Aggregation of 1,12-bis(1-pyrenyl)dodecane in sol–gel systems

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Abstract

Silica sol–gel systems were doped with a low concentration of 1,12-bis(1-pyrenyl)dodecane at two pH values. Fluorescence spectra of deaerated samples were measured at regular intervals, far beyond the gel point. At least two intramolecular pyrene dimers and two excimer-like bands (E1 and E2) were observed for pH 1.2. In contrast, at pH 2.5, only one pyrene dimer and the sandwich excimer E2 were detected. Decay curves of degassed aged gels showed that none of the excimers has a rise time at pH 1.2, but a rise-time around 8 ns was observed at pH 2.5. These results were interpreted in terms of the encapsulation of the probe in primary silica particles, whose structure and size are pH dependent. © 1997 Elsevier Science B.V.

1. Introduction

Incorporation of fluorescent probes in sol–gel systems has been useful, over the last ten years, in following the structural evolution of these systems with time [1–5]. In particular, excimer-forming probes, such as pyrene, gave relevant information based on the mode of encapsulation of the probe in the medium [6–9]. In order to avoid the high pyrene concentrations necessary to form intermolecular excimers, we have doped sol–gel systems, with chains labeled at both ends with pyrene, which have the capability of forming intramolecular excimers [10,11].

In this work, silica systems using tetraethylorthosilicate (TEOS) as a precursor were doped with 1,12-bis(1-pyrenyl)dodecane, in order to clarify the influence of the host medium on the nature and conformation of intramolecular pyrene aggregates. Additional care was taken in deaerating the recently prepared solutions, in order to avoid oxygen quenching of the fluorescent species. At pH 1.2, where silica primary particles are small, steady state fluorescence spectra showed the aggregation of pyrene forming two or more intramolecular ground-state dimers and two excimers that are directly populated (with no detectable rise-time in the decay curves). This is indicative of medium restrictions to chain flexibility. In the absence of relevant spatial constrictions, i.e. at pH 2.5, only one dimer and one excimer (with a rise-time of about 8 ns) were observed. This indicates that the excimers are mainly formed by a dynamic process.

2. Experimental

The probe 1,12-bis(1-pyrenyl)dodecane, Py-(CH2)12-Py, was supplied by Prof. Richard Weiss, of Georgetown University.

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A solution of the probe in ethanol (spectroscopic grade, from Merck) was prepared in advance, with concentration of $1.02 \times 10^{-6}$ M.

Two homogeneous starting solutions were prepared with TEOS (99%, from Alfa Products), water (deionized) and probe solution, so that the molar ratios in the final solutions were $1$(TEOS):$4$(H$_2$O):$1$ (C$_2$H$_5$OH) and the probe concentration was $1.9 \times 10^{-7}$ M. The solutions differ in the hydrogen ion concentration, [H$^+$], that was set by adding calculated volumes of HCl p.a. from Merck, in order to obtain pH $= -\log [H^+]$ values of 1.2 and 2.5. The starting solutions were deaerated by several freeze–pump–thaw cycles in a Pyrex cell, transferred to a communicating silica cell under vacuum, sealed and kept at room temperature (22 ± 1°C).

Visual observation indicated that the gel point occurred about 16 and 13 days after preparation, for pH 1.2 and for pH 2.5 respectively. This is only an approximate indication, as the process is not accompanied by solvent evaporation or volume change.

The gelation process was monitored by steady state fluorescence spectra, recorded twice a day for each sample, for a period of 5 months. Measurements were performed at room temperature, in a Spex Fluorolog 112 spectrofluorimeter.

Decay curves were obtained by the single-photon timing technique, with a picosecond laser excitation. The system consists of a mode-locked Coherent Innova 440-10 argon ion laser that synchronously pumped a cavity dumped Coherent 701-2 DCM dye laser, delivering 5–6 ps pulses at a repetition rate of 460 kHz. The fluorescence was recovered using a polarizer at the magic angle and the scattered light was eliminated by a cut-off filter. Detection was done by passing the emission fluorescence through a depolarizer and then through a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm. The fluorescence was detected by a Hamamatsu 2809U-01 microchannel plate photomultiplier: the instrument response function had an effective FWHM of 35 ps.

Decay data analysis was performed with the Globals Unlimited software package (Laboratory for Fluorescence Dynamics, University of Illinois, Urbana, IL). The excitation wavelength used to obtain the decay curves was 330 nm.

### 3. Results and discussion

Fluorescence spectra of the deaerated silica system at pH 1.2, obtained at different times, are shown

![Fig. 1. Fluorescence spectra of the 1,12-bis(1-pyrenyl) dodecane incorporated in a pH 1.2 sol–gel system, normalized to 1.0 at 377 nm. (A) Excitation wavelength 345 nm; (B) excitation wavelength 360 nm. (--) preparation day; (——) 8 days after preparation; (•••) 14 days after preparation; (•••) 19 days after preparation.](image-url)
in Fig. 1A and B, for excitation at 345 and 360 nm, respectively.

When exciting at 345 nm, where the molar absorption coefficient of pyrene monomer is high, the well resolved spectrum of the pyrene monomer (with peaks at 377, 397 and 419 nm) is modified by the emission of some ground-state pyrene aggregates. They are visible through a vibronic band appearing at around 380 nm and the broadening of the band at 397 nm. The aggregates start forming straight away and their relative amount increases with time. Another important feature of these spectra is the broad band centered at 475 nm, associated with a sandwich pyrene excimer emission, with a shoulder at around 420 nm which grows with time.

Exciting at 360 nm (where the molar absorption coefficient of pyrene monomers is low), the spectra in the wavelength region of 370–420 nm show a much more pronounced emission from ground-state aggregates (compare intensity scales in Fig. 1A and B). Close to the gel point, which occurs at around 16 days after preparation, the spectra in Fig. 1B show a large increase in the relative intensity of the excimer band at 475 nm, as another excimer-like band shifted to the blue clearly grows. This indicates that ground-state aggregates, once excited, decay to more stable excimer-like states with maxima around 475 nm ($E_2$) and 420 nm ($E_1$).

These excimer-like emissions were already observed in Langmuir–Blodgett (LB) films and silica glasses, doped with high concentrations of pyrene, by time resolved spectra. In LB films, it was shown that the pyrene excimer $E_1$ rapidly (in less than 10 ns after excitation) converts into the more stable one, $E_2$ [12,13]. Both excimers have a rise-time of about 200 ps, which is similar to the fast decay component of the dimer. In silica glasses, however, it was observed that the rise-time of $E_1$ is negligible, while the rise-time of $E_2$ is approximately 300 ps. This was interpreted assuming that $E_1$ originates from pyrene pairs in close contact, while $E_2$ are formed by deexcitation of the dimers [14].

Steady-state fluorescence spectra for the sample at pH 2.5 are shown in Fig. 2A and B.

Upon excitation at 345 nm, the presence of ground-state pyrene aggregates emission is not evident, in contrast to pH 1.2, but a similar excimer band centered at 475 nm is observed. There are no significant changes with time, as gel formation proceeds. However, by excitation at 360 nm (Fig. 2B), the spectra show a large peak at 403 nm, superimposed on the monomer emission at 397 nm, without

Fig. 2. Fluorescence spectra of the 1,12-bis(1-pyrenyl) dodecane incorporated in a pH 2.5 sol–gel system normalized to 1.0 at 377 nm. (A) Excitation wavelength 345 nm; (B) excitation wavelength 360 nm. (---) preparation day; (- - - - -) 8 days after preparation; (· · ·) 14 days after preparation; (· · · · ·) 19 days after preparation.
the band at 383 nm observed for pH 1.2 (see Fig. 1B). This peak broadens with the progress of the sol–gel reaction, suggesting that there can be a small proportion of other aggregates emitting in the same region. This seems to indicate that, at pH 2.5, the ground-state aggregates are mainly composed of one dimer, while at pH 1.2 at least two dimers are formed. The excimer to monomer intensity ratio varies slightly when compared to Fig. 1B, which shows that the dimer-excimer interconversion is not as efficient as at pH 1.2.

The decay curves obtained for the gel aged about 5 months, at several wavelengths, are complex, as the result of several species in the ground and excited states, but are also informative. Fig. 3 shows the decay curves obtained at 520 nm and 377 nm for the gel prepared at pH 2.5.

The excimer decay curve of $E_2$ ($\lambda = 520$ nm) has a rise-time of 8.9 ns and two decay components of 32.6 and 54 ns. This rise-time is attributed to excimers formed in a dynamic process from chains not cyclized in the ground state. The sum of the pre-exponential factors in the excimer decay deviates from zero, which indicates that, even for excitation at 330 nm, some excimers are populated from excited dimers that quickly decay to the excimer. The monomer decay at 377 nm shows a component of 7.7 ns, which corresponds to the rise-time component in the excimer and three more components of 262, 0.39 and 33 ns. The longest component is attributed to isolated pyrene monomers that decay with the intrinsic lifetime. The presence of common components around 8 ns and 33 ns in the excimer and monomer decay curves is characteristic of an equilibrium between the two excited states. The remaining short component in the monomer decay (not detected in the excimer fit) probably reflects the cyclization of chains with ends in close proximity. The excimer component of 54 ns, not found in the monomer decay, is due to the excimers that once excited from the dimers, remain isolated and decay with their intrinsic lifetime. The decay curves at other emission wavelengths have similar decay times, with the component of 262 ns in the monomer emission region, the 54 ns component in the excimer region or both when the monomer and the excimer spectra overlap.

Fig. 4 shows the decay curves recovered at $\lambda = 520$ nm and 377 nm by excitation at 330 nm, for the gel prepared at pH 1.2.

The decay curve of $E_2$ grows as fast as the instrumental response function and decays as a sum of three exponentials with decay times of 3.6, 28 and

\[ \frac{1}{T} = \frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_3} \]

\[ \lambda_1 = 520 \text{ nm} \]

\[ \lambda_2 = 377 \text{ nm} \]

Fig. 3. Fluorescence decay curves, of 1,12-bis(1-pyrenyl) dodecane incorporated in a pH 2.5 gel, aged for 5 months. Excimer decay curve recovered at 520 nm: $a_1 = -1.47$, $\lambda_1 = 8.9$ ns; $a_2 = 1.17$, $\lambda_2 = 54$ ns; $a_3 = 0.48$, $\lambda_3 = 33$ ns ($\chi^2 = 1.1$). Monomer decay curve recovered at 377 nm: $a_1 = 1.21$, $\lambda_1 = 0.39$ ns; $a_2 = 0.69$, $\lambda_2 = 7.7$ ns; $a_3 = 0.06$, $\lambda_3 = 33$ ns; $a_4 = 0.04$, $\lambda_4 = 262$ ns ($\chi^2 = 1.4$).
51 ns. The fit was done by fixing the component of 51 ns that was recovered using a longer time range. This component is attributed, as at pH 2.5, to excimers $E_2$ formed irreversibly from excited dimers. Nevertheless, the other components cannot be interpreted in a similar way as at pH 2.5, owing to a non-detectable rise-time. They should rather reflect the two excimer-like emissions of $E_1$ and $E_2$, which interconvert in the range of some ns. Both excimers must be populated from excited dimers, with different configurations, less than 10 ps after excitation (the time-resolution of the single-photon timing equipment). Indeed, the decay curves recovered between 420 and 450 nm do not show detectable rise-times, in contrast to the results found in LB films and silica glasses. The monomer decay curve at 377 nm can not be satisfactorily fitted even with a sum of four exponentials, reflecting the overlap of pyrene monomer and a distribution of aggregate emissions. Nevertheless, the long component of 279 ns should correspond, as with pH 2.5, to the decay of some isolated pyrenes.

The whole set of results indicates that the pH of the initial recipe is determinant in the types of intramolecular pyrene aggregates formed in 1,12-bis(1-pyrenyl)dodecane as the sol–gel reaction proceeds and the gel ages. At pH 1.2, at least two ground-state intramolecular pyrene aggregates are formed. During the first days of reaction and in the absence of oxygen and solvent evaporation, there is evidence of one excimer-like species, emitting strongly at 475 nm ($E_2$). Just before the gel point and while the gel ages (more Si–O–Si bonds are formed inside the silica particles), there is evidence of an equilibrium between $E_1$ and $E_2$ excimer-like states, populated directly from different excited dimers. Moreover, no excimers are formed via a dynamic route, by cyclization of the chains. This is consistent with the probes being constrained by the medium, in small silica particles. At pH 2.5, there is indication of one ground-state dimer. For the aged gel, in contrast to pH 1.2, evidence has been obtained that the excimer $E_2$ is formed by a dynamic process, indicating that even at this stage there are a significant number of probes which have available free volume to cyclize. For both pH values there are probes that remain uncyclized during the monomer lifetime and are responsible for the emission of free monomers. In both cases there are also excimers $E_2$, probably adsorbed at the surface of the silica particles, which do not interconvert to other excited species.

![Fluorescence decay curves](image)

**Fig. 4.** Fluorescence decay curves, for excitation at 330 nm, of 1,12-bis(1-pyrenyl)dodecane incorporated in a pH 1.2 gel, aged for 5 months. Excimer decay curve recovered at 520 nm: $a_1 = 8.98$, $\lambda_1 = 3.6$ ns; $a_2 = 0.47$, $\lambda_2 = 28$ ns; $a_3 = 0.25$, $\lambda_3 = 51$ ns ($\chi^2 = 1.2$). Monomer decay curve recovered at 377 nm: $a_1 = 0.87$, $\lambda_1 = 3.7$ ns; $a_2 = 0.04$, $\lambda_2 = 26.2$ ns; $a_3 = 0.13$, $\lambda_3 = 37$ ns; $a_4 = 0.05$, $\lambda_4 = 279$ ns ($\chi^2 = 7.1$).
Since the main difference between the two media is the silica particles size, (of the order of ~1 nm for pH 1.2 and ~10 nm for pH 2.5 [15]), we propose that the large majority of ground-state aggregates are essentially formed inside the silica primary particles. This interpretation is not contradictory to the recent observation [16] that in gel systems formed using tetramethylorthosilicate (TMOS) as a precursor, the smaller 1,3-bis(1-pyrenyl)propane probe does not form aggregates. Indeed, the primary particles formed in this case are much larger than the ones formed in the present work, in comparison to the probe dimensions, not imposing special constraints to its aggregation.

4. Conclusion

The fluorescence spectra of 1,12-bis(1-pyrenyl)dodecane incorporated in sol–gel systems give relevant information about the time evolution of the matrix. The probe is sensitive to the formation of silica primary particles, whose diameter is strongly dependent on the initial pH. Although complex, the decay curves of the probe in the aged gel display interesting photophysical behavior that was correlated with the characteristics of the medium. It is shown that the probe forms different kinds of intramolecular pyrene aggregates and two excimer-like emissions were observed at pH 1.2, where the constraints imposed by the smaller silica particles are significant.

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