acid. e) Butylamine, octylamine, hydroxylamine. f) Amines prevented formation of molybdosilicate.

The time required for gelation was thus determined by observing the precipitation of gels. In the absence of catalyst, no precipitation was observed after 72 h.

As shown in Table 1, the polymerization rate correlated well with the gelation rate. A catalyst that accelerated silicic acid polymerization also accelerated the gelation. Poly(allylamine hydrochloride), poly(L-lysine hydrobromide), and poly(L-arginine hydrochloride) showed distinct effects on the rates of both silicic acid consumption and gelation. Liner diamine, triamine, tetramine, hexamine, and cyclic tetramine showed moderate effects. Amino acids, sugars, carboxylic acids, chitosan, and monoamines showed almost no effects. Therefore, an amine's catalytic activity depends on not only the number of amino groups but also on the relative arrangement of the amino groups. It should be noted that some of the amines disturbed the molybdosilicate formation and monitoring the silicic acid concentration by this method was not successful. For such cases, only gelation time was used to estimate their catalytic activities.

In the condensation reactions of silicic acid, proton transfer from the Si–OH group and to the $Si–O^-$ group should be important.[10] We suggest that the cooperative action of amino groups that are arranged in appropriate positions can stabilize the transition state of the condensation reaction by aiding the proton transfer. This assumption leads to a significant advantage of polyamines over oligoamine, where the former has higher density of amino groups and would likely supply a favorable assembly of amino groups for efficient catalysis.

Characterization of the Silica Gels: The precipitated silica gel was collected by contrifugation and washed thoroughly with distilled water. After being freeze-dried, the samples were used for elemental analysis, thermogravimetric analysis (TGA), infra-red (IR) spectroscopic studies, and powder X-ray diffraction. As a reference gel, we prepared silica gel by dissolving 0.45 M of NaCl in 10 mM of silicic acid in a borate buffer at pH 8.5. We call this purely inorganic gel normal silica gel. The elemental analysis for nitrogen is summarized in Table 2. The amines are incorporated in the gel and the amounts of incorporated amines appear to be parallel to the catalytic activity of these amines. Thus, diamine showed only moderate catalytic power and the amount of incorporated amine was small. On the other hand, polyamines showed distinct catalytic effects and a large portion of polyamines were incorporated. These results indicated that the amines are not just a simple catalyst, but they are also reactants reacting with silicic acid. Results obtained by TGA also supported the above conclusion. Poly(L-lysine hydrobromide) and poly(L-arginine hydrochloride) showed 43 and 45% weight loss upon heating to 500 °C, while normal silica gel showed 11% weight loss. We thus call the silica gel prepared here silica gel–amine hybrids.

We prepared silica gel–poly(allylamine) hybrids from varying ratios of $Si(OH)_4$ to poly(allylamine hydrochloride) in the reaction mixtures. Thus, 10 mM of $Si(OH)_4$ and $0.2/n$, $1/n$, $2/n$, $5/n$, and $10/n$ mM of poly(allylamine hydrochloride), where n is the degree of polymerization of poly(allylamine hydrochloride), were allowed to react. From elemental analyses for nitrogen of the resultant gels, the N/Si molar ratios in the gels were calculated and plotted against the N/Si ratio in the reaction mixture in Fig. 2. The N/Si ratio reached a plateau as the N/Si ratio in the reaction mixture increased. This observation indicated that the hybrid is not a solid solution but has a definite stoichiometric ratio.

The IR spectrum of the silica gel–amine hybrids showed some characteristic bands. Firstly, the hybrids showed signals owing to C–H stretching and N–H stretching, supporting the results that amines are incorporated in the gel. Second, the Si–O stretching wavenumber was shifted to a shorter wavelength. The wavenumbers of Si–O stretching of normal silica gel and silica gel–amine hybrids are listed in Table 3. Normal silica gel exhibited the Si–O stretching at 1085 cm^{-1} while silica gel–amine hybrids showed the peaks at 1078—1039 cm^{-1}. Similar downshifts are seen in the IR of phyllosilicates, where tetrahedral silicate is bonded to magnesium or aluminium. For instance, talc, a magnesium phyllosilicate, exhibits the Si–O stretching at 1017 and 1045 cm^{-1}. We speculate that, as Mg and Al act as Lewis acids and weaken the Si–O bond, the NH_3^+ groups of polyamines also work similarly by forming hydrogen bonds to the silica gel. These downshifts in the IR Si–O stretching strongly suggest that organic and inorganic phases exist together and silica gel and amines are interacting at the molecular level. These shifts are a good measure for the extent of hydrogen bonding interaction between amine and silica gel.

Table 2. Elemental Analyses of Silica Gel Prepared over Amine Catalysts[a)]

	N %	wt % of organic component
1,3-Diaminopropane	1.84	4.9
Diethylenetriamine	2.52	6.2
Triethylenetetramine	4.22	11.0
Pentaethylenehexamine	5.31	14.7
Poly(allylamine hydrochloride)	4.86	19.8
Poly(L-lysine hydrobromide)	5.26	24.7
Poly(L-arginine hydrochloride)	11.60	32.3
Poly(L-histidine hydrochloride)	2.29	29.4
Poly(allylamine hydrochloride)[b)]	2.08	8.5

a) All hybrids were prepared from 10 mM of silicic acid and 2/*n* mM of amine in pH 8.5 borate buffer 50 (mM), where *n* is the number of amino groups in amines. See also footnote a to Table 1. For poly(histidine hydrochloride) no gelation was observed at this pH so that the gel was obtained in a buffer at pH 6.0. b) Poly(allylamine hydrochloride) was adsorbed on the normal silica gel. To an aqueous suspension of normal silica gel (115 mg) was added poly(allylamine hydrochloride) (14 mg), and then the gel was collected by centrifugation and freeze-dried in vacuo.

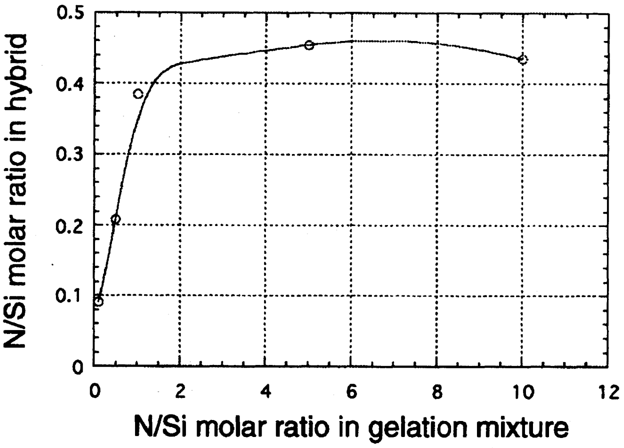

Fig. 2. Plot of the N/Si ratios in the silica gel–poly(allylamine) hybrid against the N/Si ratio in the reaction mixtures. The hybrids were prepared from 10 mM of silicic acid in 50 mM borate buffer at pH 8.5 in the presence of varying amounts of poly(allylamine hydrochloride).

Table 3. The Si–O Stretching in the IR Spectra of the Silica Gel–Amine Hybrids

Catalyst	$\nu_{\max}$ for Si–O stretching wavenumber (cm^{-1}) of the gel
No catalyst	1085
1,3-Diaminopropane	1078
Diethylenetriamine	1079
Triethylenetetramine	1073
Pentaethylenehexamine	1063
Cyclen	1081
Poly(allylamine hydrochloride)	1039
Poly(L-lysine hydrobromide)	1060
Poly(L-arginine hydrochloride)	1055

As a control experiment, we also added poly(allylamine hydrochloride) to the aqueous suspension of normal silica gel to obtain a silica gel adsorbing poly(allylamine hydrochloride). However, such a silica gel showed the Si–O stretching at 1080 cm^{-1}, showing that simple adsorption of poly(allylamine hydrochloride) on the inorganic silica gel did not cause appreciable downshifts in the Si–O stretching wavenumber. In Table 4 are compared the Si–O stretching of silica gel hybrids and those of silica gel adsorbing polyamines.

Powder X-ray diffraction with Cu *Kα* radiation indicated that the poly(allylamine)–silica gel showed a broad peak at 3.80 Å, while normal silica gel had this peak at 3.39 Å. If silica gel and poly(allylamine) exist in different phases, we expect the superimposed X-ray diffraction patterns of the two phases. Thus, the observed peak shift also supported the conclusion that poly(allylamine) and silica gel are mixed at the molecular level.

Adsorption Properties: The silica gel–amine hybrid showed characteristic adsorption properties in water. Normal silica gel has a negative ζ-potential in neutral water and adsorbs cationic dyes from water. For instance, normal silica gel adsorbed rhodamine 6G. In contrast, the silica gel–poly(allylamine) hybrid did not adsorb rhodamine 6G, while it adsorbed an anionic dye, indigo carmine. To investigate the adsorption equilibrium in a more quantitative way, the adsorption rate was measured. As shown in Fig. 3, adsorption of indigo carmine reached equilibrium after 40 h. Adsorption isotherm for indigo carmine at 20 °C in a phosphate buffer at pH 7 is shown in Fig. 4a. The adsorption showed saturation behavior and the Langmuir plot according to Eq. 1 (Fig. 4b) showed a linear relationship between *m*/*x* and 1/*c*:

$$x/m = (x/m)_{\max}ac/(1+ac), \tag{1}$$

where *x* is the adsorbed dye (mol), *m* is the amount of silica gel–poly(allylamine) hybrid (g), *c* is the equilibrium con-

Table 4. Difference in the Si–O Stretching Wavenumber Shifts between the Normal Silica Gel (SiO_2) Adsorbing Polyamines and the Silica Gel–Polyamine Hybrids

Silica gel	ν_{max} for Si–O stretching wavenumber (cm^{-1})
SiO_2 adsorbing poly(allylamine hydrochloride)	1080
Poly(allylamine)–silica gel hybrid	1039
SiO_2 adsorbing poly(L-lysine hydrobromide)	1079
Poly(L-lysine)–silica gel hybrid	1060

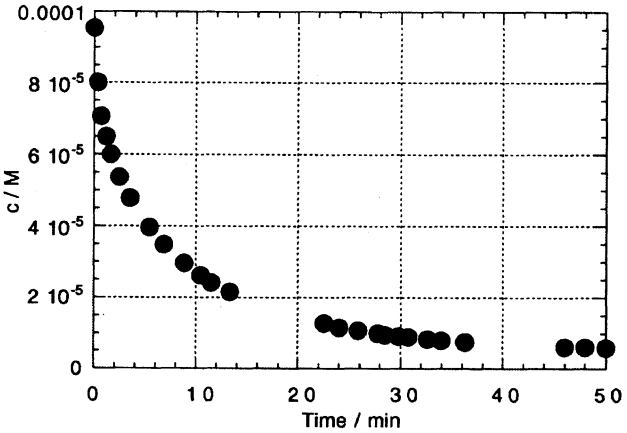

Fig. 3. Decrease in absorbance at 608 nm owing to indigo carmine as a function of time. Silica gel–poly(allylamine) (0.978 mg) was added to 3 mL of 0.1 mM of indigo carmine in water under nitrogen atmosphere at 20 °C.

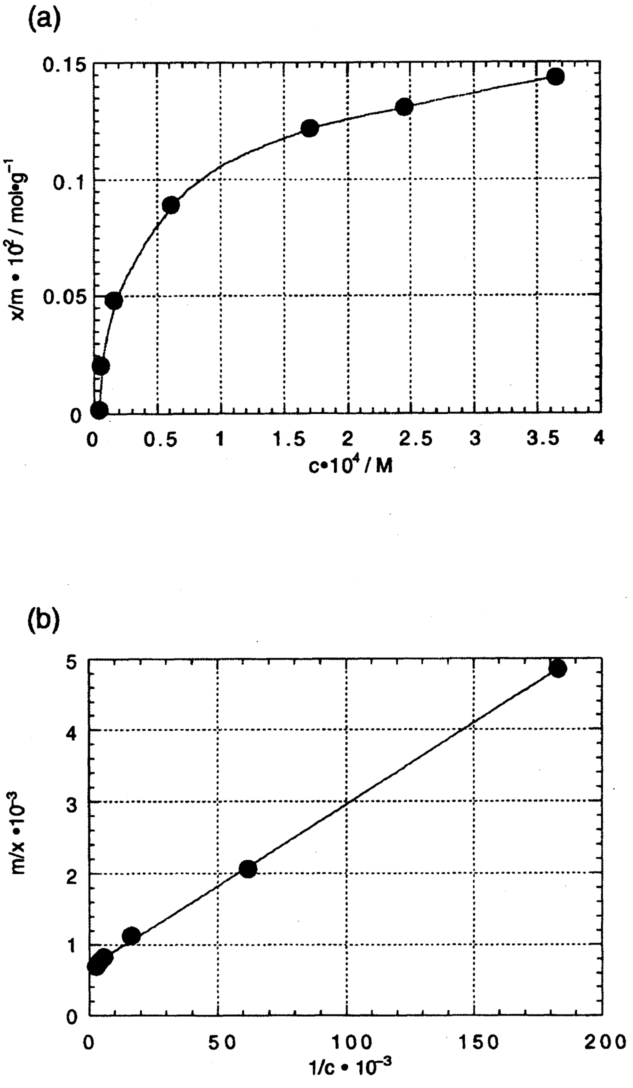

Fig. 4. Adsorption isotherm of indigo carmine to silica gel–poly(allylamine) hybrid in water at 20 °C. (a) Plot of *x*/*m* against the equilibrium concentration of the dye. (b) Langmuir plot.

centration of dye (M), and *a* is a constant. The monolayer capacity, $(x/m)_{max}$, estimated from the Langmuir plot was 1.5×10^{-3} mol g^{-1}. If we assume that indigo carmine molecules are adsorbed on the silica gel surface with the aromatic plane parallel to the surface, the surface area of silica gel is estimated to be 1000 m^2 g^{-1} as a maximum. Considering that 3.4×10^{-3} mol g^{-1} of poly(allylamine) is incorporated in the hybrid, we can estimate that one molecule of indigo carmine is bound through two amino groups of the hybrid, as schematically shown in Fig. 5.

Similarly, adsorption of indigotetrasulfonate was examined. The adsorption followed the Langmuir-type adsorption and the monolayer capacity was 7.2×10^{-4} mol g^{-1}. Therefore, the ion-exchange capacity of the hybrid was 3.0×10^{-3} equiv g^{-1} for both indigo carmine and indigotetrasulfonate. Therefore, the adsorption of these anionic dyes occurred by an ion-exchange mechanism.

Circular Dichroism Spectroscopic Study: Since the silica gel–poly(L-amino acid) hybrids are chiral, we can expect that the hybrid can provide a chiral environment to the adsorbed molecule. By adding indigo carmine to the aqueous suspension of the silica gel–poly(L-lysine hydrobromide) hybrid, we obtained a hybrid silica gel adsorbing the anionic dye. The hybrid was dispersed in KBr pellets and the circular dichroism (CD) spectrum was recorded. As shown in Fig. 6a, the hybrid showed Cotton effects induced in the indigo's band. For comparison the CD spectra of an aqueous solution of poly(L-lysine hydrobromide) and indigo carmine are shown in Fig. 6b.

The induced CD of the hybrid adsorbing indigo carmine indicates that the dye is adsorbed on the surface of the hybrid and the hybrid provides a chiral environment to the adsorbate.

Experimental

IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR. UV-vis spectra were taken on a Hewlett–Packard HP8452A.

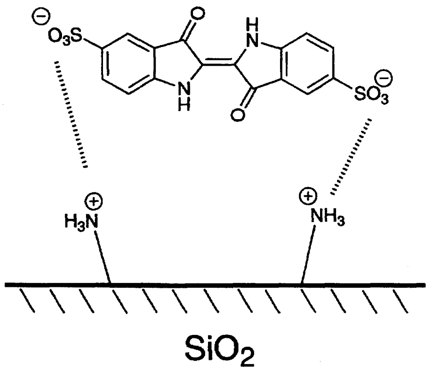

Fig. 5. Schematic representation of adsorption of indigo carmine to the surface of silica gel–poly(allylamine) hybrid.

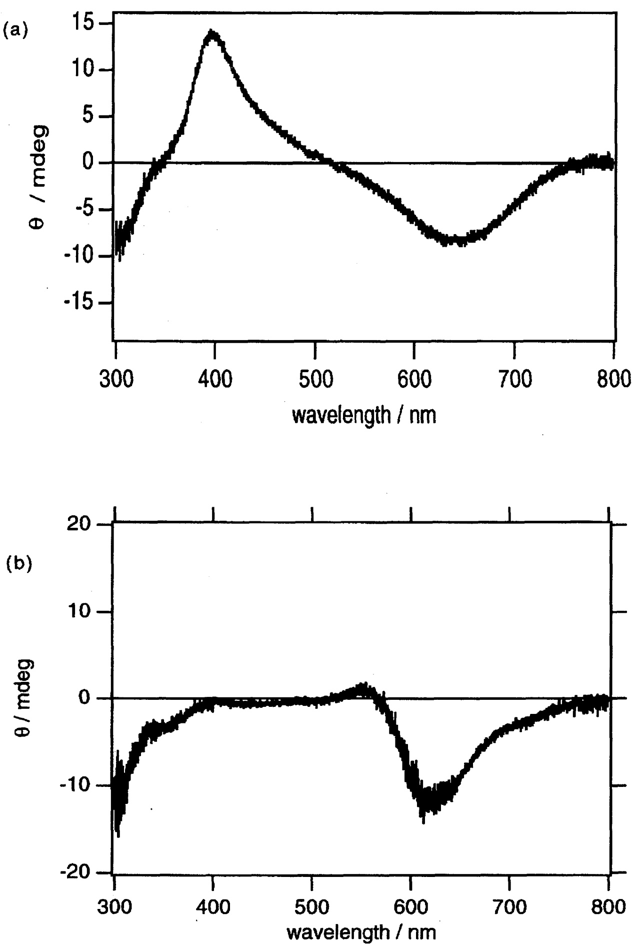

Fig. 6. CD spectra of (a) the silica gel–poly(L-lysine) hybrid adsorbing indigo carmine, and (b) an aqueous solution of indigo carmine and poly(L-lysine hydrobromide). [indigo carmine]=0.10 mM, poly(L-lysine hydrobromide) 0.026 mg mL^{-1}.

CD spectra were obtained on a JASCO J-600 spectropolarimeter. The pH's were measured on a Horiba pH meter F14. Powder X-ray diffraction results were obtained with a Rigaku RAD-B system.

Materials: Tetrasodium monosilicate *n*-hydrate was purchased from Wako Pure Chemical Industries, Ltd. and was used without further purification. Poly(allylamine hydrochloride) was purchased from Nittoboseki; its molecular weight was 8500—11000. Poly(L-lysine hydrobromide) and poly(L-arginine hydrochloride) were purchased from Sigma and their molecular weights were 8400 and 8900 based on viscosity determinations. Poly(L-histidine hydrochloride) was purchased from Aldrich, whose molecular weight was 14100 (viscosity determination).

Measurement of Silicic Acid Polymerization Rate by a Molybdosilicate Method: The decrease in the concentration of monomeric and oligomeric silicic acid (molybdate reactive silicic acids) was monitored by the molybdosilicate method as a function of time. This absorptiometry method for the formation of yellow molybdosilicate was well established for the measurement of silicic acid polymerization rate in an aqueous solution. Monosilicic acid will react with molybdic acid to form the yellow molybdosilicate. Disilicic and oligosilicic acids but not polysilicic acid will decompose to monosilicic acid and then react with molybdic acid.

To a clear solution of Na_4SiO_4 (73.5 mg) in 40 mL of a borate buffer (pH 8.5), an organic additive was added at 20 °C. The borate buffer contains 50 mM of BO_3^{3-}, 50 mM of KCl and the pH was adjusted with NaOH. An aliquot of 400 μL of this solution was taken and diluted with distilled water to 5 mL, followed by the addition of 200 μL of 1.5 M H_2SO_4 solution and 200 μL of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ solution (10 g dissolved with 100 mL of distilled water). After vigorous stirring, the sample was stood for exactly 10 min, then absorbance due to the yellow molybdosilicate was measured at a wavelength of 400 nm. Standard conditions: $[Si(OH)_4]=10$ mM, $[\text{amine}]=1/n$ mM, where n is the number of amino groups in amines.

Preparation of Silica Gel–Poly(allylamine) Hybrid: To a solution of Na_4SiO_4 (73.5 mg) in 40 mL of a borate buffer (50 mM, pH 8.5) was added poly(allylamine hydrochloride) (7.48 mg). After we aged the solution at 20 °C overnight, the gel was collected by centrifugation, washed thoroughly with distilled water and freeze-dried in vacuo. This dried gel was used for IR, XRD, and adsorption experiments.

Conclusions

Catalytic activity of various organic compounds toward silicic acid polymerization was investigated. We found that (1) amines and polyamines have catalytic activity for silicic acid polymerization in water at neutral pH, (2) the resultant silica gel was comprised of a hybrid of organic and inorganic networks though hydrogen bonding, (3) unique adsorption properties of the hybrid gels, and (4) chiral induction in the adsorbate.

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