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Fluorescence Spectra of Pyrene and Humidity Effects on Them during the Sol-to-Gel-to-Xerogel Transitions of Mixed Silicon–Aluminum Alkoxide Systems

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The fluorescence spectra of pyrene of four sol systems comprising silicon and aluminum alkoxides(Si : Al= 99.4 : 0.6 ; 93.6 : 6.4; 85.9 : 14.1; and 50 : 50) have been observed during sol-to-gel-to-xerogel transitions under at relatively low concentration, on the order of 10^{-4} mol dm^{-3}, uncatalyzed, and constant temperature (300 K) conditions. The influence of relative humidity on the relative intensities of pyrene monomer and excimer-like fluorescence in the four xerogel states has also been observed. In three of the four systems studied (all but Si : Al=99.4 : 0.6), fluorescence spectra revealed that excimer concentration increased with time and reached a maximum near 55 days after which it decreased. From our data, it is apparent that the ratio of the intensity of the excimer-like fluorescence to that of the monomer fluorescence increases with relative humidity.

The sol–gel process is a fascinating method with unfulfilled potential for creating functionalized materials such as glasses and ceramics.$^{1-6)}$ As first reported by Avnir et al.$^{7)}$ the process offers a low-temperature synthetic route for the encapsulation of luminescent organic molecules in inorganic matrices on a molecular level.$^{7-30)}$ Pyrene is a typical fluorescence probe molecule, which reflects its physicochemical environment through its long singlet lifetime, well-resolved vibronic structure, and excimer formation.$^{31-41)}$ Therefore, pyrene has been used as a photoprobe molecule for understanding the sol-to-gel-to-xerogel processes based on metal alkoxides, such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS)$^{11,24,42-46)}$

Kaufman et al. reported that the relative fluorescence intensity of pyrene excimer, I_E, to the monomer, I_M, given by the expression, E/(M+E), showed oscillatory behavior during the sol-to-gel transition in systems containing surface active agents.$^{42)}$ On the other hand, Brusilovsky and Reisfeld reported that no time oscillation of the relative fluorescence intensity of pyrene during the sol-to-gel process was found.$^{43)}$ Matsui and Usuki have studied the fluorescence and excitation spectra of pyrene at high concentration (on the order of 10^{-3} M) at various stages during the sol-to-gel-to-xerogel transitions of the sol-gel silica formed by the acid hydrolysis of TEOS.$^{45)}$ The E/(M+E) ratio and the ratio of the intensity of the third vibrational peak (383 nm), I_{III}, to the first vibrational peak (372 nm), I_I, of the fluorescence spectra given by the expression, I_{III}/I_I, (referred to hereafter as III/I ratio) of the monomer fluorescence showed no daily variation. Their results agree with a later report by Kaufman and Avnir.$^{11)}$

Silica–alumina is a well-known and important acid catalyst.$^{47-49)}$ The surface structure of silica–alumina and zeolites has been discussed from the standpoint of surface acidity and chemical reactions occurring on the surfaces. It has been pointed out that the acidity of the silica–alumina surfaces is very strong. However, pure silica gel is a poor catalyst for acid-catalyzed reactions because surface –SiOH groups have only a weak acid strength.$^{47)}$ The chemical reactions which occur on the silica–alumina surfaces are characterized by a silicon-aluminum (–Si–O–Al–) composition.$^{48)}$ Therefore, it is both interesting and important to determine what factors influence the intensity of the monomer and excimer-like fluorescences of pyrene during the sol-to-gel-to-xerogel transitions and in the solid state.

In this paper we report the fluorescence spectrum of pyrene at relatively low concentration during the sol-to-gel-to-xerogel transitions in the following systems of mixed silicon and aluminum alkoxides Si : Al=99.4 : 0.6; 93.6 : 6.4; 85.9 : 14.1; and 50 : 50, abbreviated systems A, B, C, and D, respectively. A system containing no aluminum is not reported here, since the system showed no gelation. The III/I and E/(M+E) ratios were observed during the course of the reaction. The value of the III/I ratio indicates the polar character of the environment around the doped pyrene molecules with higher III/I values indicating less polar character.$^{31-33)}$ The E/(M+E), III/I, and V/I(similar meaning as III/I, with the fifth vibronic band occurring at 392 nm) ratios in the xerogel state have also been observed in three relative humidity (RH=100, 88, and 33%) conditions. Silicon to aluminium ratios were controlled by the use of TEOS and diisobutoxyaluminium triethyl silicate ($(OBu^i)_2Al–O–Si(OEt)_3$(SAE). It became apparent that the E/(M+E), III/I, and V/I ratios increase with relative humidity.

Experimental

Pyrene (Wako, JIS S grade) was purified by repeated recrystallizations from ethanol. TEOS and ethanol from Wako, and SAE from Dynamit Nobel were used without further purification.

A 1.5×10^{-4} M (1 M=1 mol dm^{-3}) solution of pyrene in ethanol was prepared. The starting solutions of the reaction systems contained 20 mL of the pyrene solution and appropriate volumes of TEOS and SAE. Total volumes were adjusted to 30 mL. The volumes of TEOS and SAE were 9.9 mL and 0.1 mL (A); 8.9 mL and 1.1 mL (B); 7.5 mL and 2.5 mL (C); and 0 mL and 10 mL (D), respectively. Therefore, the molar ratios of Si : Al were 99.4 : 0.6; 93.6 : 6.4; 85.9 : 14.1; and 50 : 50, for systems A, B, C, and D, respectively. No catalyst was used for the sol–gel reaction in the present study. The mixtures were thoroughly stirred for 10 min and then 3 mL of the mixed solutions were poured into individual plastic cells. These cells were covered with a thin polymer film (polyvinylidene chloride) with five pinholes and allowed to undergo sol-to-gel-to-xerogel reactions at 303 K under dark conditions. Gelation occurred at 25 d, 11 d, 6 d, and 11 d, for the systems A, B, C, and D, respectively. The prepared gels were transparent.

The emission spectra were observed using a Shimadzu RF-5000 fluorescence spectrometer by the right-angle emission method for the observation during the sol-to-gel-to-xerogel transition, and by the surface-emission method for the observation of the effect of humidity on the fluorescence spectra of encapsulated pyrene. The influence of relative humidity on the whole fluorescence spectra of encapsulated pyrene was studied as follows: After final observation (85 d) of the whole fluorescence spectra of the four specimens, the specimens were placed in a 500 mL vessel covered by a thin film. A varying amount of water was added to the vessel which was allowed to stand over 10 h at 303 K in the dark. Then the samples were immediately transfer to a sample holder for emission measurements. The relative humidity was measured just before observation of the fluorescence spectra by using a Yamato YM-22-P2 temperature and humidity converter (sensor).

Results and Discussion

Fluorescence Spectra during Sol-to-Gel-to-Xerogel Transitions. Figures 1 and 2 show the fluorescence spectra of pyrene excited at 350 nm during the sol-to-gel-to-xerogel transitions of the samples as a function of time. Just after mixing the solutions, the fluorescence band of the excited pyrene monomer with a fine vibrational structure is well defined. The contribution of the excimer emission around 480 nm is poorly characterized.

During the progress of the reaction, H_2O, ethanol, and isobutanol are produced in the reaction systems by the sol–gel reaction. They escape through the pin holes from the reaction systems. Therefore, during the progress of the reaction, the effective concentration of pyrene molecules gradually increased; a small increase in the excimer emission is observed. After the gelation the relative intensity of excimer (-like) emission[50)] to that of monomer emission remained constant, in system A (see Fig. 1).

Figures 2a, 2b, 2c, and 2d (for systems B, C, and D) shows different fluorescence behavior at 55d compared with the spectral behavior for system A. Just after mixing the solutions, the spectra have a fine vibrational structure and the contribution around 480 nm is small. The spectral contribution around 480 nm is not largely changed after the gelation until ca. 40 d. The spectra observed at 55 d, especially for systems B and C, are completely different from those observed earlier. The excimer (-like) emission is much stronger than the monomer emission. However the spectra taken at 85 d resemble the spectra recorded in the early stages of the reaction. In addition to this, Fig. 2(b and c) shows that the fluorescence spectra of pyrene in system C showed the excitation-wavelength dependence. The fluorescence spectra of systems B and D also showed the similar excitation-wavelength dependence, though not shown here. This dependence indicates that there are more than one ground-state species of pyrene, one is monomeric form and the other is probably bimolecular ground-state associations (BGSA's) or configurations that lead to excimer-like emission.[34,38—40,45)]

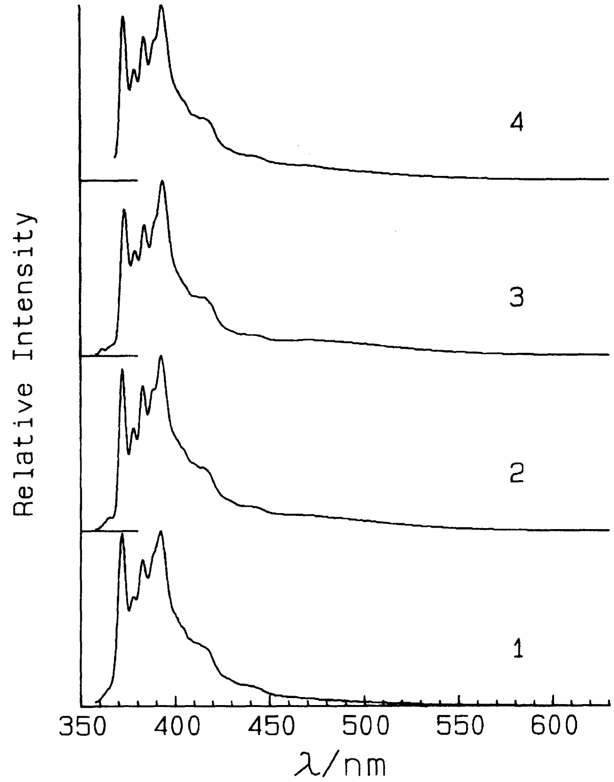

Fig. 1. The fluorescence spectra of pyrene in the TEOS and SAE mixed solutions during the sol-to-gel-to-xerogel transitions (Si : Al=99.4 : 0.6; A). Excitation wavelength is 350 nm: after 10 min (1); 25 d (gelation was first observed) (2); 55 d (3); and 85 d (4).

These results for systems B, C, and D are similar to those observed for pure Si systems studied at relatively higher concentrations of pyrene studied by Kaufman and Avnir,[11)] and Matsui and Usuki.[45)] These results are interpreted as follows: In the first stage of the reaction, the effective concentration of pyrene in the systems

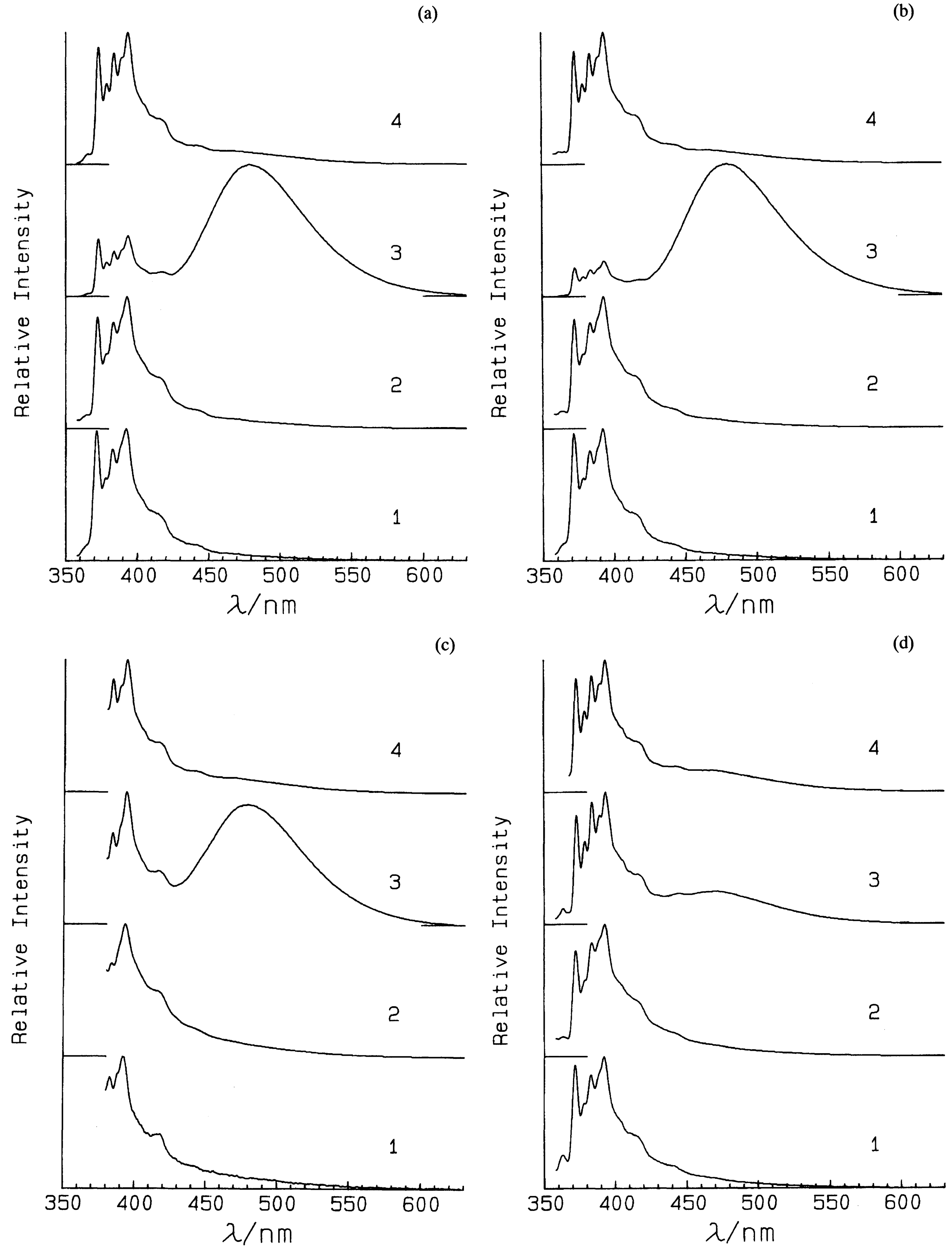

Fig. 2. The fluorescence spectra of pyrene in the TEOS and SAE mixed solutions during the sol-to-gel-to-xerogel transitions. (a): Si : Al=93.6 : 6.4 (B), after 10 min (1); 11 d (gelation was first observed) (2); 55 d (3); and 85 d (4). (b) and (c): Si : Al=85.9 : 14.1 (C), after 10 min (1); 6 d (gelation was first observed) (2); 55 d (3); and 85 d (4). (d): Si : Al=50 : 50 (D), after 10 min (1); 11 d (gelation was first observed) (2); 55 d (3); and 85 d (4). Excitation wavelength is 350 nm for (a), (b), and (d) and 372 nm for (c).

(ca. 1.0×10^{-4} M) is not enough to form an excimer during its lifetime.[51] Therefore, we cannot observe explicit excimer emission. During the sol–gel reaction, the relative concentration of pyrene gradually increases. After gelation, an –O–Si–O–Al–O– network spans completely over the inner sites of the reaction systems. Pores are formed in the reaction systems. The pyrene molecule(s) is(are) wrapped with –O–Si–O–Al–O– and –O–Si–O– etc. structures. Therefore, if there are more than two pyrene molecules in the same pore, it is possible to form the BGSA's or configurations that lead to excimer-like emission discussed in previous subsection.[34,38—40,45]

The other possible route to forming excimer geometry in the liquid state is by one ground-state molecule and one excited-state molecule diffusing together.[51] The spectra observed at 55 d in systems B, C, and D shown in Figs. 2a, 2b, 2c, and 2d support the first route (BGSA's formation) because the reaction systems are rigid gels. As the H_2O, ethanol, and isobutanol continue to escape from the reaction system during the progress of the sol–gel reaction, the systems shrink resulting in smaller, distorted pores; some pyrene molecules that had been encapsulated in the same pore are separated. Therefore, the excimer-like emission decreases in the xerogel state as the BGSA's are destroyed.

Evidently the presence of aluminum atoms to a certain extent increases the probability of formation of the BGSA's of pyrene molecules and hence increases the intensity of excimer (-like) fluorescence around 480 nm. The results shown in Fig. 2 indicate that there is a optimum Si : Al ratio for the formation of BGSA's and appearance of the excimer (-like) fluorescence. Relation among Si : Al composition, structural change, and surface acidiry or catalytic activity of silica–alumina catalysts is in any event interesting and important. Holm and Clark showed that reaction efficiencies of *o*-xylene isomerization, *n*-octane cracking, et al. show maxima between 25 to 30%-Al among Si–Al binary catalysts.[48] They suggested that the variation in the reaction efficiencies are attributable to the change of ratio of strong adsorption site to weak adsorption site. It is well known that the isomorphous substitution between Si atom and Al atom is a typical case.[52,53] Then substituted Al becomes a tetravalent atom. Leonard et al. have investigated structure defect in alumina and in two series of cogelled silica–alumina catalysts.[54] The three main kinds of structure defects were distinguished. (1) aluminum ions tetrahedrally coordinated to oxide ions. They constitute the Bronsted acid sites over the entire composition range from 0 to 100% Al. (2) aluminum cations in a perturbed tetrahedral arrangement. They are related to Lewis acidity and most probable in alumina. (3) silicon cations in a perturbed tetrahedral arrangement. They exist at Al contents greater than 50% and provide a new Lewis acidity.

In the present case, we prepared the xerogels from alkoxides composed of Si and Al atoms by the sol–gel method. Trivalent Al atoms are consequently surrounded by tetravalent Si atoms at relatively small amount of Al ratio. At relatively small Al content, the incorporated Al atoms into –O–Si–O– network become tetrahedrally-coordinated atoms. In addition to this, pyrene molecules were mixed from the starting solutions of the sol–gel reaction. Pyrene molecules are encapsulated into pores which exist at inner side of the surface of the xerogel. Then pyrene molecules interact with tetravalent Al atom at relatively small amount of Al range. Under these circumstances pyrene molecules seem likely to adsorb relatively adjacent adsorption sites, resulting in easy formation of BGSA's especially seen for the systems B and C.

The Change of III/I during the Sol–Gel Process. Figures 3, 4, and 5 show III/I and E/(E+M) ratios as a function of time. The III/I ratio is a measure of the polar character surrounding the encapsulated pyrene. Just after mixing, the values of the III/I ratio are 0.85, 0.86, 0.87, and 0.92 for systems A, B, C, and D, respectively. These values correspond to the value reported in ethanol.[31,32] The values of the III/I ratio increase rapidly at $t=1$ day and reach 0.94, 0.93, and 0.95 for systems A, B, and C as shown in Figs. 3 and 4. This increase indicates a decrease in the polar nature of the environment of the doped pyrene molecules, because their solvation shells change from polar ethanol and water molecules to less polar moieties, including silanol, –O–Si–O–Al–O– and –O–Si–O–Si–O– structures due to the progress of the hydrolysis and polycondensation reactions. On the other hand, the III/I ratio for system D gradually increased in the first several days.

The III/I ratios do not show large increases or de-

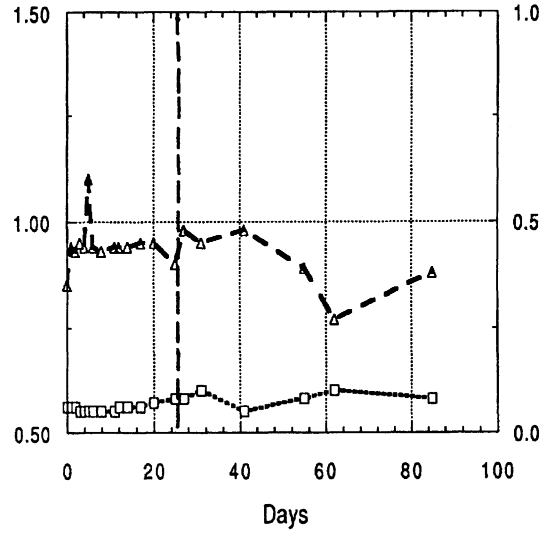

Fig. 3. The values of III/I (△) and E/(E+M) (□) ratios as a function of time for the reaction system having Si : Al=99.4 : 0.6 (A). E is the intensity at 470 nm and M is the intensity at the fifth peak at 392 nm. Excitation wavelength is 350 nm. The gelation time is represented by a vertical broken line.

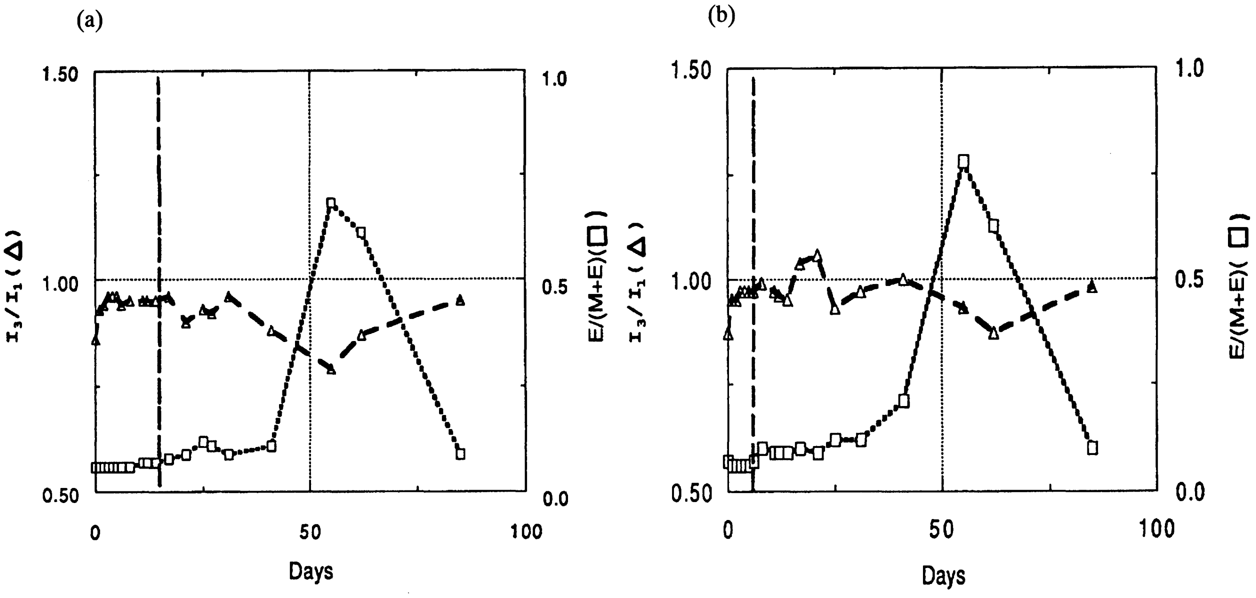

Fig. 4. The values of III/I (△) and E/(E+M) (□) ratios as a function of time for the reaction systems having Si : Al ratio of (a) 93.6 : 6.4 (B) and (b) 85.9 : 14.1 (C). E and M have the same meaning as in Fig. 3. Excitation wavelength is 350 nm. The gelation time is represented by a vertical broken line.

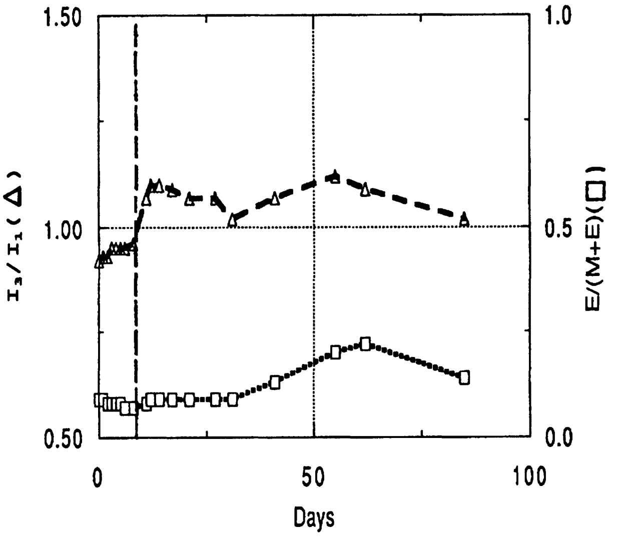

Fig. 5. The values of III/I (△) and E/(E+M) (□) ratios as a function of time for the reaction system having Si : Al=50 : 50(D). E and M have the same meaning as in Fig. 3. Excitation wavelength is 350 nm. The gelation time is represented by a vertical broken line.

creases before and after 10 d for systems A, B, and C through the time of gelation. In the case of system D, however, the III/I ratio is characterized by a rapid increase from 0.96 to 1.07 at the gelation point. This indicates a rapid decrease of the polar nature around the encapsulated pyrene molecules in the pores. This value of 1.07—1.10 is the highest value observed in the present experimental systems. The III/I ratio of system D remains nearly constant until 85 d. On the other hand, the III/I ratio in systems A, B, and C are characterized by decreases especially at 55 d to 0.89, 0.79, and 0.93, respectively, followed by increases at 85 d to 0.88, 0.95, and 1.02, respectively. These changes indicate that the environment of the encapsulated pyrene molecules become more polar around at 55 d and less polar at 85 d especially for systems B and C.

The Change of $I_E/(I_E+I_M)$ during the Sol–Gel Process. The change of E/(E+M) ratio is also shown in Figs. 3, 4, and 5. The E/(E+M) ratio in the liquid is a measure of the ability of pyrene molecules to diffuse during their excited state lifetime inside of the reaction systems. The E/(E+M) ratio for system A (Fig. 3) is characterized by small changes during the whole course of the sol–gel transitions. This flatness of the E/(E+M) ratio for system A during the sol–gel process indicates that the effective concentration of pyrene is low enough so that very little excimer is formed during the sol–gel transitions in this system. Systems B, C, and D (shown in Figs. 4 and 5) are characterized by large relative intensity of excimer emission at 55 d. The ratios decrease at 64 d. At 85 d the values are similar to those observed before 40 d.

The increase of excimer-like emission at 55 d can be interpreted as follows: The encapsulation of pyrene molecules into pores produced during the progress of the sol–gel reaction increases the effective local concentration of pyrene molecules inside the pores.[45] It is interesting to note that the increase of the E/(M+E) ratio corresponds to the decrease of the III/I ratio. The decrease of the E/(M+E) ratio at 85 d indicates that two or more encapsulated molecules in a single pore are separated by the shrinkage of the pores and are unable to approach each other.[11,43,45] The characteristic change of E/(M+E) and III/I near 55 d especially for the systems B and C suggests the occurrence of the geometrical change of the xerogels around encapsulated pyrene molecules. The weight decrease of the reaction systems around 55 d caused by the escape of alcohols and H_2O through the pinholes of the reaction systems is very small.[27,28] There is a slight and continuous geometrical change caused by the progress of the sol–gel reaction including relative replacement of conformation between pyrene molecules and surrounding alcohols, H_2O, and silanol groups of the pore surface. The characteristic behavior of the E/(M+E) and III/I ratios during the sol–gel process is attributable to the above change.

The Influence of Humidity on the Fluorescence Spectra of Pyrene Encapsulated in the Xerogel State. The influence of humidity has been examined at three relative humidities of 33, 88, and 100% and typical results are shown in Fig. 6 for system A and Fig. 7 for system C. It is seen from Fig. 6 that the change in the fluorescence spectrum of encapsulated pyrene is small for system A. The results indicate that humidity has no effect on the whole fluorescence spectrum of pyrene in systems containing small amounts of Al. The influence of humidity on the fluorescence spectra of encapsulated pyrene became apparent in systems B, C, and D. Figure 7a shows that the fluorescence spectrum of encapsulated pyrene excited at 350 nm for the system C at 33% relative humidity is very similar to that observed for system A. The fluorescence spectrum of system C changes entirely at 88% relative humidity: The intensity of the excimer-like fluorescence becomes strong relative to that of the monomer. Figure 7b shows the influence of relative humidity on the fluorescence spectra of pyrene excited at 372 nm, encapsulated in the xerogel state. Compared with the results shown in Fig. 7a, it is seen that there is an excitation-wavelength dependence in the whole spectrum. This dependence indicates the formation of BGSA's in this system as discussed in the results of Fig. 2.[11,38—40,45] Similar fluorescence behavior was also observed for systems B and D.

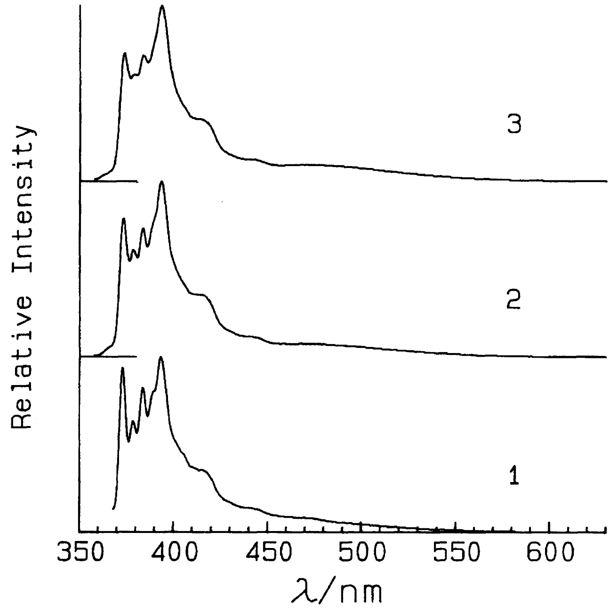

Fig. 6. The influence of humidity on the total fluorescence spectra of pyrene encapsulated in pores of the prepared xerogel state for the system Si : Al=99.4 : 0.6 (A). Excitation wavelength is 350 nm. 1, 2, and 3 correspond to the spectra under relative humidities of 33, 88, and 100%, respectively.

The influence of humidity on the E/(E+M) and III/I ratios are shown in Figs. 8 and 9. In Fig. 9, we plot a I_5/I_1 ratio (abbreviated as V/I ratio) together with the III/I ratio. The V/I ratio is also a measure of the polar character of the circumstance around pyrene molecules in solutions.[31,32] From E/(M+E) point of view shown in Fig. 8, system C among the samples is the most sensitive to relative humidity. System B is the next most sensitive and system D is still less sensitive. System A is not sensitive to relative humidity from stand point of E/(M+E) ratio. On the other hand, the values of V/I and III/I ratios increase with relative humidity, regardless of their Si : Al composition.

It is well known that a large number of H_2O molecules are physisorbed onto the surfaces of pores of gels. The influence of co-adsorbed compounds and chemical modification of pore surface on the photophysical properties of pyrene adsorbed in silica gel has been reported.[55—58] The intensity of the excimer-like emission of pyrene increases with the addition of co-adsorbed materials in the pores of silica gel. This increase indicates that the excited-state diffusion or the formation of BGSA's of pyrene molecules on the surface of pores is facilitated by adding the co-adsorbed materials. The increase of excimer-like emission of pyrene encapsulated in pores shown in Figs. 6, 7, and 8 indicates that similar circumstances are brought about for the gels in this study by high relative humidity.

The decrease of III/I ratio from non-polar solvents to polar solvents is characteristic in solutions.[31,32] As shown in Fig. 4, the decrease of the III/I ratio corresponds to the increase of E/(M+E) ratio near 55 d. On the other hand, the results shown in Figs. 8 and 9 indicate that the increase of E/(M+E) ratio by the adsorption of H_2O molecules corresponds to the increase of the III/I and V/I ratios especially for the systems B and C. This difference seen among Figs. 3, 4, 8, and 9 indicates that there is another reason, which is not originated from BGSA's formation, for increase E/(M+E) in high humidity conditions. One reason for the formation of excimer (-like) geometry under the high humidity condition especially for the systems B and C can be attributable to the diffusion of the pyrene molecules by co-adsorbed H_2O molecules on the surface of pores.

The results indicate that the observation of E/(M+E) ratio of pyrene adsorbed onto the silica gel is a good

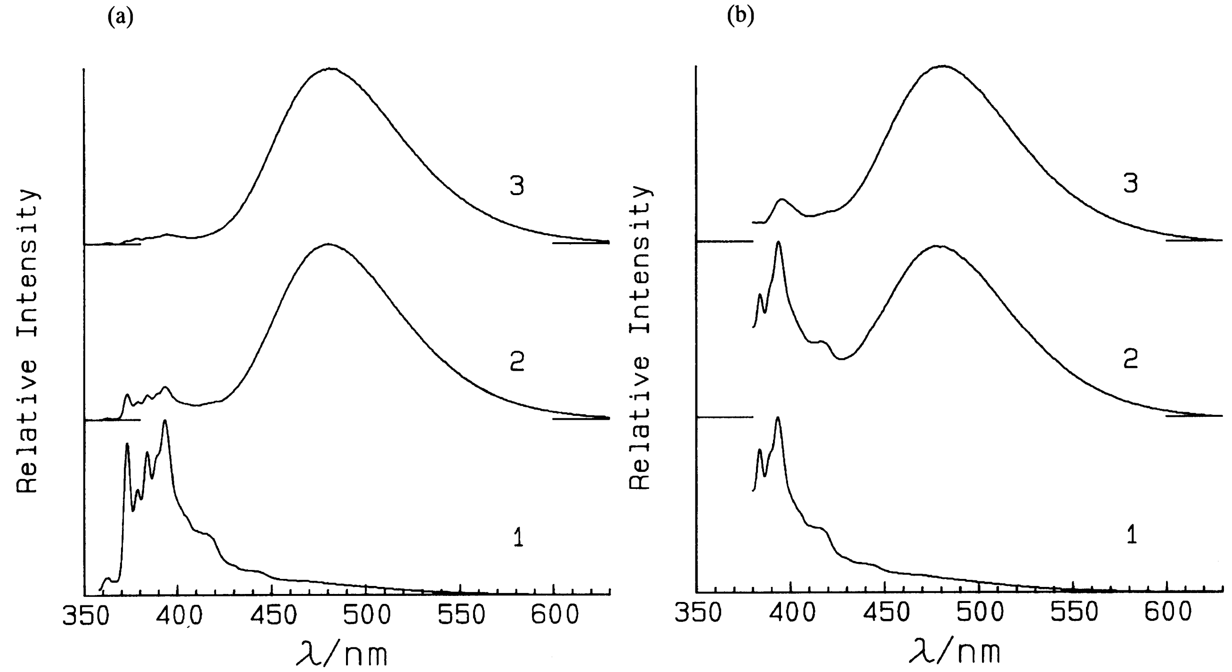

Fig. 7. The influence of humidity on the total fluorescence spectra of pyrene encapsulated in pores of the prepared xerogel state for the systems: Si : Al is 85.9 : 14.1 (C). Excitation wavelength is 350 nm for (a) and 372 nm for (b). 1, 2, and 3 have the same meaning as in Fig. 6.

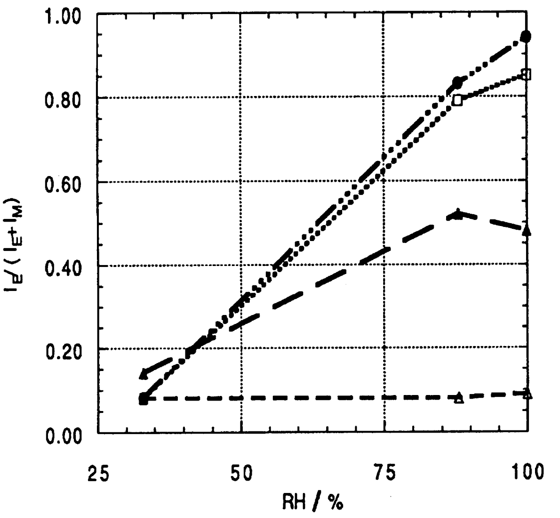

Fig. 8. The influence of humidity on the E/(E+M) ratio for the four systems. Excitation wavelength is 350 nm. Si : Al is 99.4 : 0.6 (△), 93.6 : 6.4 (□), 85.9 : 14.1 (●), and 50.0 : 50.0 (▲) for the E/(E+M) ratio.

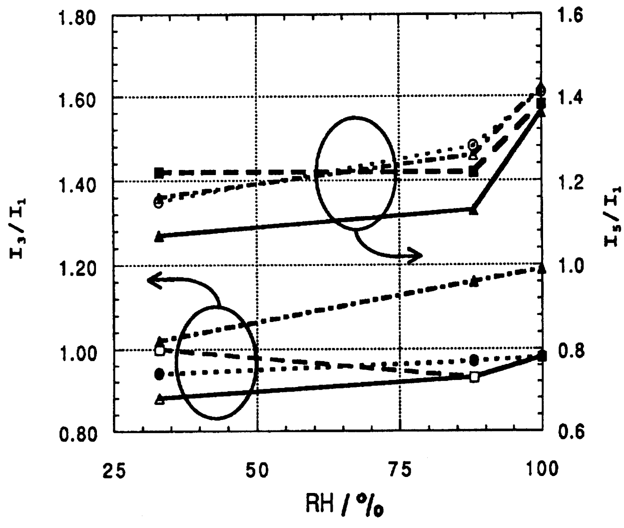

Fig. 9. The influence of humidity on the III/I and V/I ratios for the four systems. Excitation wavelength is 350 nm. Si : Al is 99.4 : 0.6 (△,▲), 93.6 : 6.4 (□,△), 85.9 : 14.1 (●,○), and 50.0 : 50.0 (▲,■) for the III/I and V/I, ratios respectively.

measure or a good sensor of relative humidity. The results also suggest that the adsorption of H_2O onto the surface of pores of gels changes not only the chemical structure of the surface but also the geometry.

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References

1) H. Dislich, *Angew. Chem., Int. Ed. Engl.*, **10**, 363(1971); H. Dislich, *J. Non-Cryst. Solids*, **57**, 371 (1983).
2) B. E. Yoldas, *J. Mater. Sic.*, **12**, 1203 (1977).
3) "Ultrastructure Processing of Advanced Ceramics," ed by J. D. Mackenzie and D. R. Ulrich, Wiley, New York (1988).

4) S. Sakka, "Zoru Geru Houno Kagaku (Science of the Sol–Gel Method," Agune Shoufuusha, Tokyo (1988).

5) C. J. Brinker and G. W. Schere, "Sol–Gel Science—The Physics and Chemistry of Sol–Gel Processing," Academic Press, San Diego (1990).

6) L. L. Hench and J. K. West, *Chem. Rev.*, **90**, 33 (1990).

7) D. Avnir, D. Levy, and R. Reisfeld, *J. Phys. Chem.*, **88**, 5956 (1984).

8) B. Dunn and J. I. Zink, *J. Mater. Chem.*, **1**, 903 (1991); J. I. Zink and B. S. Dunn, *J. Ceram. Soc. Jpn.*, **99**, 878 (1991).

9) T. Fujii, *Hyoumen*, **30**, 821 (1992).

10) D. Avnir, V. R. Kaufman, and R. Reisfeld, *J. Non-Cryst. Solids*, **74**, 395 (1985).

11) V. Kaufman and D. Avnir, *Langmuir*, **2**, 717 (1986).

12) D. Levy and D. Avnir, *J. Phys. Chem.*, **92**, 4743 (1988).

13) A. Slama-Schwok, D. Avnir, and M. Ottolenghi, *J. Am. Chem. Soc.*, **113**, 3984 (1991); A. Slama-Schwok, D. Avnir, and M. Ottolenghi, *Photochem. Photobiol.*, **54**, 525 (1991).

14) R. Reisfeld, M. Eyal, and D. Brusilovsky, *Chem. Phys. Lett.*, **153**, 210 (1988).

15) R. Gvishi and R. Reisfeld, *J. Non-Cryst. Solids*, **128**, 69 (1991).

16) T. Tani, H. Namikawa, K. Arai, and A. Makishima, *J. Appl. Phys.*, **58**, 3559 (1985).

17) A. Makishima and T. Tani, *J. Am. Ceram. Soc.*, **69**, C-72 (1986).

18) J. McKiernan, J. C. Pouxviel, B. Dunn, and J. I. Zink, *J. Phys. Chem.*, **93**, 2129 (1989).

19) D. Preston, J. C. Pouxviel, T. Novinson, W. C. Kaska, B. Dunn, and J. I. Zink, *J. Phys. Chem.*, **94**, 4167 (1990).

20) J. M. McKiernan, S. A. Yamanaka, B. Dunn, and J. I. Zink, *J. Phys. Chem.*, **94**, 5652 (1990).

21) E. T. Knobbe, B. Dunn, P. D. Fuqua, and F. Nishida, *Appl. Opt.*, **29**, 2729 (1990).

22) K. Matsui, T. Matsuzuka, and H. Fujita, *J. Phys. Chem.*, **93**, 4991 (1989).

23) K. Matsui, T. Nakazawa, and H. Morisaki, *J. Phys. Chem.*, **95**, 976 (1991).

24) Y. Takahashi, T. Kitamura, K. Uchida, and T. Yamanaka, *J. Appl. Phys.*, **28**, L1609 (1989).

25) T. Fujii, A. Ishii, H. Nagai, N. Niwano, N. Negishi, and M. Anpo, *Chem. Express*, **4**, 1 (1989); T. Fujii, A. Ishii, and M. Anpo, *J. Photochem. Photobiol.*, **54**, 231 (1990).

26) T. Fujii, O. Kawauchi, Y. Kurihara, A. Ishii, N. Negishi, and M. Anpo, *Chem. Express*, **5**, 917 (1990).

27) T. Fujii, H. Kitamura, O. Kawauchi, T. Mabuchi, and N. Negishi, *J. Photochem. Photobiol.*, **61**, 365 (1991).

28) T. Fujii, T. Mabuchi, H. Kitamura, O. Kawauchi, N. Negishi, and M. Anpo, *Bull. Chem. Soc. Jpn.*, **65**, 720 (1992).

29) T. Fujii, Y. Murata, and M. Matsui, *Res. Chem. Intermed.*, **18**, 87 (1992).

30) M. Nakamura, H. Nasu, and K. Kamiya, *J. Non-Cryst. Solids*, **135**, 1 (1991).

31) A. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 3272 (1971).

32) K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, **99**, 2039 (1977).

33) P. Lianos and S. Georghiou, *Photochem. Photobiol.*, **30**, 355 (1979).

34) K. Hara, P. de Mayo, W. R. Ware, A. C. Weedon, G. S. K. Wana, and K. C. Wu, *Chem. Phys. Lett.*, **69**, 69 (1980).

35) R. K. Bauer, R. Borenstein, P. de Mayo, K. Okada, M. Rafalska, W. R. Ware, and K. C. Wu, *J. Am. Chem. Soc.*, **104**, 4635 (1982).

36) R. K. Bauer, P. de Mayo, W. R. Ware, and K. C. Wu, *J. Phys. Chem.*, **86**, 3781 (1982).

37) S. L. Suib and A. Kostapapas, *J. Am. Chem. Soc.*, **106**, 7705 (1984).

38) T. Fujii and E. Shimizu, *Chem. Phys. Lett.*, **137**, 448 (1987).

39) T. Fujii, E. Shimizu, and S. Suzuki, *J. Chem. Soc., Faraday Trans. 1*, **84**, 4387 (1988).

40) T. Fujii, A. Ishii, H. Satozono, S. Suzuki, M. Che, and M. Anpo, *Bull. Chem. Soc. Jpn.*, **63**, 2475 (1990).

41) C. H. Lochmuller and T. J. Wenzel, *J. Phys. Chem.*, **94**, 4230 (1990).

42) V. R. Kaufman, D. Levy, and D. Avnir, *J. Non-Cryst. Solids*, **82**, 103 (1986).

43) D. Brusilovsky and R. Reisfeld, *Chem. Phys. Lett.*, **141**, 119 (1987).

44) K. Matsui and T. Nakazawa, *Bull. Chem. Soc. Jpn.*, **63**, 11 (1990).

45) K. Matsui and N. Usuki, *Bull. Chem. Soc. Jpn.*, **63**, 3516 (1990).

46) T. Yamanaka, Y. Takahashi, T. Kitamura, and K. Uchida, *Chem. Phys. Lett.*, **172**, 29 (1990); T. Yamanaka, Y. Takahashi, T. Kitamura, and K. Uchida, *J. Lumin.*, **48/49**, 265(1991); T. Kitamura, Y. Takahashi, T. Yamanaka, and K. Uchida, *J. Lumin.*, **48/49**, 373 (1991).

47) H. A. Benesi and B. H. Winquist, "Advanced in Catalysts," Academic Press, New York(1978), p. 97.

48) V. C. F. Holm and A. Clark, *J. Catal.*, **2**, 16 (1963).

49) B. C. Gates, J. R. Katzer, and G. C. A. Schuit, "Chemistry of Catalytic Processes," McGraw-Hill, New York (1979).

50) An excimer is defined as the excited-state dimer formed when an excited-state molecule and a ground-state molecule of the same species diffuse together during the excited-state lifetime.(51) Although diffusion is limited in the gel state, the fluorescence spectra around 480 nm of pyrene in the gel state is very similar to that observed ("excimer-like") as the usual excimer fluorescence of pyrene in the liquid state.

51) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York (1970).

52) S. Morimoto, I. Sunagawa, and A. Miyashiro, "Koubutu Gaku," Iwanami, Tokyo (1975).

53) R. Kiriyama, "Kotai Kouzou Kagaku," Kyouritu, Tokyo (1978).

54) A. J. Leonard, P. Ratnasamy, F. D. Declerek, and J. J. Fripiat, *Discuss. Faraday Soc.*, **52**, 98 (1971).

55) R. K. Baur, P. de Mayo, W. R. Ware, and K. C. Wu, *J. Phys. Chem.*, **86**, 3781 (1982); R. K. Bauer, P. de Mayo, L. V. Natarajan, and W. R. Ware, *Can. J. Chem.*, **62**, 1279 (1984).

56) P. de Mayo, L. V. Natarajan, and W. R. Ware, *J. Phys. Chem.*, **89**, 3526 (1985).

57) J. Stahlberg and M. Almgren, *Anal. Chem.*, **57**, 817 (1985).

58) A. L. Wong, M. L. Humnicutt, and J. M. Harris, *J. Phys. Chem.*, **95**, 4489 (1991); A. L. Wong and J. N. Harris, *J. Phys. Chem.*, **95**, 5895 (1991); A. L. Wong, M. L. Hunnicutt, and J. M. Harris, *Anal. Chem.*, **63**, 1076 (1991).