

Molecular Forms of Rhodamine B in Dip-Coated Thin Films

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Thin sol–gel films including rhodamine B (RB) which were dip-coated using the sol–gel reaction of tetraethyl orthosilicate have been prepared as a function of time after mixing of the reaction systems. The absorption and fluorescence spectra of the individual thin films have been observed as a function of time after the preparation of the individual thin films. The relative contribution of the monomer, H-dimer, and J-dimer of RB existing in the individual thin films to the total absorption and fluorescence spectra of the individual samples was obtained as a function of time. RB molecules were encapsulated in a certain structural region (prestructure of the pores) long before the gelation point. With the progress of the sol–gel reaction, dimerization in the prepared film was gradually prevented, and the monomer RB became the preferential species. On the other hand, dimerization of RB in the thin film was pronounced just after dip-coating until the SiO₂ network was almost formed, and the dimerization was enhanced progressively with the time course of the reaction under a specific reaction condition. Water plays an important role in the dimerization process.

Introduction

The sol–gel reaction of metal alkoxides proceeds via hydrolysis and polycondensation reactions. The molecular-order physicochemical properties of the reaction system would vary according to the progress of the reaction. Although the properties are scarcely known at the present time, the changes are interesting and important not only for understanding the fundamental chemical reactions but also for practical applications such as solar energy conversion and devices for photonics.^{1,2} The absorption and fluorescence spectra are a useful probe for understanding the changes.^{1–11} The sol–gel method is therefore expected to be a synthetic route to making new organic–inorganic hybrid materials which can be utilized in devices for photoelectric mutual conversion. One of the methods for increasing the conversion efficiency is using organic dyes, which have higher absorption coefficients compared with inorganic metals, as semiconductors.

Rhodamines which have a higher absorption coefficient and fluorescence yield are fine dyes for collecting and utilizing photoenergy. Because the thin film form is required in using the dyes as functional materials, it is important to investigate the photophysical and photochemical properties of the dyes encapsulated in dip-coated thin films and to clarify the environment. The properties of these dyes depend on the concentration and type of solvents used, indicating the existence of an association of the dyes.^{12–27} According to the molecular exciton theory,²⁸ the spectral features of the absorption depend on the dimer configurations. They are of a sandwich geometry (nonfluorescent H-dimer) and oblique or coplanar geometry with an inclined transition dipole (fluorescent J-dimer).

Reisfeld et al. observed that the stability of encapsulated rhodamine 6G in sol–gel glass and PMMA films is increased as compared with the solutions.⁶ They also showed luminescent enhancement of rhodamine 6G in sol–gel films containing silver aggregates.⁷ Narang et al. reported that there is a small amount of aggregates of rhodamine 6G in the spin-coated films compared with the solvent because aggregation is prevented by the sol–gel reaction.²⁹ In addition to this, they indicated that

the rotational reorientation time of rhodamine 6G in the sol–gel reaction system changes remarkably during the drying process.³⁰ Winter et al.³¹ found that rigidity at the microscopic level of the sol–gel reaction system is not accompanied by macroscopic dynamics, like the viscosity exhibiting drastic changes during gelation. The mobility of probe molecules in the system is hardly affected by gelation. Only small changes in the molecular motion occur in the course of the sol–gel reaction.

The results by Narang et al. and Winter et al. indicated that it is important to study the behavior of dye molecules along with the change in the environment surrounding the mixed molecules in the sol–gel reaction system. In a preliminary letter,³² we showed that one monomer and two dimers (H- and J-types) are clearly and simultaneously resolved in the absorption spectra of rhodamine B (RB) in water–ethanol mixed solvent and in the dip-coated thin films,^{33–35} which have been prepared as a function of time after mixing of the reaction systems, using the sol–gel reaction of tetraethyl orthosilicate (TEOS). The obtained absorption spectra suggested that the RB molecules are encapsulated in a certain structural region (pores) long before the gelation point of the sol–gel reaction of TEOS.

In this paper, we report the details of the absorption and fluorescence spectra in water–ethanol mixed solvents and those of the films observed as a function of time after the preparation of the thin films in order to clarify the chemical species (monomer, H-dimer, and J-dimer) of RB existing in the films and the structure of the pores in the films. On the basis of the experimental findings, a systematic and detailed investigation of the change in the molecular forms of RB in the film as a function of time will be discussed.

Experimental Section

Materials. RB, ethanol, and hydrochloric acid (Wako Chemicals, JIS S grade), rhodamine 6G (Tokyo Kasei), and TEOS (Wako Chemicals and Shin-Etsu Chemicals) were used without further purification. The water was deionized and distilled. Slide glasses for use as the substrate (Matsunami S-1126) were washed with neutral detergents, soaked in 0.1 M (M = mol dm⁻³) aqueous HCl solution for 1 h, washed with water, and finally dried at room temperature.

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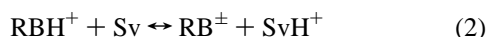
Sample Preparation. Acid and basic solutions were obtained by adding 0.04 mL of 1 M HCl and 1 M NaOH to 10 mL of 1.0×10^{-6} M aqueous or ethanol solutions of RB. In order to investigate the concentration dependence, aqueous and ethanol solutions of RB were prepared in a concentration range from 1.0×10^{-6} to 5.0×10^{-2} M. RB was dissolved in ethanol at 1.0×10^{-2} M for the sol-gel reaction. The starting solutions of the sol-gel systems contained 21.0 mL of RB in ethanol solution, 20.0 mL of TEOS, and 6.5 mL of 1.0×10^{-5} M aqueous HCl solution as catalyst (two systems, A1 and A2, were prepared). The other starting solution contained 21.0 mL of RB in ethanol solution, 20.0 mL of TEOS, and 1.6 mL of 4.0×10^{-5} M aqueous HCl solution as catalyst (system B). The solutions were stirred during the addition, stirred thoroughly for an additional 30 min, and then poured into individual polypropylene vials (50 mL). The vials were closed with a holed cover and kept in a thermostat at 35 °C. The dip-coated thin films were made as a function of reaction time of the prepared solutions. The dipping substrates were withdrawn vertically from the sol-gel solution in the vial at a speed of 10 mm min⁻¹ at room temperature. The prepared films were kept at room temperature.

Spectral and Weight Measurements. The absorption spectra and fluorescence spectra were observed using a Hitachi U-3210 recording spectrophotometer and a Shimadzu RF-5000 fluorescence spectrophotometer, respectively. The data were transferred to an NEC PC-9801 personal computer and recorded. The spectra in dilute solutions were obtained using matched quartz cells of 1.0 or 0.1 cm path lengths. The spectra in highly concentrated solutions were obtained by interposing the solution between two slide glasses. Plastic tape was wound around the two overlapped slide glasses to prevent evaporation of the solvent. The measurement of the sample weight was carried out using a Sartorius H160 electronic balance.

Results and Discussion

Molecular Forms of RB in Aqueous and Ethanol Solvents.

Although there have been reports on the absorption spectra of RB in aqueous and ethanol solvents, the relation between the fluorescence and absorption spectra and their concentration dependence is not well understood. We investigated the dependence of the spectra on the concentration of RB and the acid or basic conditions of the solvents. RB molecules in a polar solvent must give rise to the following equilibria generated by the dissociation of a chloride ion and a proton³⁶⁻³⁸



where RBH^+Cl^- , RBH^+ , RB^\pm , and Sv are the neutral salt, cation, zwitterion, and solvent, respectively. The equilibrium (1) tends toward the right side in a high dielectric solvent such as water but moves to the left side in highly concentrated hydrochloric acid solutions, where the solubility of RB is reduced in the solvent.

In order to clarify the relationship between the molecular forms and their corresponding absorption spectra in solvents and in the dip-coated films, the absorption spectra in acidic and basic aqueous and ethanol solutions were observed and are shown in Figure 1. To clarify the relationship represented in eq 2, Figure 1 shows the absorption spectra of RBH^+ and RB^\pm which were obtained in acidic and basic solvents of (A) aqueous and (B) ethanol solutions of RB. The peaks of the spectra of RBH^+ and RB^\pm are 558 and 554 nm in aqueous solutions and

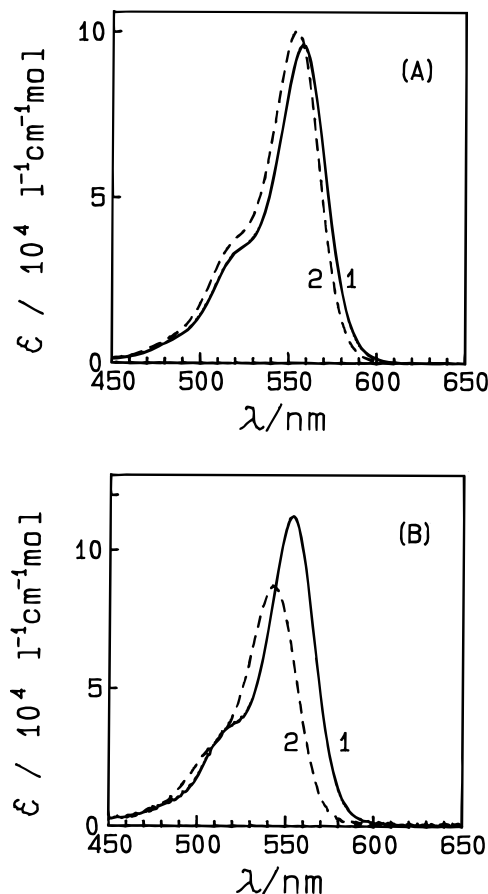


Figure 1. Absorption spectra of rhodamine B in (A) aqueous and (B) ethanol solvents in (1) acidic and in (2) basic circumstance: concentration, 1.0×10^{-6} M.

553 and 543 nm in ethanol, respectively. These values agree well with those in the literature.^{21,23,36-38}

Figure 2 shows the fluorescence spectra of RBH^+ and RB^\pm in aqueous and ethanol solutions. The peaks of the spectra of RBH^+ and RB^\pm are 581 and 578 nm in aqueous solution and 576 and 566 nm in ethanol solution, respectively. The values correspond to those in the literature.^{23,37,38} The absorption and fluorescence spectra are mirror images of each other.

Figure 3A shows the concentration dependence of the absorption spectra of RB in water. The spectrum in dilute solution has a strong peak at 554 nm and a shoulder at 525 nm. The spectrum can be assigned to the RB^\pm monomer. The relative intensity of the higher energy band increased with increasing concentration of the dye. The well-defined isosbestic points at 538 and 568 nm indicate that an equilibrium exists between the species including the RB^\pm monomer and a dimer. These isosbestic points correspond to the values in the literature.^{13,16,17,26,27} These spectral changes result from the exciton splitting by formation of the dimer with the increasing concentration of the dye. The molecular form of RB monomer constituting the dimer will be discussed in a later section.

The concentration dependence in ethanol solution is shown in Figure 3B. The spectrum in dilute solution has a peak at 543 nm which can be assigned to originate from the RB^\pm monomer. On increasing of the concentration of the dye to 1.0×10^{-3} M, the molar absorption coefficient increases and the peak red-shifts to 553 nm as in the case of increased acidity. Little change in the peak and form of the spectrum occurred at concentrations higher than 1.0×10^{-3} M. All spectra pass through isosbestic points at 543, 523, and 506 nm, indicating

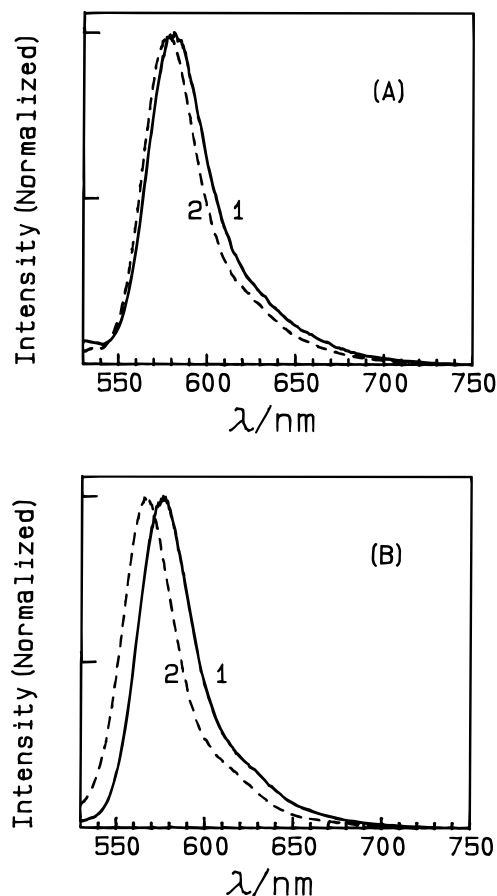


Figure 2. Fluorescence spectra of rhodamine B in (A) aqueous and (B) ethanol solvents in (1) acidic and (2) basic circumstance: concentration, 1.0×10^{-6} M; excitation wavelength, 525 nm.

an equilibrium between two species including RBH^+ and RB^\pm monomer. This behavior corresponds to that reported in the literature.¹⁶

The peak positions of the spectra in aqueous and ethanol solutions indicate that the equilibrium (2) tends to move toward the right side. On increasing of the concentration of the dye, the equilibrium moves back to the left side because the relative amount of the medium, which accepts a proton, decreases.³⁶ This change causes the concentration dependence of the absorption spectra of the dye in ethanol. Arbeloa et al.²² have reported the presence of aggregates of RB (J-dimer) in ethanol solutions at concentrations higher than 5.0×10^{-3} M. The absorption spectra which we observed in highly concentrated solutions in ethanol (5.0×10^{-2} M), however, corresponded to those of acidic ethanol solutions at a concentration of 1.0×10^{-6} M (see Figure 1B). This shows that the RBH^+ monomer exists in highly concentrated ethanol solutions. The difference from the results of Arbeloa et al. is due to the fact that they added HCl to the highly concentrated solution. Although the results are not shown here, the spectra in concentrated ethanol solutions shifted to the blue with addition of NaOH. The resulting spectra are almost the same as those obtained in the dilute solutions. It was also observed that the spectra of rhodamine 6G, whose carboxyl groups are esterified, shifted little with the changes in acidity (not shown here).

In order to assign the molecular forms of RB in the dip-coated films, we have observed the absorption spectra of RB in various water–ethanol mixed solvents. The concentration of this solution was 1.0×10^{-3} M, and the results are shown in Figure 4. The volume ratios of water to ethanol were adjusted to 0:100, 20:80, 50:50, 60:40, 70:30, 80:20, 90:10, 95:5, and

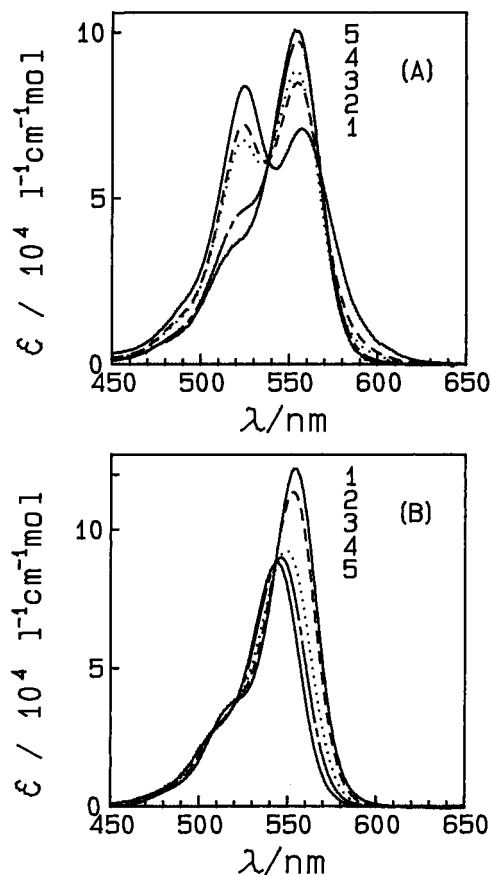


Figure 3. Absorption spectra of rhodamine B in aqueous and ethanol solvents: (A) (1) 1.0×10^{-2} M, (2) 1.0×10^{-3} M, (3) 5.0×10^{-4} M, (4) 1.0×10^{-4} M, (5) 1.0×10^{-6} M in water; (B) (1) 1.0×10^{-3} M, (2) 1.0×10^{-4} M, (3) 2.0×10^{-5} M, (4) 1.0×10^{-5} M, (5) 1.0×10^{-6} M in ethanol.

100:0. Using the same simple trial and error procedure used in previous paper,³² we have resolved the absorption spectra to the monomer and H- and J-dimers of RB in these solvents, and the results are shown in Figure 5. The monomer spectrum has a peak at 555 nm. This spectrum is the intermediate one of RBH^+ in water and ethanol. The transition moment for the dimers (a unit comprised of two molecules) is summed from the two constituent monomer transition moments, and the resulting average transition moment for the molecules constituting the dimers is equal to that of the monomer. Therefore, it is a reasonable assumption that the average absorption coefficients for the two split dimer peaks are roughly similar to the monomer absorption coefficient.

Under this condition and based on the results shown in Figures 1 and 3–5, we estimated the relative contribution of the three chemical species of RB (the monomer and H- and J-dimers) to the total absorption spectra of the water–ethanol mixed solutions using the Simplex method.^{39,40} The values obtained are given in Table 1. The spectrum in pure ethanol solution (0% water content) has a peak at 553 nm, which originates from the RBH^+ monomer. Increasing of the water content to 50% caused a red shift of the absorption peak at 558 nm. The spectrum with a peak at 558 nm is seen in acidic aqueous solutions at a concentration of 1.0×10^{-6} M (see Figure 1A) and is assumed to be due to the presence of the RBH^+ monomer. Further increasing of the water content caused the dimerization of RB molecules. The J-dimer exists in the solutions which contain 60–80% water, and the relative abundance increases with water content. The H- and J-dimers coexist in solutions which contain 90% water or more, and the

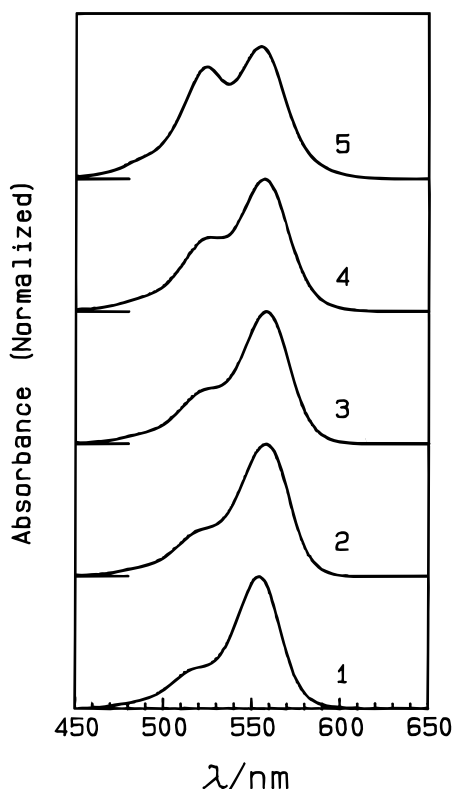


Figure 4. Normalized absorption spectra of rhodamine B in mixed water-ethanol solutions: water:ethanol (in volume ratio), (1) 0:100, (2) 50:50, (3) 80:20, (4) 90:10, and (5) 100:0. The original solutions of water and ethanol to obtain mixed solutions were both 1.0×10^{-3} M.

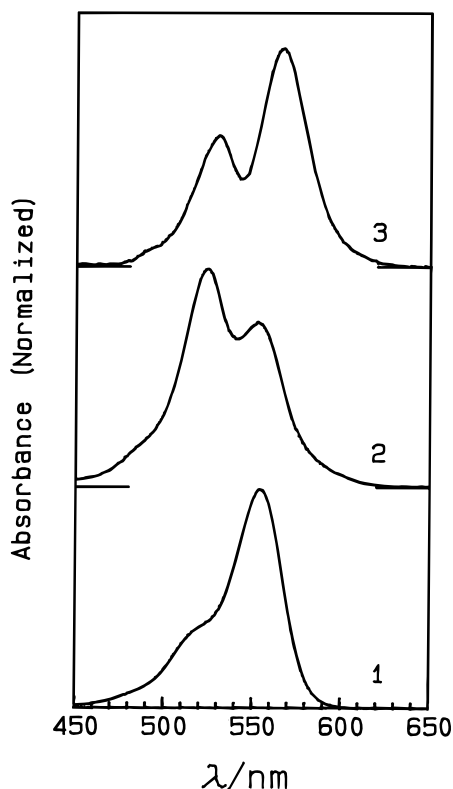


Figure 5. Resolved absorption spectra for the monomer and two dimers of rhodamine B in water-ethanol mixed solvents: (1) monomer, (2) H-dimer, and (3) J-dimer.

sum of these relative abundance increases with water content. The amount of the H-dimer in pure water is about 3 times that of the monomer. These results indicate that the formation of

TABLE 1: Relative Contribution of the Chemical Species of Rhodamine B to the Total Absorption Spectra of the Water-Ethanol Mixed Solutions

water:ethanol	monomer	H-dimer	J-dimer
0:100	1.00	0.00	0.00
20:80	1.00	0.00	0.00
50:50	1.00	0.00	0.00
60:40	0.95	0.00	0.05
70:30	0.92	0.00	0.08
80:20	0.78	0.00	0.22
90:10	0.58	0.26	0.16
95:5	0.44	0.38	0.18
100:0	0.29	0.61	0.10

dimers requires a high dielectric environment and that the two dimers are formed by association of the two RBH^+ monomers. Because water molecules would be required to interact between two dye molecules and the interaction minimizes the electrostatic repulsion, the dimerization of the dye requires some amount of water.

System A1

Absorption Spectra of RB in the System of the Sol-Gel Reaction of TEOS. Figure 6 shows the absorption spectra of RB in a fluid sol along with the progress of the sol-gel reaction until gelation occurred. It took 78 h for gelation in this system. There was little change in the spectra, which have a peak at 555 nm, during the progress of the sol-gel reaction. This spectral behavior indicates that the monomer becomes the preferential species in the system until gelation occurs. The weight of the system decreased to 73% of the initial value during the sol-gel transition; therefore, there was not a large change in the concentration of the dye in the system. The effective pH value of the sol-gel reaction systems was examined by using the absorption spectrum of thymol blue.¹⁰ It is concluded that the value does not largely change during the whole sol-gel-xerogel transitions. Consequently, the pH change does scarcely influence the molecular forms of RB dye during the reaction.

Relative Contribution from the Monomer, H-Dimer, and J-Dimer with the Progress of the Sol-Gel Reaction. We have prepared thin films including RB which were dip-coated using the sol-gel reaction of TEOS as a function of time after mixing of the reaction systems. Using the same procedures reported in the previous section, we newly obtained the resolved absorption spectra for the monomer, H-dimer, and J-dimer of RB in thin films, and they are shown in Figure 7. According to the results obtained in the solutions, it is reasonable to assume that these species consist of RBH^+ and they are the monomer (1), H-dimer (2), and J-dimer (3). Considering that the average transition moment for the molecules constituting the dimers is equal to that of the monomer, we estimated the relative abundance of the three chemical species of RB. Figure 8 shows the relative contribution of the three chemical species of RB to the total absorption spectra observed 72 h after making the films using the Simplex method. The abscissa indicates the reaction time of the fluid sol-gel solution at which the thin films were prepared. In the films prepared just after mixing of the reaction systems, the proportional of the dimers is significant. At 2 h after mixing of the reaction systems, the amount of H- and J-dimers are nearly equal and the sum of two dimers is 70%. As the sol-gel reaction proceeded, the relative abundance of the J-dimer decreased remarkably, while that of the H-dimer was approximately constant. The change in relative abundance among the three chemical species became small after the sol-gel reaction proceeded to some extent (after 30 h), at which the sum of the two dimers was $37 \pm 4\%$.

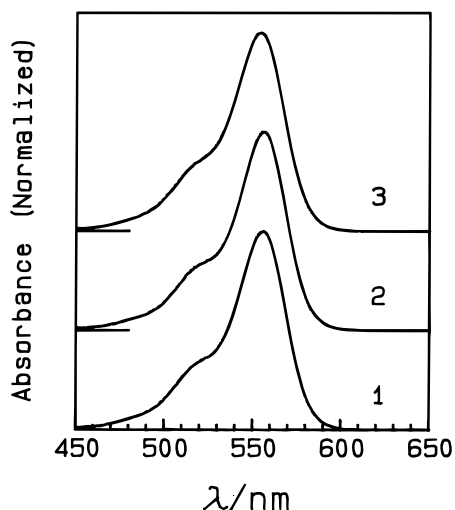


Figure 6. Absorption spectra of rhodamine B in the sol-gel reaction system, observed (1) 2, (2) 12, and (3) 60 h after start of the sol-gel reaction.

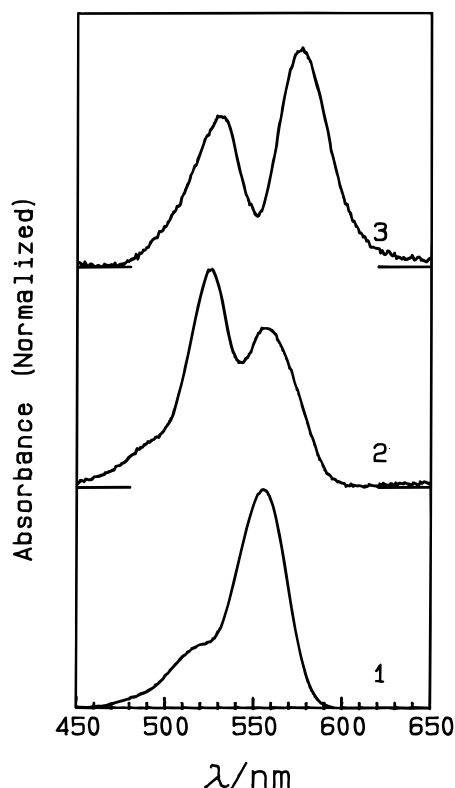


Figure 7. Resolved absorption spectra for the monomer and two dimers of rhodamine B in the sol-gel reaction system: (1) monomer, (2) H-dimer, and (3) J-dimer.

In acid-catalyzed sol-gel systems in the same manner as this work, the $-\text{SiOSi}-$ polymers lengthen linearly and form cross-linked networks along with the progress of the sol-gel reaction.^{33,34} These results lead to the concept of the microscopic configurational relationships between RB molecules and the $-\text{SiOSi}-$ polymers in fluid sol and in the dip-coated films, and this is illustrated in Scheme 1. In the fluid system, two RB molecules or more can be in a certain structural region (prestructure of the pores) at the initial stage of the sol-gel reaction (long before the gelation point). Separation of the RB molecules in such a region gradually increases with the progress of the reaction by growing $-\text{SiOSi}-$ networks around RB molecules, and the configuration at the final stage of the reaction becomes gradually unchanged after the sol-gel reaction pro-

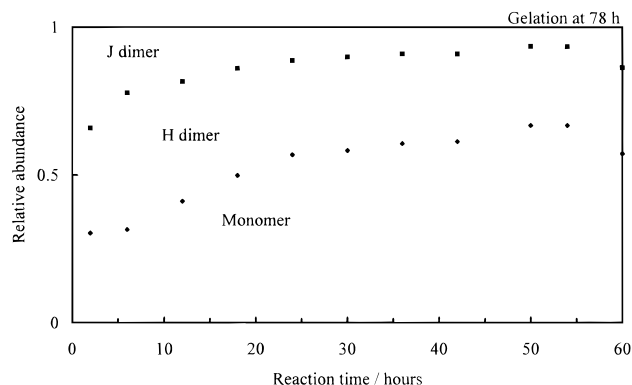
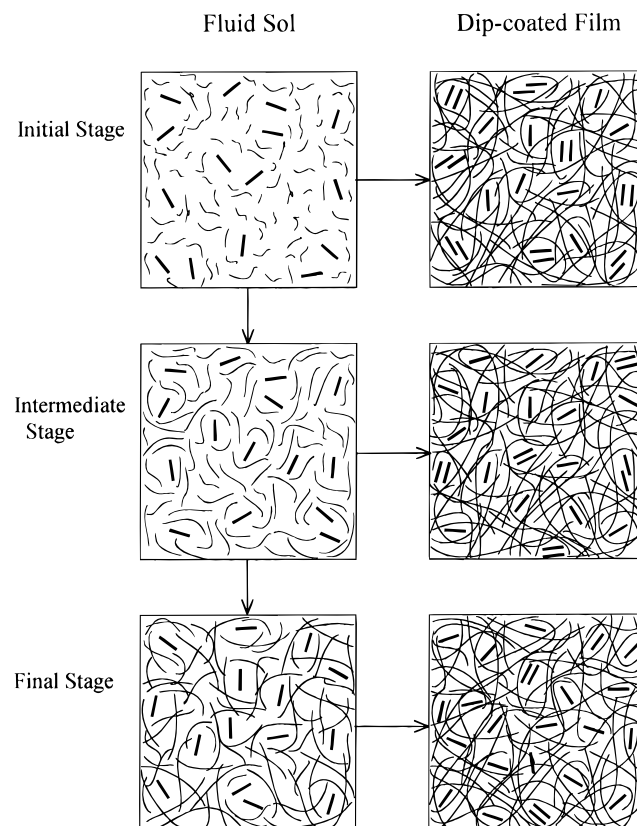


Figure 8. The relative contribution of the chemical species of rhodamine B to the total absorption spectra observed 72 h after the films were made. Each film was prepared along with progress of the sol-gel reaction system.

SCHEME 1: Illustration of the Microscopic Configurational Relationship between Rhodamine B Molecules and the $-\text{SiOSi}-$ Polymers in Fluid Sol and in the Dip-Coated Films^a



^a For the sake of simplicity, the branched parts in the polymers are neglected.

ceeded to some extent. On the other hand, preparing a film rapidly makes further networks and condensation in the system. The distribution of RB molecules in the dip-coated film reflects the situation in fluid sol at which the film was prepared; the extent of the dimerization of RB molecules in the film depends on physical restraint in the fluid system. As the reaction proceeded further, the relative abundance of the J-dimer in the films decreased, indicating that steric hindrance arising from the specific structure of the matrix by growing $-\text{SiOSi}-$ networks around the encapsulated RB molecules prevents the dimerization. The change in the distribution of RB molecules during the sol-gel transition of the fluid system (the change

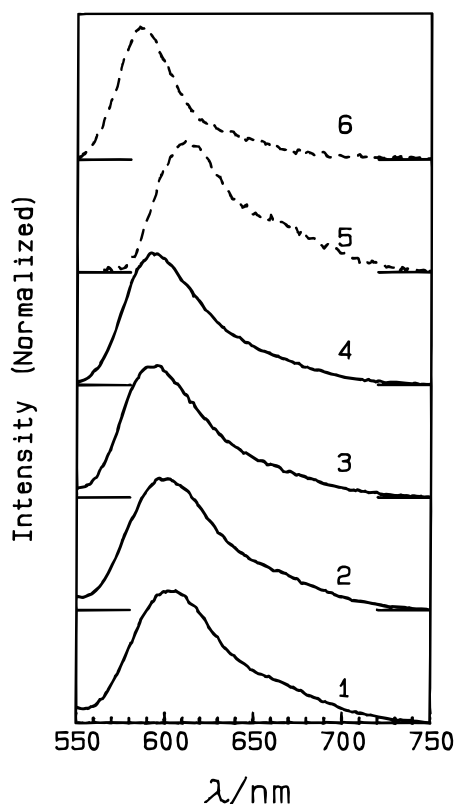


Figure 9. Fluorescence spectra of rhodamine B encapsulated in a dip-coated thin film prepared by the sol-gel reaction of TEOS 72 h after the films were made (lower): excitation wavelength, 525 nm; prepared (1) 6, (2) 12, (3) 24, and (4) 60 h after start of the sol-gel reaction. Resolved fluorescence spectra for a dimer and a monomer of rhodamine B in the sol-gel reaction system (upper): (5) dimer, (6) monomer.

shown in the left column of Scheme 1) indicates that they are encapsulated in a certain structural region (prestructure of the pores) long before the gelation point (at initial stage) of the sol-gel reaction of TEOS. On the other hand, the change in the distribution of RB molecules with the preparing a film (the changes shown in the rows of Scheme 1) indicates that they are already encapsulated in a certain structural region (prestructure of the pores) in fluid sol at which the film is prepared.

Fluorescence Spectra of Monomer and J-Dimer in the Dip-Coated Thin Films. It is difficult to observe the dimer fluorescence spectrum of a highly concentrated solution because of the inner filter effect or a high concentration quenching. The preparation of the dip-coated thin film, whose thickness is about $400 \pm 100 \text{ Å}$,³² enabled us to observe the fluorescence spectra of the highly concentrated dye.

The fluorescence spectra of RB encapsulated in the dip-coated thin films, which were prepared by dip-coating along with the progress of the sol-gel reaction of TEOS, observed 72 h after the films were made are shown in Figure 9. Spectra 1–4 indicate the films which were prepared 6, 12, 24, and 60 h after mixing of the reaction system, respectively. The spectrum of the film prepared 6 h after mixing of the reaction system is broad and has a peak at 606 nm. As the sol-gel reaction of TEOS proceeded, the peak of the spectrum of the prepared film shifted to 595 nm (spectrum 4). The change in these spectra depends on the relative abundance of the monomer and J-dimer which are fluorescent species. On the basis of these conditions, the resolved fluorescence spectra for a dimer and a monomer of RB in the films were obtained (Figure 9-5 and -6). The spectra of the dimer and monomer have peaks at 611 and 585

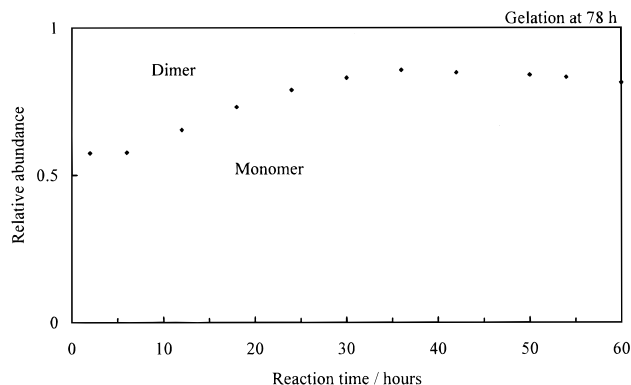


Figure 10. The relative contribution of the chemical species of rhodamine B to the total fluorescence spectra observed 72 h after the films were made. Each film was prepared along with progress of the sol-gel reaction system.

nm, respectively. The obtained peak of the monomer correspond to the spectra of acidic aqueous solution (Figure 2A-2).

The dimer fluorescence peak is reported at ca. 620 nm in 10 M LiCl–water at 77 K^{18,19} and at 595 and 623 nm in submono-, mono-, and multilayer systems adsorbed on fused quartz at 77 and 295 K.²⁴ These differences suggest that there is some geometrical difference in the dimer conformation in these matrices. According to the molecular exciton theory,²⁸ the spectral features of the absorption and fluorescence spectra depend on the dimer configuration (H- or J-types). The transition to the upper level of two split excited states of the H-dimer is allowed compared with the weak lower level, so that this species is nonfluorescent. On the other hand, the transition to the lower level of the J-dimer is allowed, so that this species is strongly fluorescent. There is a mirror image relation between the absorption spectrum of the J-dimer and the dimer fluorescence, indicating that the dimer fluorescence originates from the excited state of the J-dimer.

We can estimate the relative contribution to the total fluorescence spectra from the two fluorescent species of RB in the films. The results are plotted as a function of the reaction time of the fluid sol-gel solution, where the abscissa indicates the time of preparation of the thin films and the results are shown in Figure 10. The contributions from the dimer are 42, 35, 21, and 19% for spectra 1, 2, 3, and 4 in Figure 9, respectively. Figure 10 shows that the relative abundance became constant after around 30 h, indicating that structural change along with the progress of the sol-gel reaction is no longer responsible for the force which causes change in the monomer–dimer equilibrium after 30 h. This behavior indicates that RB molecules are encapsulated in a certain structural region (prestructure of pores) long before the gelation point of the sol-gel solution of TEOS. The results correspond well with those obtained from the absorption spectra, assuming that the monomer and the J-dimer are the only fluorescent species in the thin films.

System A2

Change in Absorption and Fluorescence Spectra of RB in the Thin Sol-Gel Films after Preparing the Thin Films.

In order to clarify the three chemical species of RB in the fluid sol-gel reaction system and in the thin sol-gel films and the structure of the pores in the films, thin films including RB which were dip-coated using the sol-gel reaction of TEOS have been prepared as a function of time after mixing of the reaction systems. The absorption and fluorescence spectra of the films

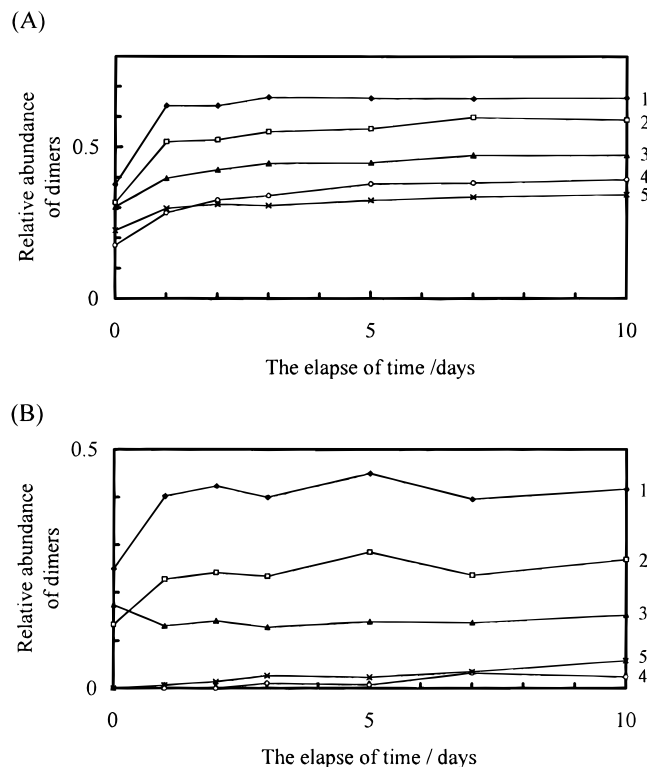


Figure 11. The relative contribution of the dimer of rhodamine B to the total absorption spectra (A) and to the total fluorescence spectra (B) of the film observed as a function of time; prepared (1) 2, (2) 4, (3) 12, (4) 22, and (5) 30 h after start of the sol-gel reaction.

were observed as a function of time after preparation of the thin films. It took 42 h for gelation in this sol-gel reaction system. We can estimate the relative abundance of the dimer of RB using the same procedure as reported in the previous section.

Figure 11A shows the relative contribution of the dimer of RB to the total absorption spectra, which were observed as a function of time after preparation of the thin films, where 1, 2, 3, 4, and 5 indicate the films which were prepared 2, 4, 12, 22, and 30 h after mixing of the reaction systems, respectively. The monomer component became the preferential species in the fluid sol until gelation occurred in the reaction system. In the films prepared at every reaction time of the sol-gel system, the sum of the abundance of the H- and J-dimers increased after preparation of the film. The increase in the dimer contribution at the first day is most remarkable. The sum of the values of the dimers at 10 days after preparation of the thin films are 66, 59, 47, 39, and 34% for the thin films 1, 2, 3, 4, and 5, respectively. The degree of dimerization of RB is higher in the film prepared at the initial stage of the sol-gel process. As the sol-gel reaction proceeded, the degree of dimerization in the dip-coated film decreased. In the films prepared after the sol-gel reaction proceeded to some extent, the change in the degree of dimerization of RB in the thin films of Figure 11A-5 became small.

Figure 11B shows the relative contribution of the dimer of RB to the total fluorescence spectra observed just after observing the absorption spectra, where the dimer is the fluorescent J-dimer. The proportions of dimer at 10 days after preparation of the thin film are 42, 27, 15, 3, and 6% for the thin films 1, 2, 3, 4, and 5, respectively. The results correspond to those obtained from the absorption spectra, assuming that the values are the proportions of only the two fluorescent species, the monomer and the J-dimer.

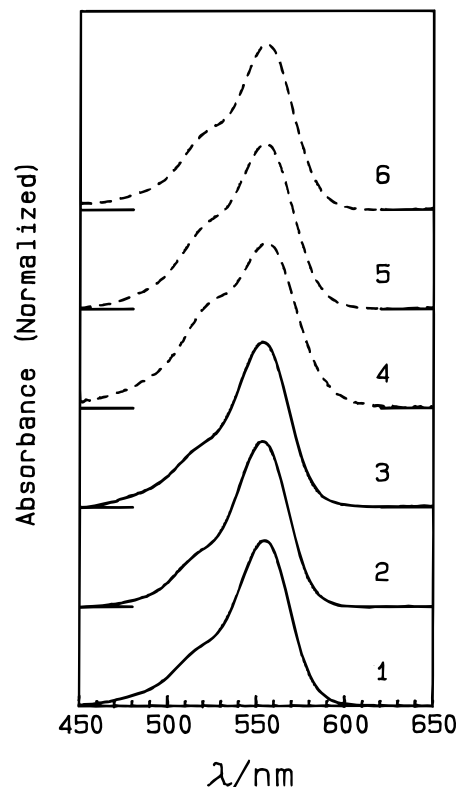


Figure 12. Absorption spectra of rhodamine B encapsulated in a dip-coated thin film prepared by the sol-gel reaction of TEOS with a small amount of water: observed just after the films were made (lower: 1, 2, and 3) and observed 5 days after the films were made (upper: 4, 5, and 6). They were prepared (1 and 4) 20 h, (2 and 5) 90 h, and (3 and 6) 144 h after start of the sol-gel reaction.

The results shown in Figure 6 indicate that monomer RB becomes the preferential species in the systems of the sol-gel reaction of TEOS until gelation occurs. Two RB molecules tend to interact with each other just after mixing of the solutions compared with the situation in which the reaction proceeded. The dimerization of RB molecules in the thin film is pronounced just after dip-coating until formation of the SiO_2 network in the system proceeds to some extent, although the progress depends on the reaction conditions of the sol-gel system. A decrease in the degree of dimerization with the elapse of reaction time of the sol-gel system shown by the films (lines) 1 \rightarrow 5 in Figure 11 corresponds to the results shown in Figures 8 and 10. Under the reaction conditions, following the evaporation of ethanol, there is an increase in the relative proportion of water in the dip-coated film, and the dimerization in the film is enhanced progressively with the elapse of time (increasing of the values on the abscissa in Figure 11). It is interesting that the dimerization of RB was promoted in the thin sol-gel films with aging of their films, while the interaction of two RB molecules was prevented in fluid sol with the progress of the sol-gel reaction. This indicates that the dimerization is enhanced at the initial stage of the sol-gel reaction in the thin film along with the decrease of the space in the pore structure.

System B

Effect of Water in the Sol-Gel Reaction. In order to clarify the effect of water in the sol-gel reaction system on the dimerization of RB, thin films including RB were prepared using the sol-gel reaction of system B which contains 25 vol % water compared with system A. It took 500 h for gelation in this sol-gel reaction system. Figure 12 shows the absorption spectra of RB in those films prepared 20, 90, and 144 h after starting

TABLE 2: Relative Contribution of the Chemical Species of Rhodamine B to the Total Absorption Spectra of Individual Films Prepared along with Progress of the Sol–Gel Reaction with a Small Amount of Water

reaction time/h	monomer	H-dimer	J-dimer
(A) Observed Just after the Films Were Made			
20	0.80	0.09	0.11
90	0.86	0.05	0.09
144	0.78	0.11	0.11
(B) Observed 5 Days after the Films Were Made			
20	0.46	0.26	0.28
90	0.58	0.23	0.19
144	0.66	0.21	0.13

the sol–gel reaction, which were observed just after preparation (1, 2, and 3) and 5 days after preparation (4, 5, and 6). The higher energy side shoulders of the spectra 1, 2, and 3 are smaller than those of the spectra 4, 5, and 6, respectively. The relative contribution of the three chemical species of RB to the total absorption spectra estimated using the Simplex method is summarized in Table 2. Monomeric RB is the preferential species in the films just after the preparation, where the effective dimerization cannot occur just after preparation of the films because of little water. However, a slight dimerization of RB is noticed in the films kept at room temperature for 5 days, indicating that a certain amount of water is adsorbed into the thin films from the surrounding atmospheric water.

These results indicate that water plays an important role in the dimerization process and is essential for the formation of the dimers. Water molecules in the sol–gel system are excessive compared with the quantity used by hydrolysis of TEOS; they remain in the pores of the dip-coated thin film. Dimerization of RB occurs during the process in which the proportion of water increases following the evaporation of ethanol. However, there is no process of dimerization in the case of little water contained in the system. Furthermore, water molecules in air would be adsorbed into the film and hence enhance the dimerization of RB.

Conclusions

The RB cation becomes the preferential species under high water content and high RB concentration, where two cations form the H- and J-dimers. Monomer RB becomes the preferential species in the systems of the sol–gel reaction of TEOS. Two RB molecules interact with each other just after mixing of the solutions compared with the situation in which the reaction proceeded. RB molecules are encapsulated in a certain structural region (prestructure of the pores) long before the gelation point. Therefore, with the progress of the sol–gel reaction, dimerization in the prepared film is gradually prevented by the steric hindrance of the SiO₂ network and the monomer RB becomes the preferential species. Dimerization of RB in the thin film is pronounced just after dip-coating until the SiO₂ network is almost formed. Under the reaction conditions, the proportion of water increases after the evaporation of ethanol, and the dimerization in the thin films is progressively enhanced with the time course of the reaction.

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