Excimer Fluorescence of Pyrene in Sol-Gel Silica

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The fluorescence and excitation spectra of pyrene at high concentrations were studied along the sol to xerogel stages of the sol-gel silica formed by the acidic hydrolysis of tetraethyl orthosilicate. The monomer and excimer fluorescence of pyrene were observed in the reaction system. Their relative intensities revealed that complex changes occurred that depended on the reaction time and the excitation wavelengths. The environmental polarity of the probe molecules also changed as shown by the fluorescence vibronic structure. The excitation spectrum of the excimer fluorescence in some stages was red shifted in comparison with that of the monomer fluorescence, indicating the existence of bimolecular ground-state pyrene associations. The mechanism by which pyrene molecules are trapped in the silica network is discussed on the basis of the results.

The photophysics of pyrene molecules adsorbed on solid surfaces has been extensively studied as a photochemical and photophysical model system of adsorbed molecules,[1-8] because of the unique excited-state properties of such molecules, such as the sensitivity of their fluorescence vibronic structure to environmental polarity[9,10] and their ability to form excimers.[11]

A longer-wavelength broad band emission as well as the monomer fluorescence have been observed in pyrene on silica.[1] The excitation spectrum of the broad-band emission was red shifted in comparison with that for the monomer emission. The broad-band emission was interpreted as excimer fluorescence originating from the bimolecular ground-state associations (BGSAs) of pyrene.[1] A dimeric configuration of the BGSAs and a kinetic scheme from the BGSA to the excimer state have already been proposed.[1,5,6]

Recently, the doping of silica-gel glass with organic molecules has become possible by using the sol-gel process.[12,13] It has been shown by using this technique that the excimer intensity of pyrene changes during the sol-gel-xerogel stage, and that the final silica xerogel is an efficient trap that isolates organic molecules, as indicated by the fact that the excimer intensity becomes barely detectable.[14] The trapping mechanism has been fully discussed. However, the excitation spectrum of the excimer fluorescence was markedly red shifted in comparison with that of the monomer fluorescence in some stages. This is indicative of the formation of BGSAs, which were not completely taken into consideration in the discussion of the trapping mechanism. More specifically, the excimer fluorescence in the sol-gel system originates from both the conventional excimer formed from monomers and also the BGSAs. Therefore, a number of points are open to discussion regarding the mechanism by which pyrene is trapped during the sol-gel process.

In this study the changes in the excimer fluorescence of pyrene during the sol-gel-xerogel stages were examined by varying the excitation wavelength, and the changes in the excitation spectra were studied as well. The ratio of the intensity of the third peak to the first peak (I_3/I_1) of the monomer fluorescence was also measured during the process.[15] These results indicate that (1) excimer states are formed from an excited monomer and a ground-state monomer in the initial stages; (2) BGSAs, which are formed during the evaporation of ethanol solvents, also show excimer fluorescence; and finally, (3) most of the BGSAs are forced to decompose into monomers by the shrinkage of the silica cage and show little excimer fluorescence after the shrinkage.

Experimental

Chemicals. Pyrene (Aldrich, >99%) was recrystallized several times from ethanol. Tetraethyl orthosilicate (TEOS) from Tokyo Kasei and ethanol of spectroscopic grade were used without further purification. The water was deionized and distilled.

Sol-Gel Process. A solution was prepared as described in a previous paper[15] from 10.0 mL of TEOS, 5.0 mL of water, and 10.0 mL of ethanol containing 2.5×10^{-3} mol dm^{-3} of pyrene. The solution was adjusted to a pH of 3.2 by the addition of HCl and stirred for 1 h. Samples of an appropriate volume were taken from the mixture and used in the measurements. A small amount that was taken from the mixture just before gelation and spread on a Petri dish was used for the measurements after gelation. This procedure was used in order to minimize the scatter in the data, which showed a positional dependence in bulk gel.

Measurements. The fluorescence and fluorescence excitation spectra were taken with a JASCO FP-770 spectrofluorometer in rectangular excitation at room temperature. The excitation wavelengths for the fluorescence were 340 and 360 nm. The 340-nm wavelength was settled because the excitation spectra for the monomer fluorescence showed a strong peak around 340 nm, and the 360-nm wavelength was also settled because the excitation spectra for the excimer fluorescence showed a strong peak around 375 nm, and 360 nm was the longest excitation wavelength at which the fluorescence 0-0 band could be measured.

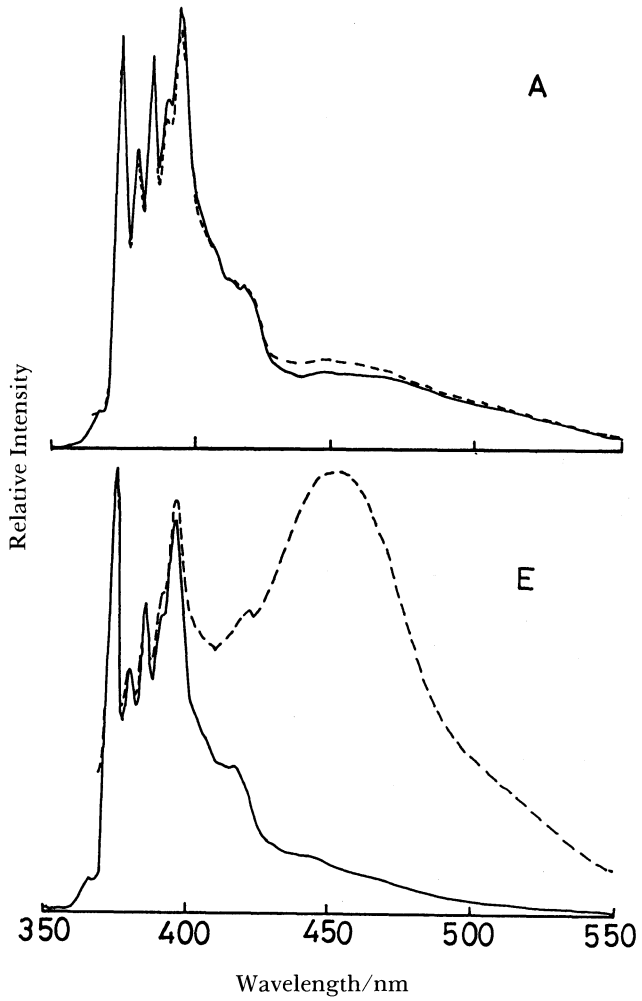

Fig. 1. Fluorescence spectra of pyrene in the sol-gel system at t=0 h (A) and t=260 h (E): λ_{ex}=340 nm (——) and λ_{ex}=360 nm (----).

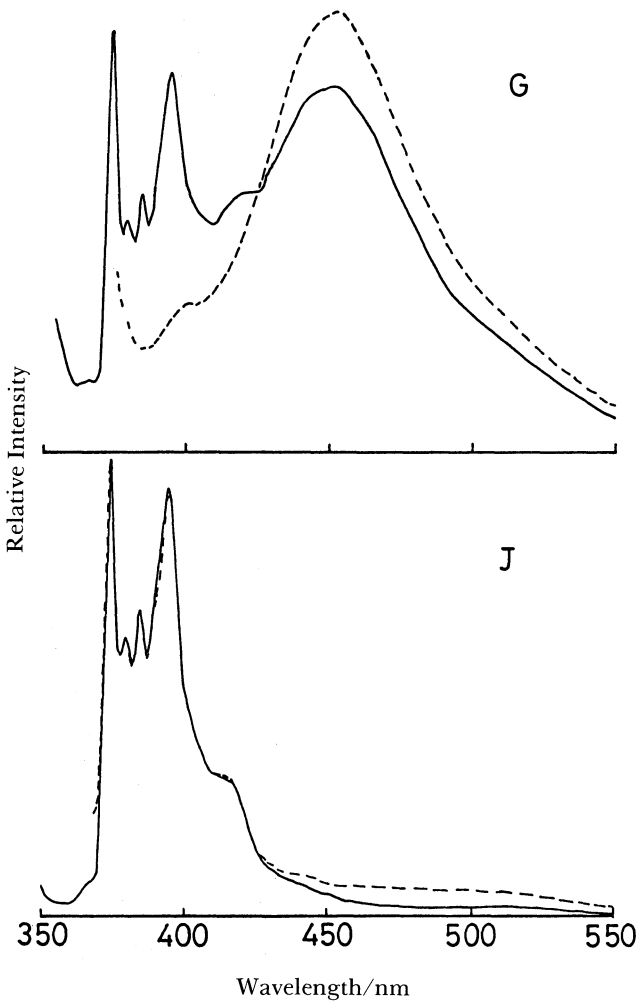

Fig. 2. Fluorescence spectra of pyrene in the sol-gel system at t=400 h (G) and t=1700 h (J): λ_{ex}=340 nm (——) and λ_{ex}=360 nm (----).

Results and Discussion

Figures 1 and 2 show the fluorescence spectra of pyrene in the sol-gel system excited at 340 nm (^{1}La) and 360 nm(^{1}Lb). Just after mixing (Fig. 1A), the peak intensities of the excimer fluorescence are much weaker than those of the monomer fluorescence and the intensity ratio did not depend on the excitation wavelength. Figure 1E shows the spectra after gelation (260 h). Here the excimer fluorescence excited at 360 nm is much greater than in Fig. 1A, while the monomer fluorescence is dominant for 340-nm excitation. This difference is caused by the coexistence of monomers and BGSAs. The excitation spectrum of the excimer fluorescence originating from the BGSAs is red shifted in comparison with the absorption responsible for the monomer fluorescence.[1] Therefore, the excimer fluorescence is stronger for 360-nm excitation than for 340-nm excitation, which will be discussed later. After 400 h, the excimer intensity for 340-nm excitation increased dramatically and that for 360-nm excitation rose still higher (Fig. 2G). This result indicates that equilibrium between monomers and BGSAs shifts to the BGSAs.[6] Finally they both become very small after 1700 h (Fig. 2J), which exhibits pyrene is isolated and trapped in the silica cage.[14] The changes in the ratio of the third band to the 0-0 band intensity of the monomer fluorescence, I_3/I_1, were monitored during the process.

Figure 3 shows the changes in the excimer fluorescence and I_3/I_1 during the whole sol-gel process from A (t=0 h) to J (t=1700 h). The relative intensity of excimer fluorescence is represented by $I_E/(I_E+I_M)$ as used by Kaufman and Avnir,[14] where I_E and I_M are the fluorescence intensities of excimer (455 nm) and monomer (395 nm, the fifth peak). The fifth peak is used for normalization because the intensity is less sensitive to the environmental polarity.[10] It should be noted that the excimer fluorescence and monomer fluorescence are not resolved here, therefore the relative intensity of the excimer is only a rough measure. The general features are almost similar to those

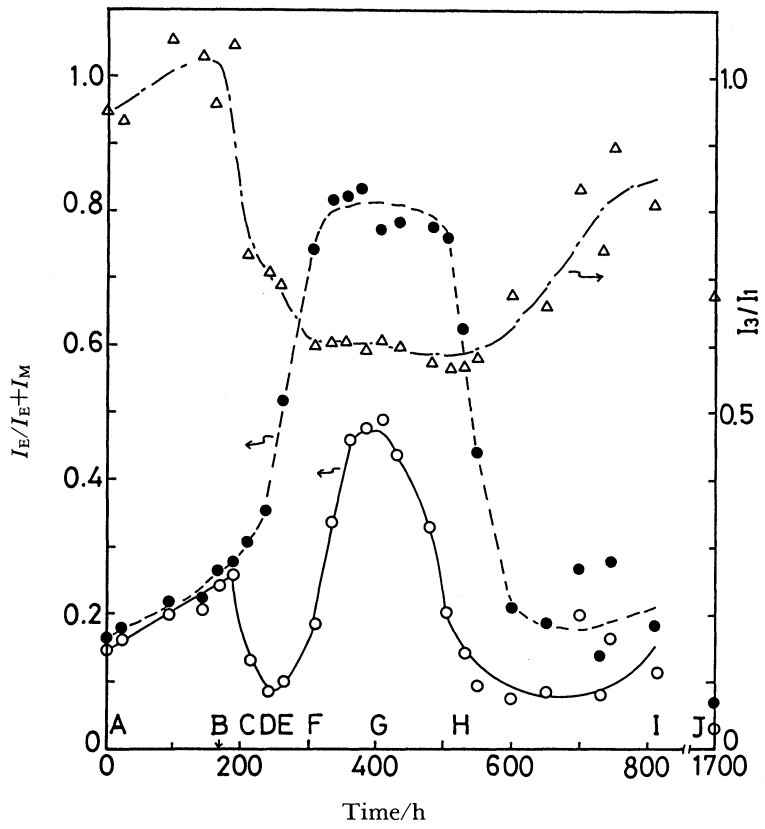

Fig. 3. Changes in relative excimer fluorescence intensity over time of pyrene ($I_E/(I_E+I_M)$) at λ_{ex}=340 nm (○) and λ_{ex}=360 nm (●), and I_3/I_1 (△) during the sol-gel process. The arrow indicates a gelation point.

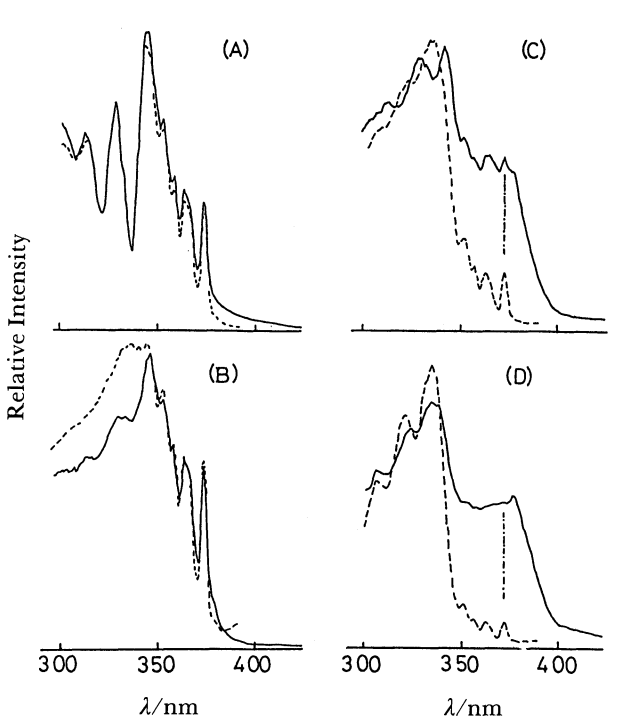

Fig. 4. Excitation spectra of pyrene in the sol-gel system at four stages (A-D) shown in Fig. 3: λ_{em}=395 nm (----) and λ_{em}=455 nm (——).

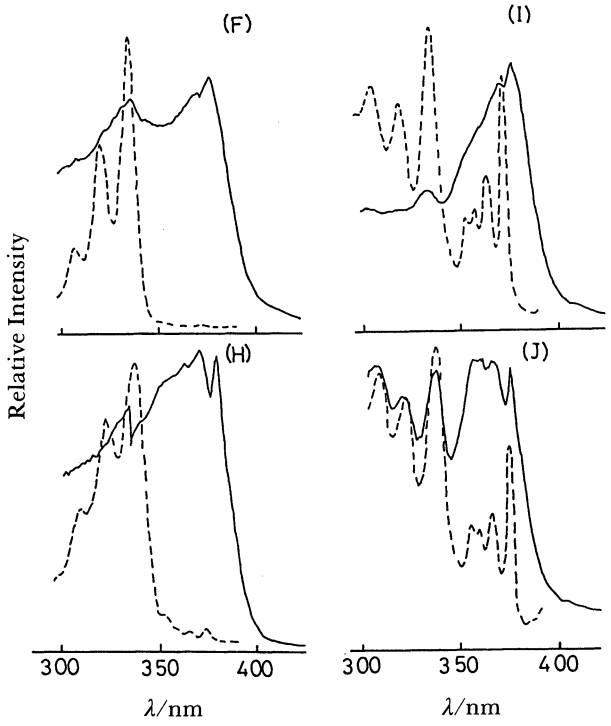

Fig. 5. Excitation spectra of pyrene in the sol-gel system at four stages (F-J) shown in Fig. 3: λ_{em}=395 nm (----) and λ_{em}=455 nm (——).

obtained by Kaufman and Avnir.[14] The excimer intensity for 340-nm excitation (○) rises from its initial value in the solution (A) to a small peak after the gelation point (B), and then drops to a low value (D) and rises again to a maximum (G). It then becomes very small in the final xerogel stage (J). The excimer intensity for 360-nm excitation (●) initially rises along with the curve for 340-nm excitation, but then, unlike the curve for 340-nm excitation, it increases abruptly and reaches a peak around the same time as the 340-nm curve. This difference induced by varying the excitation wavelength indicates the coexistence of the monomers and the BGSAs of pyrene molecules as mentioned above.

The changes in I_3/I_1 generally reflect the changes in the excimer intensity. The main features of the curve are that it is near a minimum when the excimer intensity is at a maximum (G), and after that, it rises as the excimer intensity falls (H-I). Initially, the behavior is more complicated as all three curves rise together (A-B) and then I_3/I_1 falls off as the excimer intensity for 340-nm excitation falls off and that for 360-nm excitation continues to rise (B-D). The initial behavior of I_3/I_1 well corresponds to that of I_1/I_5 as found by Kaufman and Avnir.[14]

Figures 4 and 5 are excitation spectra for the excimer (455 nm) and monomer (395 nm) during the sol-gel process. These spectra almost overlap in A and B. The intensity of the excitation spectra for the excimer increases in the long wavelength regions at C, and this spectrum is apparently red-shifted in comparison with that of monomer fluorescence after D. It should be noted that the C-D region shows a minimum for 340-nm excitation (Fig. 3). Between F and H, where the excimer intensities show a maximum (Fig. 3), the excitation spectra for the monomer fluorescence show prominent structures similar to the absorption spectra, while the excitation spectra for the excimer fluorescence shows broad red-shifted peaks. The structures in both spectra nearly coincident with each other at J, except that, for excimer fluorescence, the intensity is slightly stronger than for monomer fluorescence in the 350—375 nm region.

In the following, general concepts that can explain the observed changes in the excimer fluorescence, excitation spectra, and I_3/I_1 during the sol-gel-xerogel stage are discussed.

From A to B, the excimer intensity for 340-nm excitation matches that for 360-nm excitation and the excitation spectra for the monomer and the excimer coincide. These results indicate that excimer fluorescence occurs by the well-known reaction between one molecule in the ground state and one in the excited state in this stage, and that the intensity increases because of an increase in the effective pyrene concentration during the hydrolysis and polymerization of TEOS. The environment of pyrene becomes less polar because its "solvation" shell consists of neighboring pyrene molecules as well as silanols and water molecules[14] when there is an effective increase in the local concentration, and so I_3/I_1 increases.[9,10,15]

The evaporation of the ethanol encaged in the silica gel network induces the change in the solvent composition after B with the result that the concentrated pyrene molecules cannot dissolve in the solvents and/or a minimization of the contact surface between the hydrophobic pyrene molecules and the surrounding water molecules occurs. In consequence, pyrene forms aggregates, such as BGSAs. This is indicated by the decrease in the excimer fluorescence for 340-nm excitation, and by the corresponding increase in the excimer fluorescence for 360-nm excitation, which originates from the BGSAs after C. The evidence pointing to BGSAs as the origin is the red shift of the excitation spectra for excimer fluorescence in comparison to those for monomer fluorescence.[1] The decreases in I_3/I_1 can be explained by both the evaporation of ethanol[15] and the decrease in the number of molecules nearby due to the formation of the BGSAs.

Between F and H, the concentration of monomer pyrene is lowered as discussed above, resulting in the absorption spectrum-like excitation spectra for monomer fluorescence. Furthermore, the I_3/I_1 values in this region (ca. 0.60) are quite similar to those in a diluted system, as shown in the previous paper.[15] It should be noted that I_3 and I_1 are not separated from the excimer intensity. The result, therefore, indicates that the degree of overlap of these spectra is extremely small, which is expected from the previous result.[1] The second increase in the excimer fluorescence for 340-nm excitation after D can be ascribed to the increased number of BGSAs that are excited at a wavelength of 340 nm and the consequent decrease in monomers.

After passing H, the excimer intensities for 360- and 340-nm excitation decrease. This change is probably induced by the shrinkage of the silica cage, forcing the BGSAs too close together to remain stable as discussed in detail by Kaufman and Avnir.[14] The repulsive forces between the pyrene molecules push the pyrene molecules into adjacent silica cages and bring about the dispersion of the pyrene molecules.[14] From H to I are transient stages where pyrene molecules migrate form one pore to another until the intermolecular repulsive forces become a minimum. I_3/I_1 increases again because of an effective increase in the local concentration of pyrene monomer due to the dissociation of the BGSAs and a consequent decrease in polarity. In the final stage in this experiment (J), few pyrene molecules are still trapped in the form of the BGSAs, as is shown in the excimer fluorescence for 360-nm excitation, and in the slight difference between the excitation spectra.

Although the changes in I_3/I_1 were tentatively ascribed to the changes in environmental polarity, an increase in I_3/I_1 can also be attributed to a decrease in

I_1 due to reabsorption at high pyrene concentrations.[14] Naturally, when monomer concentrations decrease as a result of the formation of BGSAs, I_3/I_1 decreases because of a decrease in reabsorption of I_1. Therefore, the changes in monomer concentrations reflect the changes in I_3/I_1, which can be explained by polarity changes or by reabsorption. Further studies are required to clarify the mechanism.

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