

## PYRENE FLUORESCENCE STUDIES OF THE SOL-GEL PROCESS

Kazunori MATSUI, Department of Industrial Chemistry,  
College of Engineering, Kanto Gakuin University,  
Mutsuura-cho, Kanazawa-ku, Yokohama 236, Japan

The fluorescence of pyrene probe molecules was measured in the sol-gel reaction system of tetraethyl orthosilicate. The monomer fluorescence intensity ratio of the vibronic bands changed remarkably during the sol-gel process, indicating that the environmental polarity of the probe molecules increased upon the evaporation of the ethanol solvent. The excimer fluorescence revealed that complex changes occurred that depended on the reaction time and the excitation wavelengths, suggesting the existence of bimolecular ground-state pyrene association in some stages. The trapping of micelles and inclusion compounds in the silica glasses also was shown by the fluorescence intensity ratio of the vibronic bands.

## 1. Introduction

Recent studies have demonstrated that organic molecules can be embedded in silica gel glasses by the sol-gel process and that such a material system opens up the possibility for various new applications.<sup>1-6</sup> It has also been shown that some organic molecules in the sol-gel system show remarkable changes in fluorescence during the sol-gel-xerogel transition in silica.<sup>7-9</sup> Therefore, it is interesting and important to study the interaction between organic molecules and silica glasses. Moreover, characterization of porous silica gels also is important from a view point of glass fabrication because the porous silica gels determine the properties of the final glasses.

The photophysics of pyrene molecules adsorbed on solid surfaces has been extensively studied as a photochemical and photophysical model system of adsorbed molecules,<sup>10-17</sup> because of the unique excited-state properties of such molecules, such as the sensitivity of their fluorescence vibronic structure to environmental polarity<sup>18,19</sup> and their ability to form excimers.<sup>20</sup> By using pyrene as a probe for the sol-gel process, Kaufman and Avnir showed for the first time that the environmental polarity of the probe molecule changes along the sol-gel process and that the final silica xerogel is an efficient trap that isolates organic molecules.<sup>21</sup> However, a number of points

are open to discussion regarding the detailed mechanism.

In this work, we report the sol-gel-xerogel transitions during the polymerization of tetraethyl orthosilicate (TEOS,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) and the mechanism by which organic molecules are embedded in silica glasses by using the monomer and excimer fluorescence of pyrene.<sup>22,23</sup> We also show the trapping of micelles and inclusion compounds in silica glasses by using the monomer fluorescence of pyrene.<sup>24,25</sup>

## 2. Monomer fluorescence as a probe for the environmental changes during the sol-gel process

Figure 1 shows examples of the fluorescence spectra of pyrene as measured in the starting solution and the xerogel. It is clear that the relative intensities of the vibronic band change from the solution to the xerogel. The intensity ratio of the third peak (384 nm) to the first peak (373 nm) ( $\underline{I}_3/\underline{I}_1$ ) and that of the fifth peak (394 nm) to the first peak ( $\underline{I}_5/\underline{I}_1$ ) of the pyrene monomer fluorescence were measured in various ethanol-water mixtures. The  $\underline{I}_3/\underline{I}_1$  value decreased with an increase in dielectric constant as shown in Figure 2, while the  $\underline{I}_5/\underline{I}_1$  parameter (not shown here), which was used by Kaufman and Avnir,<sup>21</sup> was less sensitive than the  $\underline{I}_3/\underline{I}_1$  parameter.<sup>23</sup> Therefore, we used  $\underline{I}_3/\underline{I}_1$  as a probing parameter.

Figure 3 shows the change in  $I_3/I_1$  during the sol-gel process. The  $I_3/I_1$  value changed little initially and then it dropped sharply to a value of 0.60 and remained there. The dielectric constant estimated from the relationship in Fig. 2 is also plotted in Fig. 3. The dielectric constant was 36 in the starting solution and became 67 in the xerogel (after 900 h). Such a change is ascribed to an increase in the water composition of the encapsulated solvents upon the evaporation of the ethanol.<sup>4,22</sup> The dielectric constants for both the solutions and the xerogels are in order of the water:TEOS ratios (Table 1). It is suggested that the residual water molecules play an important role in determining the polarity of the xerogels.

### 3. Excimer fluorescence

A longer-wavelength broad band emission has been observed in pyrene on silica. The broad-band emission was interpreted as excimer fluorescence originating from the bimolecular ground-state associations (BGSAs),<sup>10</sup> because the excitation spectrum of the broad-band emission was red shifted in comparison with that for the monomer emission. In the study by Kaufman and Avnir,<sup>21</sup> the excitation spectrum of the excimer fluorescence was markedly red shifted in some stages during the sol-gel process, suggesting the

formation of BGSAs.

Figure 4 shows the changes in the excimer fluorescence intensities excited at 340 and 360 nm.<sup>23</sup> The excimer intensity for 340-nm excitation (○) rises from its initial value in the solution to a small peak around 200 h, and then drops to a low value and rises again to a maximum. It then becomes very small in the final xerogel stage (1700 h). 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. Considering the results and the excitation spectra (not shown here) together, we conclude that this difference induced by varying the excitation wavelength is ascribed to the coexistence of the monomers and the BGSAs of pyrene molecules.

In region I, excimer fluorescence occurs by the well-known reaction between one molecule in the ground state and one in the excited state. In region II, the evaporation of the ethanol occurs, resulting in the formation of the BGSAs. The excimer fluorescence arises from the BGSAs. Therefore, the excimer intensity for 360-nm excitation becomes stronger than that for 340-nm excitation. In region III, the shrinkage of the silica cage induces the decomposition of the BGSAs, bringing about the disper-

sion of the pyrene molecules.<sup>21,23</sup>

#### 4. Trapping of micelles in the sol-gel glasses

The effect of surface-active agents on the sol-gel process was first studied by Kaufman et al.<sup>26</sup> They found an oscillatory behavior of pyrene excimer intensity when the surface-active agents were added ( $3 \times 10^{-5}$ – $1.5 \times 10^{-3}$  M) to the sol-gel solution. When surfactants are added above the critical micelle concentration to a sol-gel solution, it is expected that micelles can be formed in the sol-gel system. If the entrapment of micelles is possible in the sol-gel silica, new functions will be added to silica glasses.<sup>27</sup>

Figure 5 shows how  $I_3/I_1$  changes over time for the sol-gel systems with and without sodium dodecyl sulfate (SDS). As shown above, the  $I_3/I_1$  values decreased as the reaction proceeded without SDS. On the contrary, the  $I_3/I_1$  values increased when SDS was added above  $2 \times 10^{-2}$  M into the sol-gel solution. The  $I_3/I_1$  values were similar to those for micellar solutions of SDS, indicating that the environment of pyrene resembled that of micelle-solubilized pyrene. The results suggest that the micelles of SDS are trapped in the sol-gel glasses.<sup>24</sup>

#### 5. Trapping of inclusion compounds in the sol-gel glasses

Cyclodextrin are cyclic oligomers of glucose. The cyclodextrins have a cylindrical shape and ability to form inclusion complexes with organic or inorganic guests. Trapping of inclusion complexes in silica glasses is of considerable interest.

Figure 6 show the changes in  $I_3/I_1$  for the sol-gel systems with and without  $\beta$ -cyclodextrin( $\beta$ -CD). The  $I_3/I_1$  values increased when  $\beta$ -CD was added as the  $I_3/I_1$  values without  $\beta$ -CD decreased. The increased  $I_3/I_1$  values were similar to those for the inclusion compound between  $\beta$ -CD and pyrene.<sup>28,29</sup> The results indicate that the inclusion complexes were trapped in the sol-gel glasses.<sup>25</sup>

## 6. Conclusion

We have shown that a pyrene photophysical probe is useful for studying complex changes along the sol-gel-xerogel transition. In addition, it is revealed that micelles and inclusion compounds are trapped in silica glasses prepared by the sol-gel process. Such materials will be available for new applications.

## References

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Table 1. Estimates of the Dielectric Constant for the Sol-Gel Process by Means of Pyrene Fluorescence: Ethanol/TEOS = 3.8; pH = 3.2.

Water/TEOS	Solution		Xerogel	
	$I_3/I_1$	$\epsilon$	$I_3/I_1$	$\epsilon$
1.2	0.79	30	0.62	65
3.1	0.77	34	0.61	66
6.2	0.76	36	0.60	67
12.4	0.74	43	0.57	71

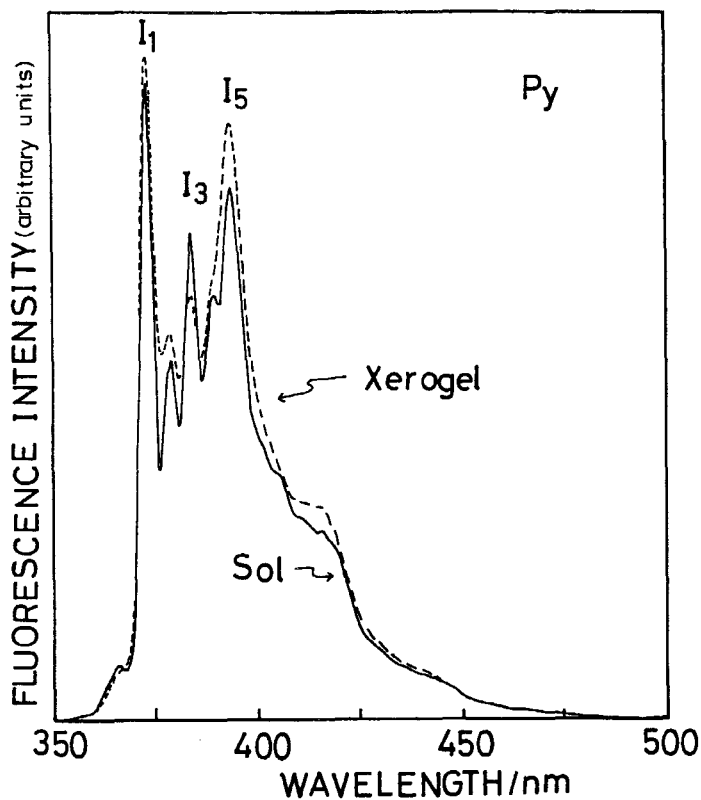


Figure 1. Typical fluorescence spectra of pyrene during the sol-gel process: TEOS: H<sub>2</sub>O: ethanol = 1:6.2:3.8 (molar ratio) at pH = 3.3.

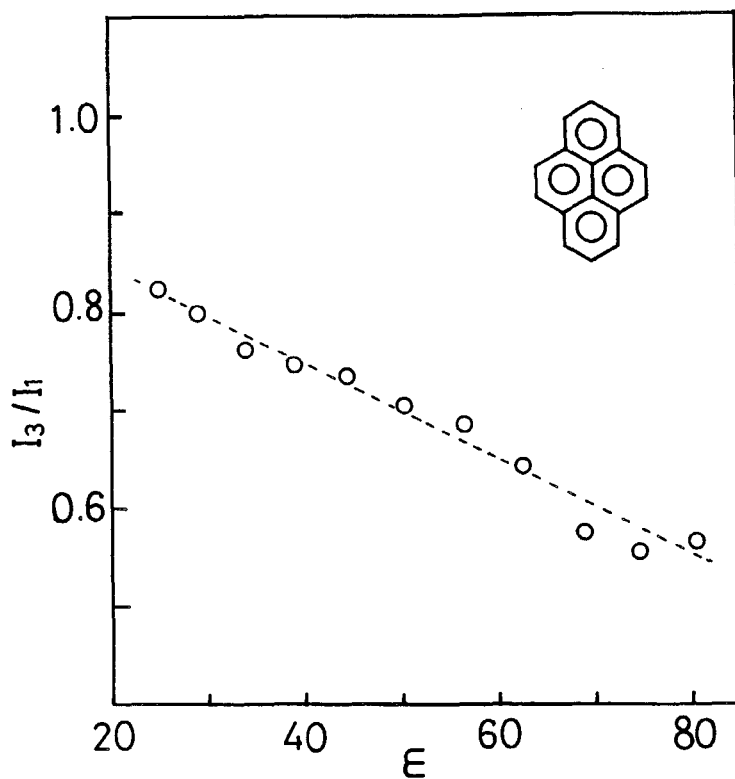


Figure 2. Variation of  $I_3/I_1$  for pyrene as a function of dielectric constant of ethanol-water mixtures.

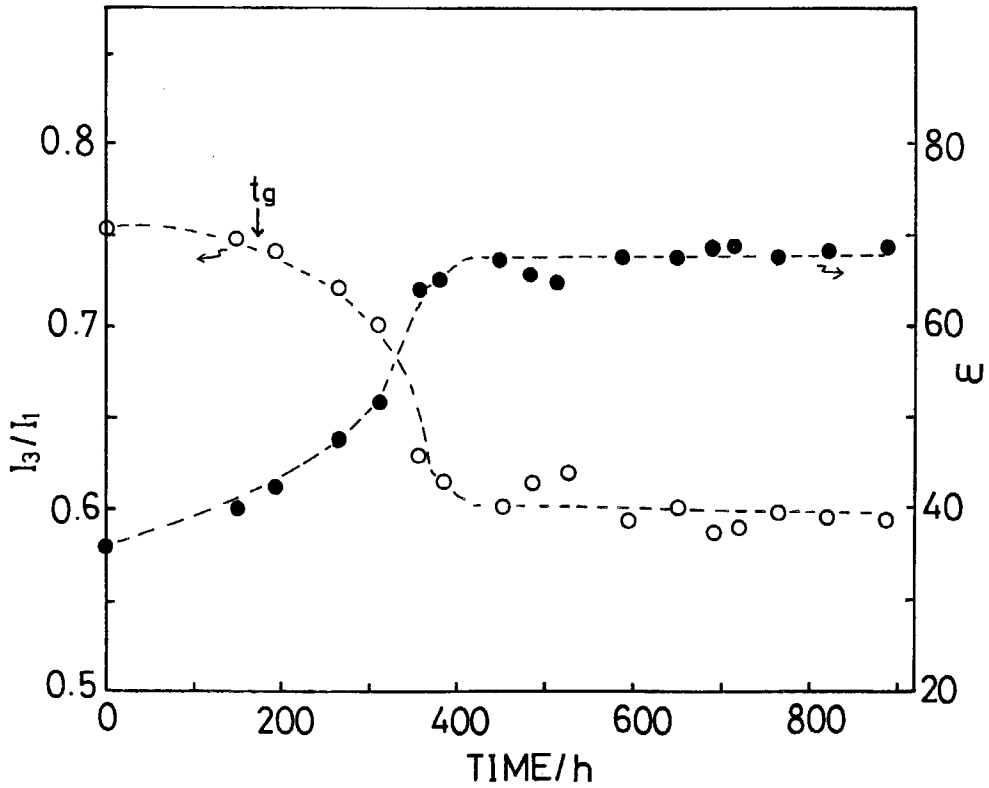


Figure 3. Changes in  $I_3/I_1$  of pyrene (O) and estimated dielectric constant (●) during the sol-gel process.

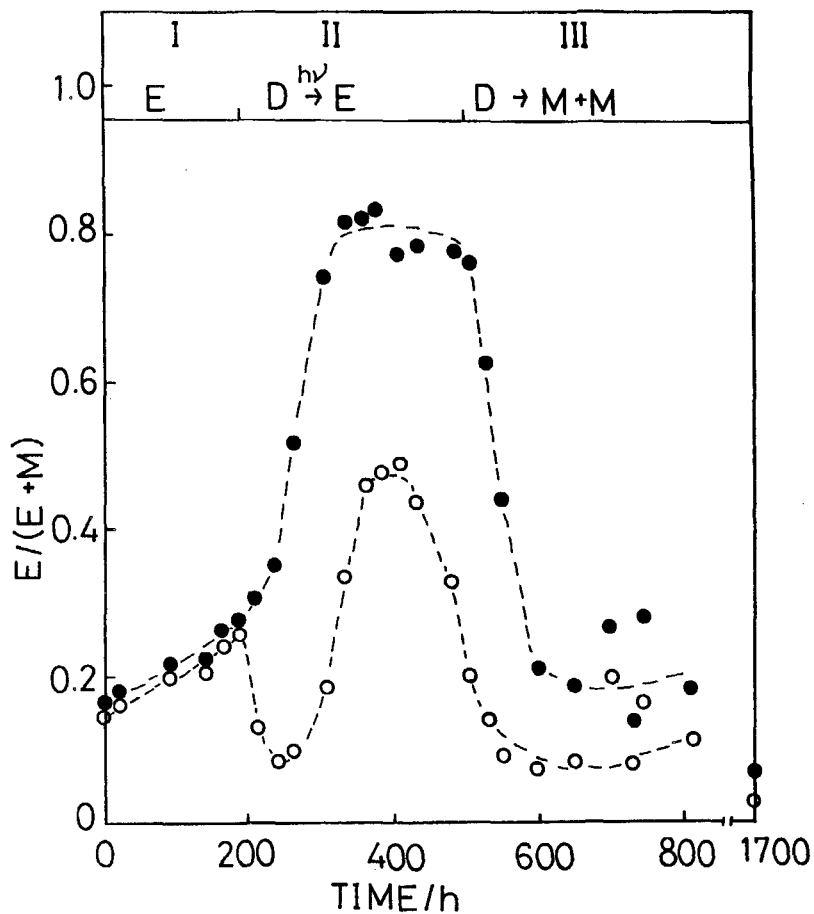


Figure 4. Changes in relative excimer fluorescence intensity ( $E/(E + M)$ ) over time during the sol-gel process at  $\lambda_{\text{ex}} = 340 \text{ nm}$  (○) and  $\lambda_{\text{ex}} = 360 \text{ nm}$  (●).

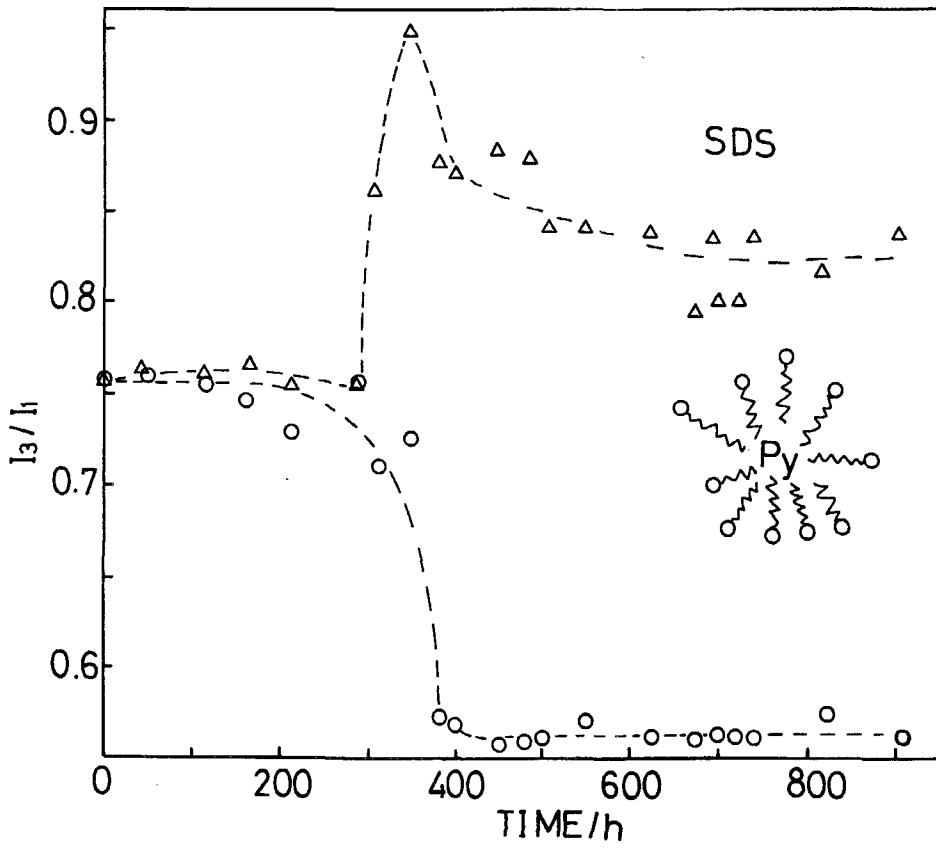


Figure 5.  $I_3/I_1$  over time during the sol-gel process without (○) and with sodium dodecyl sulfate ( $1 \times 10^{-1}$  M) (Δ).



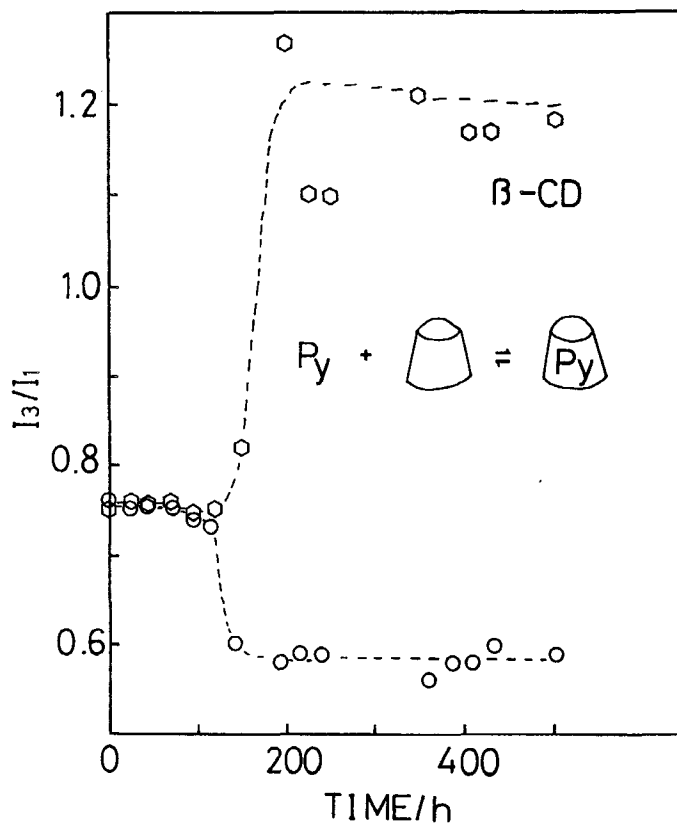


Figure 6.  $I_3/I_1$  over time during the sol-gel process without (○) and with  $\beta$ -cyclodextrin ( $1 \times 10^{-3}$  M) (◐).