Fluorescence Probes of Pyrene and Pyrene-3-carboxaldehyde for the Sol-Gel Process

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Silica sols and gels doped with pyrene (Py) and pyrene-3-carboxaldehyde (PyCHO) were prepared by the acidic hydrolysis of tetraethyl orthosilicate in ethanol. We studied the fluorescence of these molecules during the sol-gel-xerogel stages. The fluorescence intensity ratio of the vibronic bands of Py changed remarkably, while the fluorescence maximum of PyCHO showed a significant red shift as the gel dried. Such a spectral change was ascribed to an increase in the environmental polarity of the probe molecules upon the evaporation of the ethanol. The estimated dielectric constant of the gel after drying in a vacuum is about 72, just slightly less polar than water (80). The silica cage produced by the sol-gel process is probably rich in silanols, resulting in a relatively polar environment.

The polymerization of silicon alkoxides known as the sol-gel process has become an important and interesting field in material science.[1-3] Among an extensive body of studies, the doping of the silica gel with organic molecules has received considerable interest. The technique is expected to lead to new applications.[4-8] It has also been reported that some organic molecules embedded in the reaction system show remarkable changes in fluorescence during the sol-gel-xerogel transitions in silica and can be used as sensitive probes for the structural changes in the silica.[9-11] However, the detailed mechanism of these changes in the fluorescence spectra is not completely clear, for little is known about the properties of the silica cage prepared by the sol-gel process or about the interaction between the silica cage and the trapped molecules.

Meanwhile, there have been many studies regarding fluorescence probes in colloid and polymer chemistry. For example, the pyrene (Py) monomer fluorescence is known to be a typical probe. The fluorescence intensities for vibronic bands were used to study the critical micelle concentrations[12-15] and the polarity of iron(III) hydrosol,[16,17] because the intensity ratio of the third peak (384 nm) to the first peak (373 nm: 0-0 band) (I_3/I_1) is dependent on the solvent polarity.[13,15,18] The fluorescence of pyrene-3-carboxaldehyde (PyCHO) was also used to estimate the polarity at the micelle-water interfaces[19,20] and to monitor the properties of the aggregates of block copolymers.[21] This is because a linearity between the fluorescence maximum (λ_{max}) and the dielectric constant (ε) has been observed.[19]

In this work, we studied the sol-gel-xerogel transitions during the polymerization reaction of tetraethyl orthosilicate, $Si(OC_2H_5)_4$, (TEOS) by using the well-characterized Py and PyCHO molecules as fluorescence probes. The aims of the present study are to monitor the chemical changes that occur during the sol-gel process and to elucidate the nature of the silica cage and the interaction between the guest molecules and the host silica cage. It is shown that these fluorescence probes can monitor the changes in polarity along the sol-gel-xerogel transitions.

Experimental

Chemicals. The Py and PyCHO (both Aldrich products) were recrystallized several times from ethanol. The TEOS (Tokyo Kasei) and ethanol of a spectroscopic grade were used without further purification. The water was deionized and distilled.

Sol-Gel Process. The sol-gel glass was prepared by the acidic (HCl) hydrolysis of TEOS in ethanol as has been reported previously.[11] Py and PyCHO were dissolved in ethanol at 10^{-5} mol dm^{-3}. Various solutions with different ratios of TEOS : water : ethanol and pH values were prepared. The mixtures were stirred for 2 h and subsequently kept at room temperature. Typical compositions are summarized in Tables 1 and 2, along with results to be described later.

Measurement. The fluorescence spectra were taken with a JASCO FP-770 spectrofluorometer at room temperature. Samples of an appropriate volume were obtained from the mixtures during the sol-gel-xerogel stages and used for the fluorescence measurement.

Results

The fluorescence spectra for PyCHO in ethanol-water mixtures indicated the variations in the fluorescence spectra with the solvent as reported previously.[19] The parameter λ_{max} of PyCHO in these solvents is plotted against the dielectric constant of the solvents in Fig. 1. λ_{max} shifts to a longer wavelength with an increase in the dielectric constant.

Figure 2 shows same typical fluorescence spectra of PyCHO as measured in a time sequence during the sol-gel-xerogel stages. The λ_{max} value just after mixing is 454 nm, and shifts to a longer wavelength with time, resulting in a value of 467 nm after 1005 h. The parameter λ_{max} is plotted as a function of the time in the sol-gel reaction in Fig. 3. The λ_{max} value changes very little after the gelation point (ca. 230 h). Then the fluorescence spectrum shifts gradually to a longer

Table 1. Estimates of the Dielectric Constant for the Sol-Gel Process by Means of Pyrene-3-carboxaldehyde Fluorescence

r	pH	Solution		Xerogel		Vacuum-drying	
		λ_{max}/nm	ε	λ_{max}/nm	ε	λ_{max}/nm	ε
1.2	3.2	448.5	27	464.5	72	464.0	72
3.1	3.2	452.0	39	467.0	75	462.0	70
6.2	3.2	453.0	42	469.5	84	465.0	73
12.4	3.2	454.0	45	470.0	87	463.0	71
4.7	4.5	448.5	27	464.5	72	464.5	72
4.7	4.0	448.5	27	469.0	81	463.5	71
4.7	3.0	452.5	40	469.0	81	462.5	70
4.7	1.7	452.0	39	466.5	74	465.0	73

Table 2. Estimates of the Dielectric Constant for the Sol-Gel Process by Means of Pyrene Fluorescence

r	pH	Solution		Xerogel		Vacuum-drying	
		I_3/I_1	ε	I_3/I_1	ε	I_3/I_1	ε
1.2	3.2	0.79	30	0.62	65	0.56	73[a]
3.1	3.2	0.77	34	0.61	66	0.55	75[a]
6.2	3.2	0.76	36	0.60	67	0.56	73[a]
12.4	3.2	0.74	43	0.57	71[a]	(0.68)	(58)
4.7	4.3	0.80	28	0.59	68	0.56	73[a]
4.7	4.0	0.80	28	0.57	71[a]	0.55	75[a]
4.7	3.0	0.76	36	0.58	69	0.57	71[a]
4.7	1.9	0.77	34	0.61	66	0.62	65

a) These values may become slightly higher because the I_3/I_1 values correspond to two dielectric constants between 70 and 80. However, we adopt the values in Table 2, considering those results together with those for pyrene-3-carboxaldehyde in Table 1.

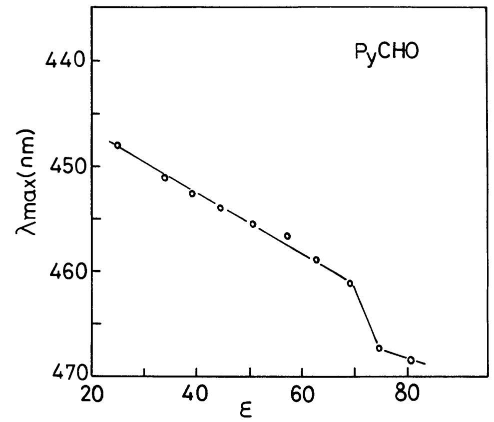

Fig. 1. Variation of fluorescence λ_{max} for pyrene-3-carboxaldehyde with dielectric constant of ethanol-water mixtures.

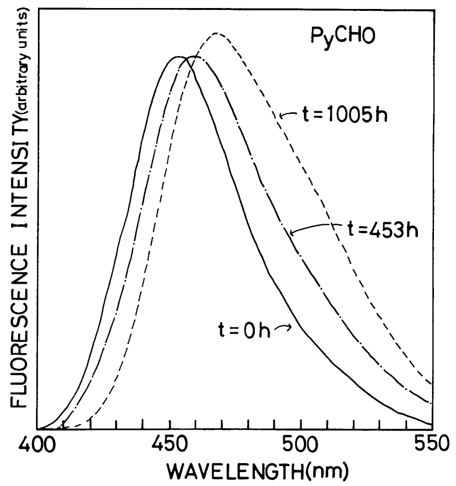

Fig. 2. Typical fluorescence spectra of pyrene-3-carboxaldehyde during the sol-gel process: TEOS: H_2O: ethanol=1 : 6.2 : 3.8 (molar ratio) at pH=3.4.

wavelength during the desiccation, reaching the longest λ_{max} value (467 nm) after about 600 h. The dielectric constant estimated from the relationship in Fig. 1 is also plotted in Fig. 3. The dielectric constant was 45 in the starting solution and became 75 in the xerogel (after 1000 h) under these preparation conditions (see the caption of Fig. 2 for the preparation conditions).

The intensity ratio of the third peak (384 nm) to the first peak (373 nm) (I_3/I_1) and that of the fifth peak (394 nm) to the first peak (I_5/I_1) of the Py monomer fluorescence were obtained in various ethanol-water mixtures. I_3/I_1 and I_5/I_1 are plotted as functions of the dielectric constant in Fig. 4. The I_3/I_1 parameter is sensitive to the solvent polarity,[13,15,18] while the I_5/I_1 parameter is not so sensitive within the range of dielectric constants tested.

Figure 5 shows examples of the fluorescence spectra

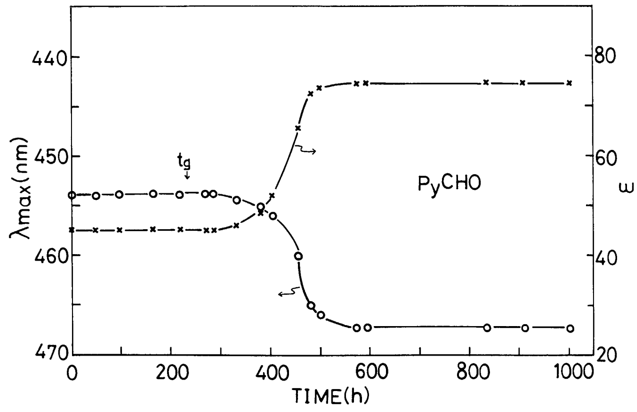

Fig. 3. Changes in fluorescence λ_{max} of pyrene-3-carboxaldehyde and dielectric constant estimated during the sol-gel process with time.

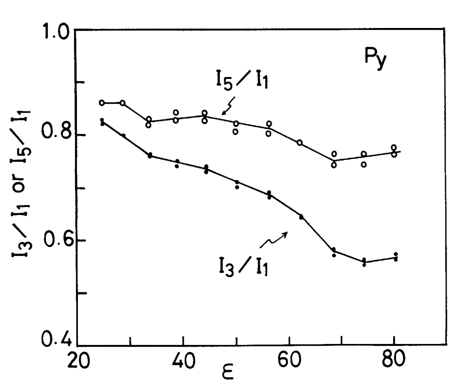

Fig. 4. Variation of I_3/I_1 for pyrene as a function of dielectric constant of ethanol-water mixtures.

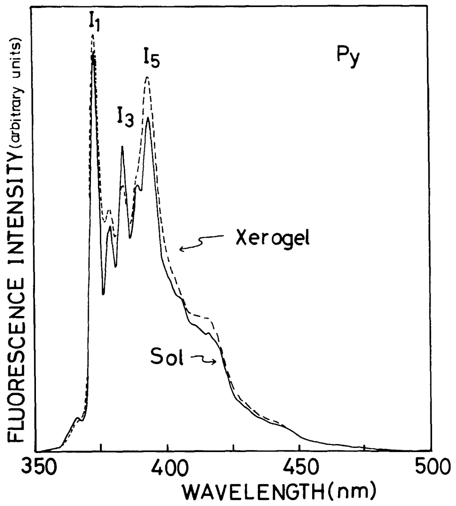

Fig. 5. Typical fluorescence spectra of pyrene during the sol-gel process: TEOS : H_2O : ethanol=1 : 6.2 : 3.8 (molar ratio) at pH=3.3.

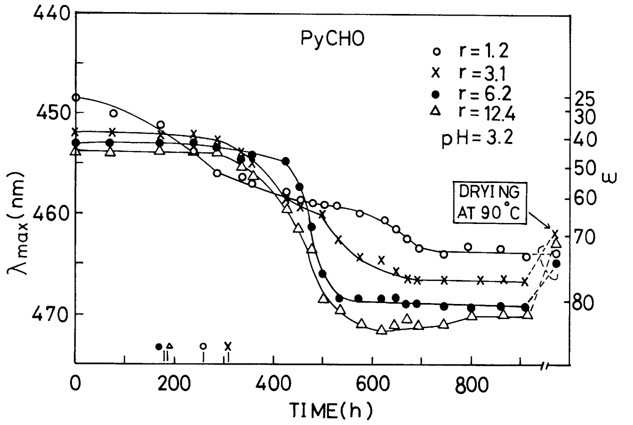

Fig. 6. Changes in fluorescence λ_{max} of pyrene-3-carboxaldehyde during the sol-gel process with time in various molar ratio of water/TEOS (r) at ethanol/TEOS=3.8 and pH=3.2. Each gelation point is indicated on the abscissa.

of Py as measured in the starting solution and the xerogel. It is clear that the relative intensities of the vibronic bands change from the solution to the xerogel, indicating a change in polarity during the desiccation.

Figure 6 shows the effect of the water-to-silane ratio (r) on the fluorescence shift of PyCHO at a constant pH value of 3.2. λ_{max} changes gradually at lower r values, such as 1.2 and 3.1, whereas λ_{max} changes steeply at around 400 h at higher r values, such as 6.2 and 12.4. The dielectric constants of the solutions are 27, 39, 42, and 45 for r=1.2, 3.1, 6.2, and 12.4 respectively. The dielectric constant does not change much during the polymerization or at the gelation point, which is shown on the abscissa. The dielectric constant does, however, increase with time after about 400 h, resulting in values of 72, 75, 84, and 87 for r=1.2, 3.1, 6.2, and 12.4 respectively, for xerogels (after ca. 900 h). The dielectric constants for both the solutions and the xerogels are in order of r: water contents. When the xerogels were heated for 10 h under a vacuum (10^{-3} Pa) at 90 °C, however, the dielectric constant showed almost the same value (around 72) (Table 1).

Figure 7 shows the effect of the r on the I_3/I_1 value of Py at a constant pH value of 3.2. The behavior of I_3/I_1 with time in relation to Py is similar to that of λ_{max} in relation to PyCHO. The dielectric constants of the solutions are 30, 34, 36, and 43 for r=1.2, 3.1, 6.2, and 12.4 respectively. These values are similar to those obtained from the PyCHO probe. However, the dielectric constants of the xerogels (after ca. 900 h) are slightly smaller than those obtained from PyCHO: ε=65, 66, 67, and 71 for r=1.2, 3.1, 6.2, and 12.4 respectively. When the xerogels were heated for 10 h under a vacuum at 90 °C, the dielectric constants were increased in this case except for r=12.4: ε=73, 75, and 73 for r=1.2, 3.1, and 6.2 respectively. (For r=12.4, an unknown reaction might occur. The spectrum after drying indicated a strange intensity alteration in the

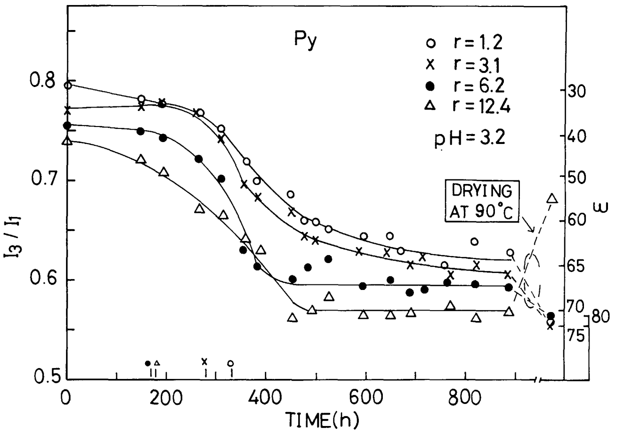

Fig. 7. Changes in I_3/I_1 for pyrene during the sol-gel process with time in various molar ratio of water/TEOS at ethanol/TEOS=3.8 and pH=3.2. Each gelation point is indicated on the abscissa.

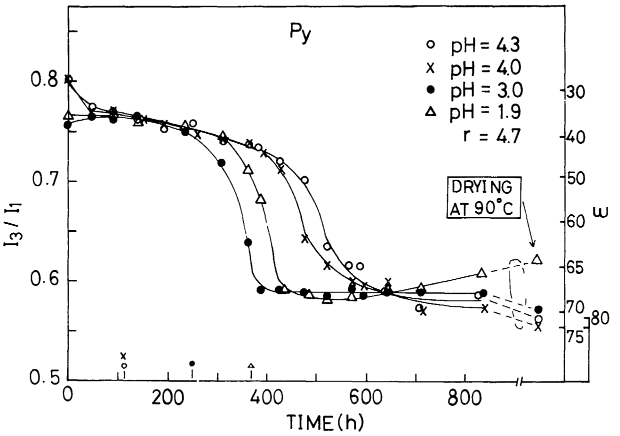

Fig. 9. Changes in I_3/I_1 for pyrene during the sol-gel process with time in various pH at molar ratio of water/TEOS (r)=4.7 and ethanol/TEOS=3.8. Each gelation point is indicated on the abscissa.

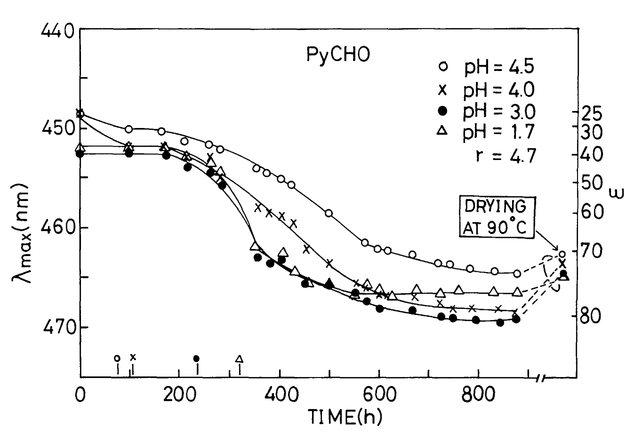

Fig. 8. Changes in fluorescence λ_{max} of pyrene-3-carboxaldehyde during the sol-gel process with time in various pH at molar ratio of water/TEOS (r)=4.7 and ethanol/TEOS=3.8. Each gelation point is indicated on the abscissa.

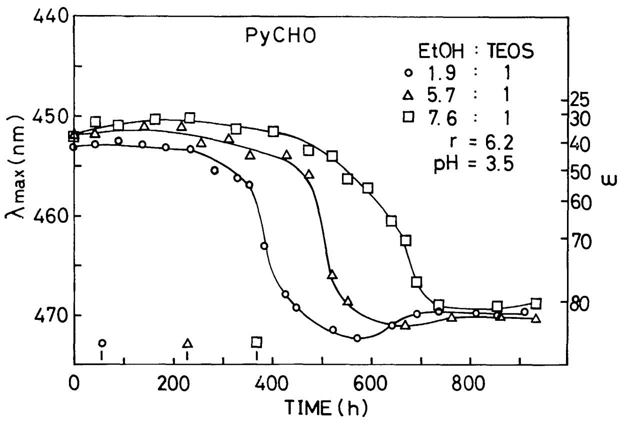

Fig. 10. Changes in fluorescence λ_{max} of pyrene-3-carboxaldehyde during the sol-gel process with time in various molar ratio of ethanol/TEOS at water/TEOS (r)=6.2 and pH=3.5. Each gelation point is indicated on the abscissa.

vibrational structures. Therefore, the result is rather exceptional and is not considered here.) The dielectric constants obtained for Py after drying are almost the same as those for PyCHO after drying (Table 2).

Figure 8 shows the effect of the pH on the λ_{max} value in PyCHO at r=4.7. A spectral shift similar to Fig. 6 was observed. The dielectric constants in the solutions were 27, 27, 40, and 39 for pH=4.5, 4.0, 3.0, and 1.7 respectively. The xerogels showed dielectric constants similar to those in Fig. 6: ε=72, 81, 81, and 74 for pH=4.5, 4.0, 3.0, and 1.7. When the xerogels were dried as has been described previously, those values decreased to be the same as those around 72 (Table 1).

Figure 9 also shows the effect of the pH on the I_3/I_1 ratio in Py at r=4.7. The dielectric constants in the solutions are 28, 28, 36, and 34 for pH=4.3, 4.0, 3.0, and 1.9, very close to those obtained for PyCHO. The dielectric constants of the xerogels are also slightly smaller for Py than for PyCHO: ε=68, 71, 69, and 66 for pH=4.3, 4.0, 3.0, and 1.9. After drying in a vacuum, those for Py increased to values around 72 similar to those for PyCHO after drying (Table 2).

Figure 10 shows the effect of the ethanol-to-TEOS ratio on the λ_{max} value of PyCHO at a constant r value of 6.2 and at pH 3.5. It is clearly seen that the transition time in the dielectric constant increases with an increase in the ethanol content, indicating that the evaporation of ethanol determines the transition in the dielectric constant.

Discussion

The results of the fluorescence probes of Py and PyCHO have shown that these probes well reveal the changes in the environment trapping of the molecules. We will consider three issues—the factors affecting the polarity of the solutions, the reason for the spectral changes, and the local structure of the trapping sites of the probe molecules.

1. Polarity of the Solutions. The dielectric constants of the solutions are in the order of the water contents (Tables 1 and 2). These results reasonably suggest that the polarity of a medium is determined by the polar water content. Naturally, water is consumed by hydrolysis. The present results thus indicate that the residual water content increases with initial water content. These results are consistent with those of a previous report.[10)]

The effect of the pH brings about the difference in the dielectric constant at a constant water content: the dielectric constant increases as the pH decreases. From the above discussion, it appears that the decrease in water content is larger at higher pH values. However, these results are in conflict with those of the previous report:[10)] that is, there is a slower decrease in the water content at higher pH values. This discrepancy can probably be explained by the reasonable assumption that the probe molecules are not homogeneously distributed in the solutions, but are on a time-average located near the surface of the aggregate or entangled in the aggregate of the silica polymers.[22–24)] Since hydrolysis slows down as the pH increases,[23,25)] the nature of the aggregate becomes rather hydrophobic at higher pH values because of an abundance of residual $\equiv$Si–OC$_2$H$_5$, while it becomes rather hydrophilic at lower pH values because of an abundance of $\equiv$Si–OH. Actually, it has been reported that a high concentration of $\equiv$Si–OC$_2$H$_5$ groups remains unreacted,[26,27)] comparable to that of $\equiv$Si–OH in some cases.[28)] Therefore, the access of the water molecules to the probe molecules surrounded by the aggregate is easier for the lower pH values than for the higher pH values. As a consequence, the local polarity around the probe molecules differs from the overall polarity of the solutions.

2. Mechanism of the Spectral Changes. The fluorescence shift of PyCHO and the change in the I_3/I_1 ratio of Py can be well explained by the increase in the polarity of the silica matrix, because those changes occur simultaneously in Py and PyCHO under the same preparation conditions and because the two estimated dielectric constants are very similar. Thus, the possibility of a specific interaction between the probe molecules and the silica surface can be discarded. Why, then, does the polarity change? This problem is elucidated by the evaporation of the ethanol molecules.[7)] Figure 10 provides proof. The transition time in the dielectric constant depends on the ethanol content. The evaporation of the less polar ethanol molecules effectively increases the polarity of the silica cage.

The change in water content does not much influence the transition time (Figs. 6 and 7); however, the effect of the pH on the transition time (Figs. 8 and 9) is significant under the present preparation conditions. In the sol–gel reaction, water is consumed and ethanol is released by:

$$H_2O + Si(OC_2H_5)_4 \longrightarrow \equiv Si\text{–}OH + C_2H_5OH,$$

while water is released by:

$$2\equiv Si\text{–}OH \longrightarrow \equiv Si\text{–}O\text{–}Si\equiv + H_2O.$$

Therefore, the overall reactions determine the solvent composition and, accordingly, the transition time in the dielectric constant. Furthermore, the polarity of the silica cage (perhaps mainly $\equiv$Si–OH) cannot be neglected, as will be described later. The situation is, however, very complicated when various preparation conditions are into account. We cannot explain the full picture at present.

It is noteworthy that no distinctive correlation between the gelation time and the transition time in the dielectric constant is seen. The macroscopic gelation time is not directly related to the microscopic gel structure probed by Py and PyCHO.[9)]

3. Structure of the Silica-Cage Trapping of Molecules. In the starting solutions, the dielectric constants in PyCHO are almost the same as those in Py. This finding indicates that PyCHO and Py are located on a time-average around the same environment of the solutions. Previous investigations in micellar systems have suggested that PyCHO resides near the outer surface of the hydrophilic shell and that Py resides near the inner surface of the hydrophilic shell.[29,21)] As has been discussed above, the aggregate of the silica polymers has a rather hydrophobic portion because of residual $\equiv$Si–OC$_2$H$_5$ groups as well as a rather hydrophilic portion because of $\equiv$Si–OH. However, the aggregate of the silica polymers in the solutions does not have such a micellar structure with a hydrophobic core and a hydrophilic shell so as to enable us to differentiate the location of Py from that of PyCHO.

In the xerogels, the dielectric constants in Py are slightly smaller than those in PyCHO, and both of the dielectric constants increase as the water content increases. It should be noted here that the difference in the dielectric constants with the r values is larger for PyCHO than for Py. However, after drying in a vacuum, those in Py increase and those in PyCHO decrease, resulting in the same dielectric constant (around 72), independent of the water content. The dielectric constants after drying in a vacuum are also independent of the pH.

The above results can be explained as follows. By analogy with the results of previous investigations,[22,30)] it may be considered that Py and PyCHO molecules become entangled and finally trapped within growing clusters as the cluster–cluster aggregation reaction proceeds. The silica-gel network also encapsulates ethanol and water molecules. During the desiccation, however, these solvents evaporate. However, this evaporation does not occur homogeneously. PyCHO is rather more hydrophilic than Py because of a hydrophilic group.[19)] Therefore, the residual solvents around PyCHO become rather rich in water molecules or, in other words, PyCHO itself adsorbes water molecules, while those around Py become rather rich in ethanol molecules. Consequently, the dielectric constants of the xerogels are larger for PyCHO than for Py, and the variation in the dielectric constant with r is larger for PyCHO than for Py.

After drying in a vacuum, the relatively polar solvents around PyCHO (mainly water) evaporate, reducing the polarity of the silica cage, while the relatively less polar solvents around Py (mainly ethanol) evaporate, increasing the polarity of the silica cage. The intrinsic polarity of the silica cage appears after these solvents have been desorbed.

It is important that the intrinsic dielectric constant ($\varepsilon=72$) is not dependent on r at pH=3.2. This is probably because the ambient moisture promotes the sol–gel reaction even if the r value is less than the stoichiometry of hydrolysis, and probably also because the excess water molecules are not directly involved in the sol–gel reaction; the excess water molecules exist as adsorbed water, not as silanol groups remaining after drying in a vacuum and increasing the polarity of the silica cage.

The value of $\varepsilon=72$ is rather larger than expected.[4,31)] The value of Kozower's Z, as estimated from the relationship previously reported,[19)] is 92, also larger than the value of 88 obtained for the conventional silica gel.[31)] The relatively polar property of the silica cage prepared by the sol–gel process is ascribed to an abundance of silanol groups. Generally, a conventional silica gel is treated at a considerably higher temperature, causing dehydroxylation. Therefore, the conventional silica gel is less polar than the silica gel prepared by the sol–gel process.

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