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Sol–gel synthesis of silica gel disc as applied to supports of organic molecules with optical functions

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In order to synthesize transparent, crack-free silica-gel bodies used as supports for organic substances with optical functions such as fluorescent, lasing, photochromic, photochemical hole burning and non-linear optical functions via the sol–gel route, the effects of the composition of the starting solution on the transparency of the gel, the occurrence of cracks and the bulk density of the gel have been investigated for Si $(OCH_3)_4$–H_2O–CH_3OH–HCl and Si $(OCH_3)_4$–H_2O–CH_3OH–HNO_3 solutions. It was found that the addition of specific amounts of water and acid gave transparent, crack-free silica gel bodies, which could be used as supports for optically functional organic substances. It was also found that organic substances such as quinizarin and rhodamine B incorporated into these gels were uniformly dispersed at the molecular level.

1. Introduction

Various organic substances are reported to show optical functions, such as fluorescence, laser oscillation, photochromism, photochemical hole burning and non-linear optical properties. One of the methods for applying these organic substances as optical elements in optoelectronic and photonic devices is to fix the organic substances in inorganic gels so that the optical function might be stabilized. For that purpose, transparent gels in which organic molecules are dispersed at the molecular level are required, and sol–gel synthesis may be a suitable method for preparing such gels. Avnir *et al.* [1, 2] and Tani and co-workers [3, 4] prepared transparent silica gel bodies embedded with optically functional organic molecules by the sol–gel method, using tetraethoxysilane (TEOS), and showed that the incorporated organic molecules were dispersed as monomers. We have prepared opalescent [5, 6] and opaque [7] silica gel monoliths by the sol–gel method using tetramethoxysilane (TMOS) as source of silica.

In the present work, we attempted to prepare transparent, crack-free silica gel bodies by the sol–gel method using tetramethoxysilane solution. For that purpose, the sol-to-gel conversion process, transparency and crack occurrence in the gel were investigated for $Si(OCH_3)_4$–H_2O–CH_3OH–HCl and $Si(OCH_3)_4$–H_2O–CH_3OH–HNO_3 solutions containing varying concentrations of water and acid. In addition, measurement of fluorescence spectra was performed on certain organic substances incorporated in the gel, in order to check the possibility of embedding the gel with well-dispersed organic molecules.

2. Experimental procedure

2.1. Preparation of starting solutions

$Si(OCH_3)$–H_2O–CH_3OH–HCl and $Si(OCH_3)$–H_2O–CH_3OH–HNO_3 solutions of varying compositions shown in Table I were prepared as starting solutions; x, y and y' represent molar ratio of H_2O, HCl and HNO_3 to Si $(OCH_3)_4$, respectively. Most of the experiments were performed on starting solutions containing no organic substance. Reagent grade chemicals were employed for TMOS (Tokyo Kasei Company), methanol (Wako Pure Chemicals Company), and hydrochloric and nitric acids (Nacalai Chemicals Company). Ion-exchanged water was employed.

For all the starting solutions, the quantity of TMOS in a batch was fixed at 0.08 mol, and other components were added in the mole ratios shown in Table I. First, half of the given amount of methanol was mixed with 0.08 mol TMOS. Then, the other half of the methanol, mixed with the given amounts of water and hydrochloric acid (or nitric acid), was added little by little whilst stirring. A homogeneous starting solution resulted. Organic substances were added to some of these starting solutions and then the solutions were stirred for a few minutes. Three kinds of organic substances were used: 1,4-dihydroxyanthraquinone (quinizarin), [9-(*o*-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene] diethyl chloride (rhodamine B) and 2-methyl-4-nitroaniline (MNA). The volume of the solution was 22–32 ml, depending on the composition of the starting solution.

2.2. Gelation of the solution and drying of the gel

The solution was placed in a cylindrical polypropylene container of 56 mm inner diameter, 73 mm height and about 150 ml volume, sealed with a polypropylene lid and kept at room temperature (about 15 °C) until gelation occurred. The time at which no flow was

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TABLE I Compositions of the starting solutions and properties of the gel

Solution no.	Composition (mole ratio)					Gelling time	Appearance of the dried gel		Bulk density (g cm^{-3})	Porosity
	TMOS	H_2O, x	CH_3OH	HCl, y	HNO_3, y'		Crack[a]	Transparency		
1	1	1.53	2	0.40		2 h	A	Opaque	0.87	0.60
2	1	2	2	0.40		1 h	A	Transparent	1.33	0.40
3	1	3	2	0.40		1 h	A	Transparent	1.23	0.44
4	1	4	2	0.40		1 h	A	Transparent	1.19	0.46
5	1	8	2	0.40		12 h	C	Slightly opalescent	0.93	0.58
6	1	10	2	0.40		12 h	C	Slightly opalescent	0.90	0.59
7	1	1.53	2	0.10		6 h	A	Opaque	0.76	0.65
8	1	2	2	0.10		3 h	A	Transparent	1.51	0.31
9	1	3	2	0.10		3 h	A	Transparent	1.40	0.36
10	1	4	2	0.10		3 h	A	Transparent	1.30	0.41
11	1	8	2	0.10		15 h	C	Transparent	1.20	0.45
12	1	2	2	0.01		4 d	B	Transparent	1.63	0.26
13	1	3	2	0.01		7 d	B	Transparent	1.44	0.35
14	1	4	2	0.01		7 d	B	Transparent	1.73	0.21
15	1	8	2	0.01		14 d	A	Transparent	1.40	0.36
16	1	10	2	0.01		14 d	A	Transparent	1.40	0.36
17	1	2	2		0.40	1.5 h	A	Transparent	1.56	0.29
18	1	3	2		0.40	3 h	A	Transparent	1.55	0.30
19	1	4	2		0.40	3 h	A	Transparent	1.51	0.31
20	1	8	2		0.40	1 d	C	Slightly opalescent	1.23	0.44
21	1	2	2		0.10	3 d	A	Transparent	1.63	0.26
22	1	3	2		0.10	3 d	A	Transparent	1.60	0.27
23	1	4	2		0.10	3 d	A	Transparent	1.56	0.29
24	1	8	2		0.10	7 d	C	Transparent	1.50	0.32
25	1	4	2		0.05	5 d	A	Transparent	1.78	0.19
26	1	10	2		0.05	7 d	A	Transparent	1.44	0.35
27	1	2	2		0.01	14 d	B	Transparent	1.91	0.13
28	1	3	2		0.01	14 d	B	Transparent	1.80	0.18
29	1	4	2		0.01	14 d	B	Transparent	1.81	0.17
30	1	8	2		0.01	30 d	B	Transparent	1.63	0.26

[a] A, no crack; B, one or two cracks; C, many cracks.

observed on tilting the container was taken as the gelation time.

After gelation, the container was equipped with a polypropylene cover having five holes of 2 mm diameter and kept in an oven at 40 °C for 2 months to dry the gel. The container was placed in a closed polypropylene box filled with silica gel drying agent during the drying period. The whole drying agent was renewed every 3 days until 2 weeks from the start of the drying process and every 1 week thereafter.

2.3. Bulk density and pore size of dried gels

The bulk density was estimated from the weight and size of a dried gel disc. The porosity was calculated from the bulk density, assuming that the silica skeleton in the gel has the same density as the silica glass.

The pore-size distribution was measured for some of the dried gel bodies. The measurement was made using the BET method with nitrogen gas using a Micromeritics Company model AccuSorb 2100E physical absorption analyser. The average pore size was estimated from the pore-size distribution curve derived from the absorption isotherm for nitrogen gas.

2.4. Measurement of fluorescence spectra of gels containing organic substances

In order to examine the state of organic molecules in the dried gel, fluorescence spectra of dried gels prepared from the solutions which would produce transparent, crack-free gel bodies were examined. Quinizarin and rhodamine B molecules were incorporated in the starting solution. The fluorescence spectra were measured using a Hitachi model 850 spectrofluorescence meter. For excitation, the maximum excitation wavelengths of 250 and 540 nm were selected for quinizarin and rhodamine B, respectively.

3. Results

Gel discs, 30–40 mm diameter and 6–8 mm thick, were prepared. Table I shows the gelation time of the starting solution, the transparency and occurrence of cracks in the gel body, and the porosity and bulk density of the gel.

3.1. Gelation and ageing process

On keeping at room temperature in the sealed container, the solution became more viscous with time and finally was solidified as wet gel. Most of the solutions were transparent, becoming transparent gels, while some of the solutions became gradually turbid during the gelation process, forming opaque gels (nos 1 and 7 in Table I).

During the subsequent ageing for 1 week in the sealed container, the gel shrank and at the same time syneresis occurred. This shrinkage produced a space of 1–5 mm between the gel body and the container wall, which was filled with a solvent excluded from the wet gel as a result of the syneresis, as shown on the right of Fig. 1. The following qualitative observations were made.

1. For the starting solutions containing the same amount of added water, gelation occurred faster with increasing acid content.
2. Solutions 1 and 7, in which the water content was small ($x = 1.53$), were opaque at the time of gelation, while all other solutions became transparent gels.
3. During ageing after gelation, a shrinkage in the volume of the wet gel occurred, accompanied by syneresis. The rate of shrinkage was larger for the compositions with higher acid content. This results in smaller gel volumes for starting solutions of higher acid content than for that of a lower acid content after ageing for 1 week.

3.2. Process of drying of wet gels

Drying the wet gel at 40 °C in the container with a perforated lid caused the vaporization of the solvent produced by syneresis and shrinkage of the gel. Opaque wet gels prepared from starting solutions with a low water content ($x = 1.53$, nos 1 and 7) remained opaque on drying, becoming opaque dried gels.

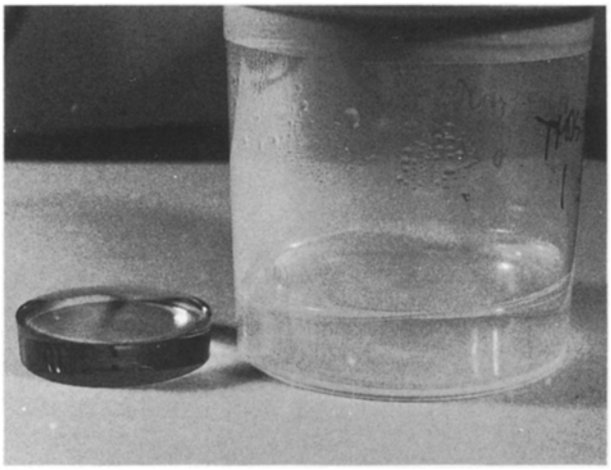

Figure 1 A wet gel (right) and dried gel (left) prepared from the starting solution 4 (TMOS:H_2O:CH_3OH:HCl = 1:4:2:0.40).

Many of the transparent wet gels exhibited a peculiar behaviour in appearance during the drying process: they became opaque or opalescent 10–15 days after the start of drying, and on further drying, they started to become less opaque, regaining the original transparency at the time of the completion of drying, as shown in Fig. 2. The phenomenon is markedly observed for starting solutions 4–6, 10, 11, 19, 20, 23 and 24, which are characterized by the acid content y (y') of 0.10 or 0.40 and a water content, x, equal to or higher than 4. It has been observed with these gel discs in which cracks were found during drying that the cracks often occur before regaining transparency.

The occurrence and degree of cracking observed in dried gel are shown in Table I. The degree of cracking is illustrated by examples in Fig. 3. In Fig. 3, (a) shows a transparent disc without cracks, (b) a low degree of cracking characterized by fracture of the disc into two or three pieces, (c) severe cracking characterized by the breakdown of the gel into small pieces, and (d) the opaque disc without cracking.

No cracking occurred for starting compositions 1–4 and 7–10, which have a high content of HCl ($y = 0.40$, 0.10), and a low content of water ($x \leq 4$). Or compositions 14–16, which have a low content of HCl ($y = 0.01$) and a higher content of water ($x > 4$).

When HNO_3 was used in place of HCl, no cracking occurred for starting compositions 17–19 and 21–23, which have high HNO_3 content ($y' = 0.40$ or 0.10) and lower water content ($x \leq 4$), but a couple of cracks were seen for compositions of a low HNO_3 content ($y' = 0.01$) even if the water content was higher than 4 (solutions 29 and 30).

A heavy warping of the gel disc is another defect which occurred during the drying process. This defect was often seen for starting solutions 14–16 and 30, which were characterized by low acid content ($y, y' = 0.01$) and high water content ($x \geq 4$).

3.3. Appearance of gel

As summarized in Table I, the dried gel discs prepared from compositions of a low water content at $x = 1.53$ (1 and 7) were not transparent but white. All the other dried gel discs were transparent.

3.4. Infrared spectra of dried gels

Fig. 4 shows near infrared spectra in the wavelength

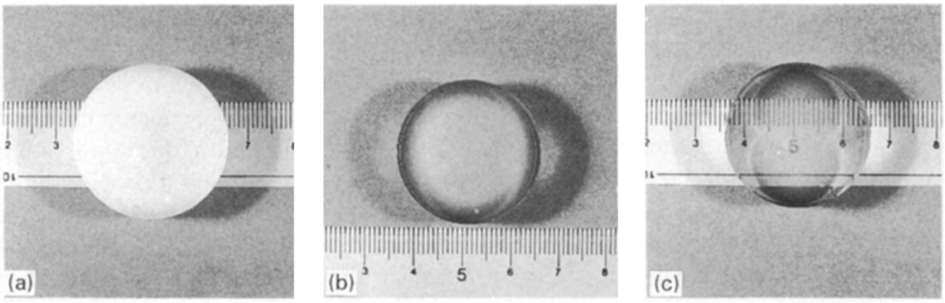

Figure 2 Appearance of the gel 4 during the drying process: (a) 14 days, (b) 17 days and (c) 21 days after gelation.

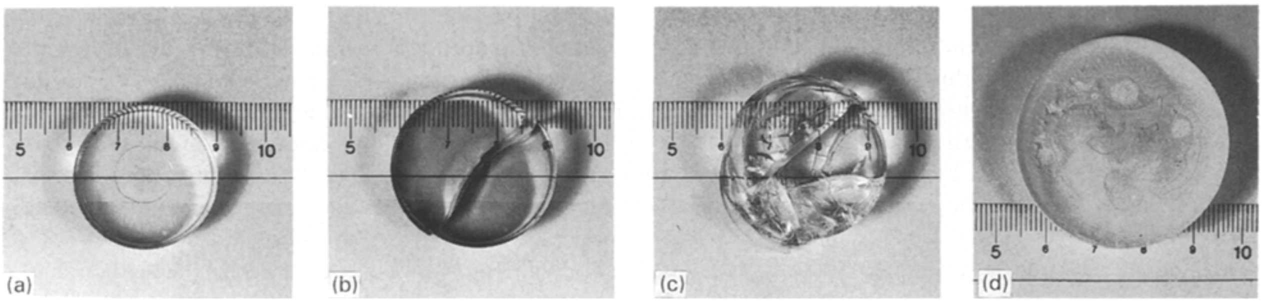

Figure 3 Appearance of the dried gel bodies containing no organic substance: (a) transparent and no cracks, (b) transparent and one or two cracks, (c) transparent and many cracks, (d) opaque and no cracks.

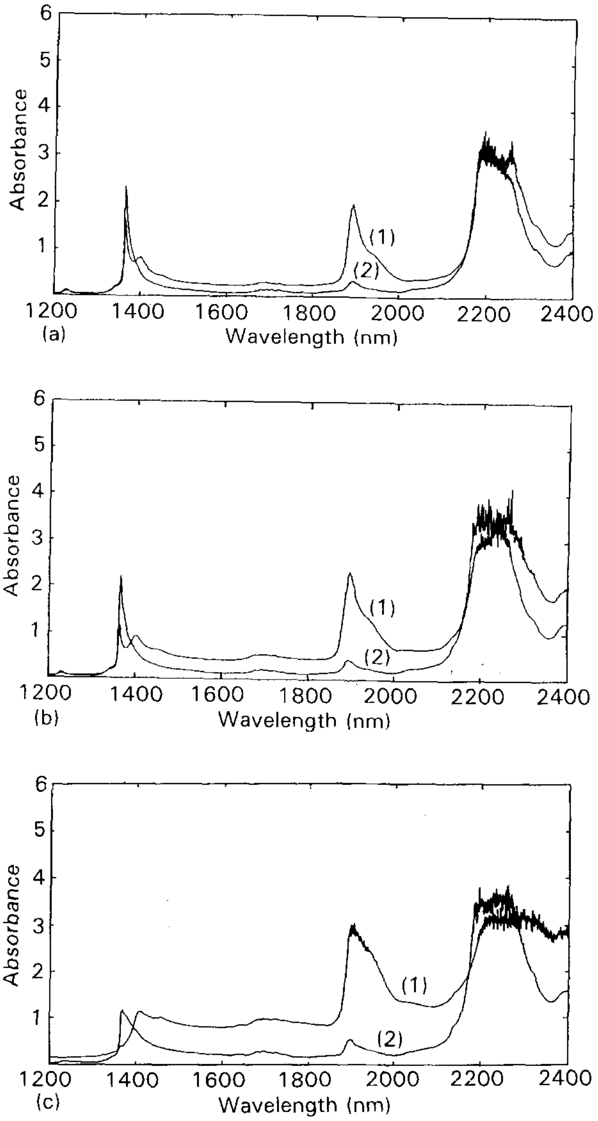

Figure 4 Near infrared spectra of the dried gel obtained from a solution of a constant water content at $x = 4$ and various HCl contents, y. (1) The gel immediately after drying, (2) the same gel after subsequent heating at 100 °C for 20 h. (a) solution 4 ($y = 0.40$), (b) solution 10 ($y = 0.10$) (c) solution 14 ($y = 0.01$)

range from 1200–2400 nm for dried gels obtained from solutions of a constant water content ($x = 4$) and varying HCl content. Fig. 4 a–c correspond to HCl contents of $y = 0.40$ (solution 4), 0.10 (solution 10) and 0.01 (solution 14), respectively. In each figure, Curve 1 is for the gel immediately after drying and Curve 2 for the same gel after subsequent heating at 100 °C for 20 h.

The band peaking at 1900 nm with a shoulder at 1950 nm is due to a combination of stretching and bending vibrations of water [8] and the intensity of the band represents the quantity of water. The band shows a marked decrease in intensity upon heating of the gel at 100 °C for 20 h, indicating that the dried gel contained a considerable amount of water.

Because the vibration of silanol groups is known to cause an absorption around 3600 cm^{-1} in the infrared region [9, 10], the absorption band around 1400 nm (7150 cm^{-1}) is thought to correspond to their overtones. It is also known that free Si–OH groups have a higher frequency in vibration than associated Si–OH groups [9, 10]. Therefore, it is possible to assume that the decrease in the intensity of the 1400 nm band and the growth of the sharp peak at 1360 nm on heating at 100 °C may be attributed to the reduction of associated silanol groups and water molecules and the formation of non-associated silanol groups resulting from the vaporization of water. It was found that when the gel heated at 100 °C for 20 h was kept in a water-vapour saturated atmosphere, the spectra returned to the form before heating.

The band peaking at 1360 nm is much smaller for the dried gel prepared from the solution of $y = 0.01$ (Fig. 4c) than those prepared from the solution of higher HCl contents at $y = 0.40$ (Fig. 4a) and 0.10 (Fig. 4b), indicating that the weakly acid-catalysed gel contains a relatively small amount of non-associated silanol groups. This is possibly due to smaller pore volume (or pore size) of the weakly acid-catalysed gel (see Table I).

3.5. Dispersion state of functional organic substances

The colour of dried gels in which organic molecules are incorporated is described in Table II. Their photographs are shown in Figs 5–7. In gels 1 and 7 which are white because of micrometre- or submicrometre-sized gel skeleton [7], organic molecules of any kind are not homogeneously dispersed, but are precipitated as specks on the surface and inside of the gel, as shown in Fig. 5. For gels 1 and 7, even a very small amount of rhodamine B has been confirmed not to be homogeneously dispersed, although a very large amount of rhodamine B can be dissolved in the starting solutions.

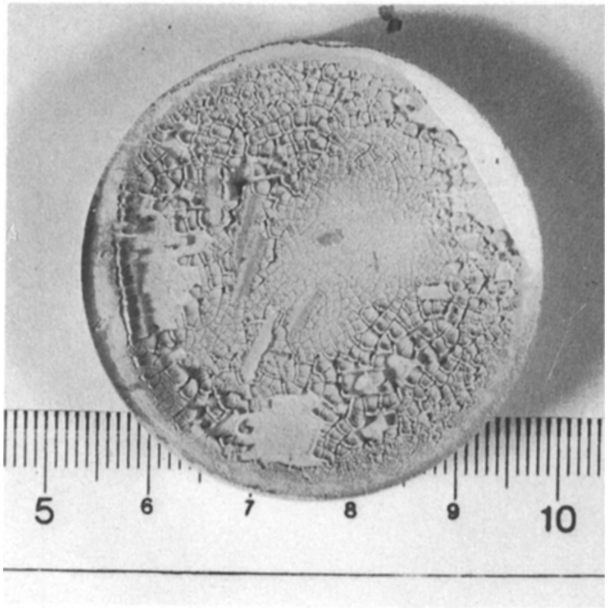

Figure 5 The appearance of dried gel 7 ($x = 1.53$, $y = 0.10$) containing rhodamine B.

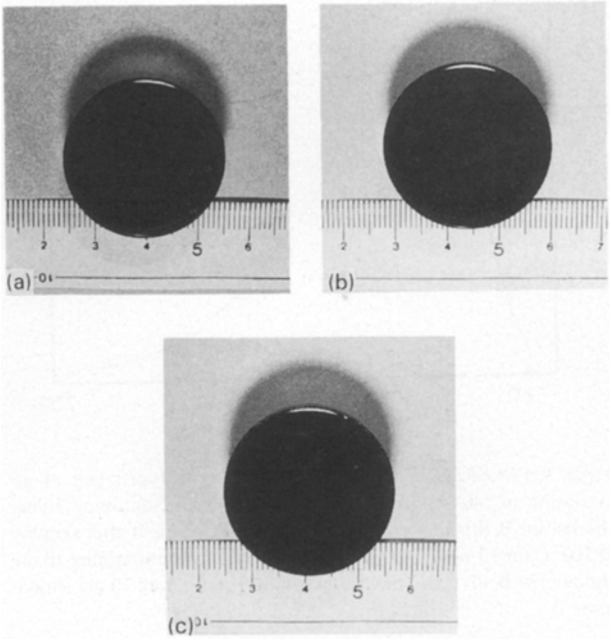

Figure 6 The appearance of dried gel 4 ($x = 4$, $y = 0.40$) containing organic substances: (a) quinizarin, (b) rhodamine B, (c) MNA.

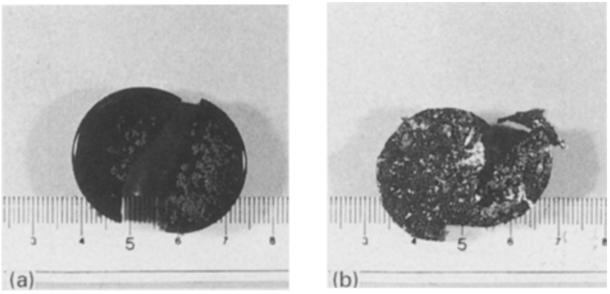

Figure 7 The appearance of the dried gel containing MNA. (a) solution 14 ($x = 4$, $y = 0.01$), (b) solution 15 ($x = 8$, $y = 0.01$).

TABLE II Dispersion of organic substances in the dried gels on the basis of the appearance

Solution no.	Dispersion of organic substances[a]		
	Quinizarin	Rhodamine B	MNA
1	I	I	I
2	H	H	H
3	H	H	H
4	H	H	H
5	H	H	H
6	H	H	H
7	I	I	I
8	H	H	H
9	H	H	H
10	H	H	H
11	H	H	H
12	H	H	H
13	H	H	H
14	H	H	H*
15	H	H	H*
16	H	H	H*
17	H	H	H
18	H	H	H
19	H	H	H
20	H	H	H
21	H	H	H
22	H	H	H
23	H	H	H
24	H	H	H
25	H	H	H
26	H	H	H
27	H	H	H
28	H	H	H
29	H	H	H
30	H	H	H

[a] I, Inhomogeneous dispersion. Opaque gel. Organic substance precipitated as specks.
H, Homogeneous dispersion. Transparent gel.
H*, Homogeneous dispersion. Transparent gel with a small amount of organic substance precipitated on the surface.

In gels of compositions other than 1 and 7, dried gels doped with organic substances show a colour characteristic of the employed organic substance, but appear transparent (Fig. 6). It should be noted, however, that a large addition of organic substance makes the gel dark.

Fig. 7 shows the appearances of dried gels doped with MNA prepared from starting solutions of compositions 14–16 which have a low HCl content ($y = 0.01$) and high water content ($x \geq 4$). The inside of these gels is transparent and homogeneous, while at the surface of the gels, MNA molecules are agglomerated, producing specks. It has been confirmed that the incorporation of organic substances has no essential influence on the gelation process of the starting solution, shape of the dried gel and occurrence of cracks, as long as the amount incorporated is not unusually high. Incorporation of an extremely high amount of organic substance tends to increase cracking in the dried gel, even if it is homogeneously dissolved in the starting solution.

3.6. Fluorescence of gels doped with functional organic substances

Fig. 8 shows the fluorescence spectra of silica gels

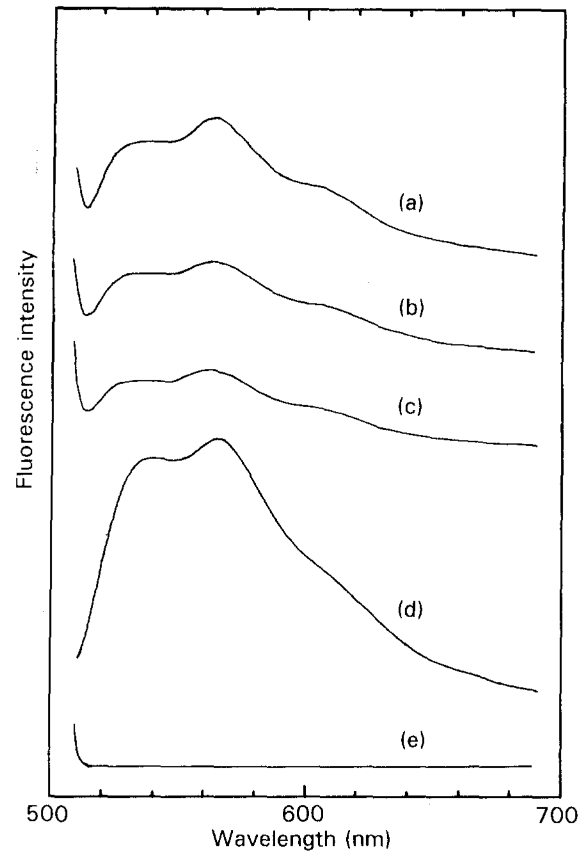

Figure 8 Fluorescence spectra of quinizarin-doped gels at an excitation of 250 nm. (a) Gel 4 ($x = 4$, $y = 0.40$) containing 3 mg quinizarin. (b) Gel 4 containing 1 mg quinizarin. (c) Gel 19 ($x = 4$, $y' = 0.40$) containing 1 mg quinizarin. (d) 50 ml methanol solution containing 5 mg quinizarin. (e) Gel 4 ($x = 4$, $y = 0.40$) without quinizarin.

doped with quinizarin. Because silica gel gives fluorescence at 500 nm, fluorescence spectra for longer wavelengths than 510 nm are shown. Quinizarin in the gel gives three broad bands peaking at 530, 560 and 610 nm. These peaks agree well with those for quinizarin molecules in methanol. In addition, no difference was found in the spectrum between starting solutions using HCl and HNO_3.

Fig. 9 shows spectra of rhodamine B in silica gels. The peak at 580 nm attributed to rhodamine B is seen both in gels and methanol. The peak of the gel prepared from HCl-catalysed solution agrees quite well with that of the methanol solution, while that of the gel prepared from HNO_3-catalysed solution shows a slight shift to longer wavelength and a larger band width. Heating of the gel prepared from HCl-catalysed solution at 100 °C broadens the band width.

4. Discussion

Incorporation of organic molecules in starting solutions does not essentially affect the transparency and occurrence of cracks of the resultant gel, and therefore, first we will discuss silica gel bodies not doped with organic substances.

4.1. Transparency of gels

Of the 30 starting solutions shown in Table I, only solutions 1 and 7 gave opaque gels; all other compositions gave transparent gels. Compositions 1 and 7 were used by Kozuka and Sakka [7] to produce large gel bodies. The gels prepared from starting compositions 1 and 7 consisted of large round particles of about 5 and 0.1 μm diameter, respectively. This caused an intense light scattering, making the gel completely opaque. The reason for the transparent nature of the other gels may be attributed to the very small diameter of pore channels in the gel. A very rough measure of the transparency may be given by

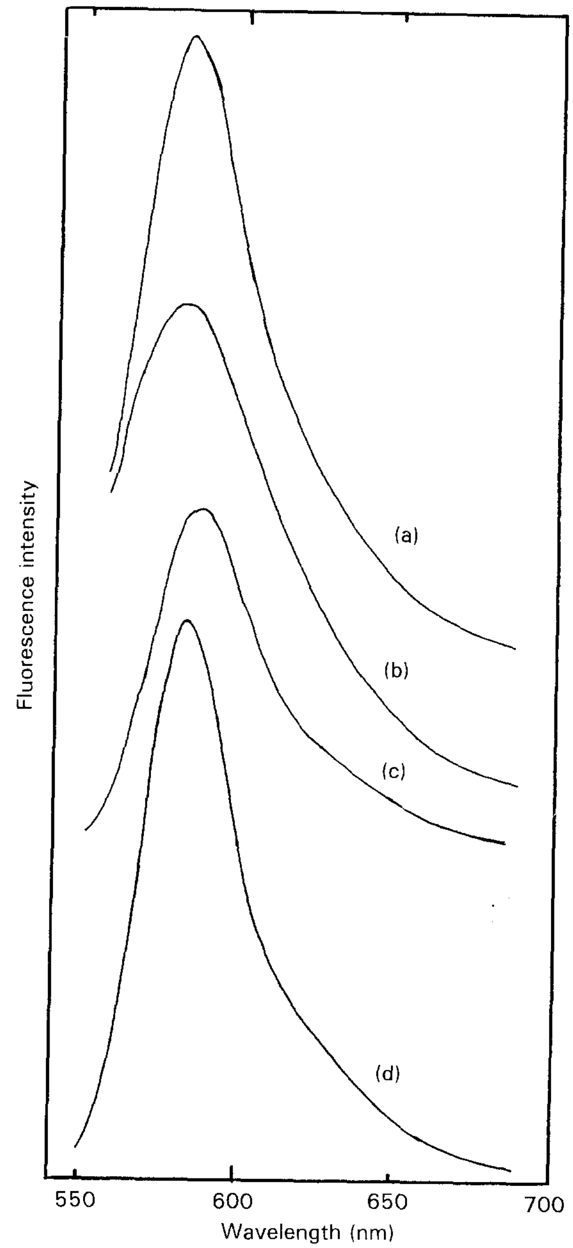

Figure 9 Fluorescence spectra of rhodamine B-doped gels at an excitation of 540 nm. (a) Gel 4 ($x = 4$, $y = 0.40$) containing 10 mg rhodamine B. (b) Gel 4 containing 10 mg rhodamine B after keeping at 100 °C for 10 weeks. (c) Gel 19 ($x = 4$, $y' = 0.40$) containing 10 mg rhodamine B. (d) 50 ml methanol solution containing 10 mg rhodamine B.

$$d \ll \frac{\lambda}{2\pi} \qquad (1)$$

where d is the diameter of light-scattering particles in a medium and λ is the wavelength of light. If we substitute the wavelengths of visible lights of 400–800 nm for λ in Equation 1, we obtain

$$d \ll 70\text{–}130\ \text{nm} \qquad (2)$$

Our measurements for some (solutions 4, 10 and 14) of the transparent dried gels showed that the pore diameter was about 2.5 nm. This satisfies Equation 2 and explains the transparent nature of dried gels other than 1 and 7.

4.2. Occurrence of cracks during the drying process

Table I indicates that some of the transparent gels have cracks and others do not. Generally, cracks may be generated during the drying process by the capillary force of the solvent filling the pores, which tends to contract the surface layer of the gel, causing tensile stress. The capillary force is expressed by [11]

$$\Delta P = \frac{4\gamma\cos\theta}{D} \qquad (3)$$

where ΔP is the capillary force, γ is the surface tension of the solvent and θ is the contact angle. This equation indicates that the capillary force, ΔP, is small when the diameter of the pores is large and the surface tension of the solvent is small. Based on Equation 3, we can cite the conditions required for producing crack-free gel monoliths.

1. The pore size should be large, resulting in a small capillary force.
2. The surface tension of the solvents filling pores at the drying stage should be small, resulting in small capillary force.
3. The siloxane network must be strong as a result of sufficient development of siloxane bondings. In the case of granular structure, siloxane bondings between neighbouring particles must be strong.

At present, the relation between the occurrence of cracks and the composition of the starting solution is not well understood. However, the following somewhat speculative explanation might be possible. In the series of starting solutions containing HCl of $y = 0.40$ (solutions 1–6) and 0.10 (solutions 7–11), no cracks occur for starting solutions of compositions with a low water content, but cracks do occur for those of high water content. In these series of high HCl content, it is assumed that the gel has a microstructure consisting of granular particles [7], and the particle size, and thus the pore diameter, become small with increasing water content. The increase in the water content would lead to an increase of capillary force causing cracking in the drying gel.

On the other hand, in the series of low HCl content at $y = 0.01$ (solutions 12–16), no cracks occur for compositions with high water content. In this series, gels may have a structure in which continuous pores are dispersed in the SiO_2 matrix. It may be assumed that the pore diameter is very small, less than 1.5 nm for lower water contents, and the pore diameter increases with increasing water content up to about 2.5 nm, making the capillary force small enough not to cause cracks.

4.3. State of organic molecules in the gel

It has been shown that for quinizarin and rhodamine B, the fluorescence spectrum of the gel is very similar to that of the methanol solution. This indicates that quinizarin and rhodamine B molecules are dispersed in the gel as individual molecules. Therefore, they are expected to display their own characteristic functions of photochemical hole-burning and dye laser effects, for example. Because individual molecules of these substances fixed in the gel are separated from each other by inorganic networks, it is reasonable to assume that these organic molecules would be quite stable against agglomeration and deterioration of their function.

5. Conclusions

In order to obtain silica gel bodies for use as supports of functional organic substances, sol–gel formation was applied to starting solutions of compositions $1\mathrm{Si(OCH_3)_4 \cdot x\,H_2O \cdot 2CH_3OH \cdot y\,HCl}$ (or $y'\,\mathrm{HNO_3}$), where $x = 1.53\text{–}10$ and $y = 0.01\text{–}0.40$, and the effect of the composition of the starting solution on the transparency, the occurrence of cracks and the fluorescence spectrum of the organic molecules has been examined. The following results were obtained.

1. Starting solutions of compositions of the lowest water content ($x = 1.53$) and higher HCl contents ($y = 0.10$ and 0.40) produced opaque gels, while all other solutions produced transparent gels.
2. Among the starting solutions from which transparent gels were obtained, the starting solutions of higher acid content and lower water content and those of low acid content and higher water content gave crack-free dried gel discs of about 30 mm diameter and 5–6 mm thickness.
3. Functional organic substances such as quinizarin and rhodamine B, dissolved in the starting solution, were confirmed to be homogeneously dispersed as molecules in the transparent gels.

Acknowledgement

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