Articles

On the Microenvironments Surrounding Dansyl Sequestered within Class I and II Xerogels

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We report on the static and time-resolved fluorescence spectroscopy of dansyl sequestered within two xerogels that were formed from tetraethylorthosilane (TEOS) mixed with ppm levels of dansylamide or dansyltriethoxysilane. These are referred to as class I and II xerogels, respectively. Experiments were performed on these samples as they progressed from liquids to xerogels over a period of 1 year. The results show that the average local microenvironment surrounding the dansyl dopant is different in the class I and II xerogels. Specifically, even though the dipolarity surrounding the dansyl dopant increases as both samples progress from liquids to xerogels, the local dansyl microenvironment within a class II xerogel is always more heterogeneous in comparison to the class I xerogel. In an aged xerogel, the local dipolarity surrounding the dansyl dopant is greater for the class I xerogel than for the class II xerogel. These results are discussed in terms of a model that has the dansyl locating preferentially within Si−OH- and SiO_2-rich regions for the class I and II xerogels, respectively.

Introduction

Sol−gel processing is a facile means to produce a variety of novel materials with many uses.[1−9] For example, sol−gel processing has been used to make lasing materials,[10,11] luminescent solar concentrators,[12] nonlinear optical components,[13] and affinity and chromatographic columns.[14−16] Sol−gel-derived materials have also been used as platforms for chemical sensors and biosensors.[17−28] Organically modified silicates (ORMOSILs)[22−29] provide another avenue for preparing novel sol−gel-derived materials that have a variety of unique catalytic, electrochemical, or optical properties.[23,30]

Sol−gel-processed materials that are based in whole or in part on ORMOSILs can be divided into two

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classes.[26] Class I xerogels are formed when dopants (e.g., chromophores, redox active species, oligomers, surfactants, or polymers) are randomly dispersed within the inorganic host matrix during the xerogel formation process. These dopants can then interact with the inorganic network by van der Waals forces, hydrophobic−hydrophilic interactions, hydrogen bonds, and/or ionic bonds.[26] In class II xerogels, the dopant is linked directly to the inorganic network by a hydrolytically stable bond (e.g., Si−C). Dopants within class II xerogels can also interact with the network in ways similar to those described for class I xerogels (vide supra).

To form class II silica xerogels, one generally incorporates the dopant (R′) by using an organoalkoxide of the form $R'_nSi(OR)_{4-n}$ as a comonomer in the presence of a $Si(OR)_4$ precursor. (Note: The "R" residues do not necessarily need to be identical in $R'_nSi(OR)_{4-n}$ and $Si(OR)_4$.) The $R'_nSi(OR)_{4-n}$ species can serve as network junctions ($n = 1$), bridges ($n = 2$), or end caps ($n = 3$). The nature of R′ and the molar ratio of $R'_nSi(OR)_{4-n}$ to $Si(OR)_4$ can also influence the xerogel properties.[31] Monofunctional organoalkoxysilane precursors ($n = 1$) where R′ is an alkyl,[32−36] vinyl,[37,38] or aryl[38,39] moiety have been reported and precursors with meth(acrylate), isocyanate, sulfhydryl, epoxide, and perfluorinated functionalities have been described.[26] There have also been reports on more sophisticated organoalkoxysilanes where R′ represents a calixarene, chromophore, crown ether, cryptand, cyclodextrin, luminophore, porphyrin, or nonlinear optical (NLO) dye.[26,28,40]

The covalent bond between R′ and Si in $R'_nSi(OR)_{4-n}$ imparts some interesting behavior in the class II xerogel relative to that of the class I xerogel. For example, some researchers have argued that the stability of the second harmonic signal from a class II xerogel doped with a NLO dye relative to that from a similarly prepared class I xerogel arises from the decreased NLO dye mobility within the class II xerogel.[28,41] In this context, Fox and co-workers[34] used steady-state fluorescence anisotropy measurements to estimate pyrene mobility within class I and II xerogels. These authors did *not* observe any significant difference in the pyrene steady-state fluorescence anisotropy between the class I and II xerogels. Their interpretation of this result was that the pyrene rotational mobility within class I and II xerogels is similar. Ueda and co-workers[42] investigated the cis to trans photoisomerization of an azobenzene derivative sequestered within class I and II xerogels. This particular photoisomerization reaction is mediated by the viscosity, polarity, porosity, hydration, and the void volume within the host network. The results of these experiments showed that there was no observable difference in the isomerization rate within class I and II xerogels.

In the context of chemical sensing, class II xerogels, where R′ is a chemically selective recognition element (RE), offer many potential advantages over class I xerogels in which the RE is randomly distributed within the xerogel. For example, in a class II xerogel, RE leaching is minimized,[28,43] RE loading densities are increased,[44] and the RE is reportedly incorporated into select or discrete microenvironments.[45] The latter claim is somewhat surprising because previous work[46] has shown that the local micoenvironment surrounding certain organic dopants that are sequestered within sol−gel-derived xerogels is heterogeneous.

In this paper, we aim to explore the issue of heterogeneity surrounding an organic dopant when it is sequestered within class I and II xerogels. Toward this end, we report on the steady-state fluorescence and time-resolved fluorescence intensity decay of ppm levels of dansylamide (class I) or dansyltriethoxysilane (class II, $n = 1$) dispersed within tetraethylorthosilane (TEOS) xerogels as a function of sample aging time. This particular system was chosen because the dansyl fluorescence spectra and its excited-state fluorescence intensity decay kinetics depend on the physicochemical properties of its immediate surroundings.[47] These features provide us with a convenient way to explore how the dansyl-siloxane covalent tether influences the local microenvironment surrounding the dansyl chromophore.

Theory

The excited-state intensity decay kinetics were recovered using multifrequency phase-modulation fluorescence.[48]

The time-resolved fluorescence intensity decay, $I(t)$, is generally given by

$$I(t) = \sum_{i=1}^{m} \alpha_i \exp(-t/\tau_i) \qquad (1)$$

In this expression α_i represents the pre-exponential factor that is associated with the ith emissive component with excited-state lifetime τ_i. Equation 1 is adequate for

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a system in which the number of emissive components is small (less than ≈4) or the photophysics are predictable.

In situations when one or more fluorophores are distributed among or converting between a multitude of micorenvironments, eq 1 is inadequate for describing the true $I(t)$. In this case the observed time-resolved intensity decay is better described by an ensemble of decay times to reflect the multitude of microdomains.[46a,49] Under these circumstances, one can often model the intensity decay kinetics by a continuous unimodal distribution of the form

$$I(t) = \sum_{\tau=0}^{\infty} \alpha(\tau) e^{-t/\tau}\, d\tau \qquad (2)$$

where simple functions can be used to describe the underlying lifetime distribution ($\alpha(\tau)$):[49d−h]

Uniform

$$\alpha(\tau) = 1;\ \langle\tau\rangle - W/2 \leftrightarrow \langle\tau\rangle + W/2$$
$$\alpha(\tau) = 0;\ \text{elsewhere} \qquad (3)$$

Gaussian

$$\alpha(\tau) = \frac{\exp[-(\tau - \langle\tau\rangle)^2/2\sigma^2]}{\sigma\sqrt{2}\pi} \qquad (4)$$

Lorentzian

$$\alpha(\tau) = \frac{1}{1 + [(\tau - \langle\tau\rangle)/(W/2)]^2} \qquad (5)$$

In eqs 3−5, $\langle\tau\rangle$ represents the center or mean excited-state fluorescence lifetime, σ is the standard deviation of the Gaussian distribution, W is the full-width at half-maximum (fwhm) for the Lorentzian and Uniform distributions, and τ is the lifetime. To determine if the experimental data are best described by a discrete (eq 1) or distributed (eq 2) model, we use a global analysis strategy[50] and a commercial software package from Globals Unlimited. We primarily base the fit quality on the reduced χ^2 and the residuals.[48−50]

Experimental Section

Reagents. The following chemicals were used as received: TEOS (United Chemical Technologies); *N*-(triethoxysilylpropyl)dansylamide (Dan-TriEOS, Gelest); dansylamide and Na_2HPO_4 (Sigma); cyclohexane and acetonitrile (Aldrich); HCl and $NaH_2PO_4{\cdot}2H_2O$ (Fisher); and 200 proof EtOH (Quantum Chemical). Aqueous solutions were prepared by using 18 MΩ distilled−deionized water. Dansyl stock solutions were kept refrigerated in the dark at 4 ± 2 °C.

Xerogel Monolith Preparation. Dansylamide and Dan-TriEOS stock solutions were prepared at 200 μM in EtOH. Xerogels were prepared by mixing TEOS, water, and HCl in the molar ratio 1:4.00:4.6 × 10^{-4}. The TEOS, H_2O, and HCl were simultaneously combined under ambient conditions with vigorous stirring to ensure a visually homogeneous solution. After prehydrolyzing for 5 h, the TEOS/H_2O/HCl solution was used to prepare xerogels. Monoliths were formed within clean, 1.0-cm^2 disposable polystyrene cuvettes (Fisher).

Class I and II xerogels were prepared by adding 150 μL of either the dansylamide (class I) or Dan-TriEOS (class II) stock solutions to 3.000 mL of the prehydrolyzed TEOS/H_2O/HCl solution. Blanks were prepared by omitting the dansyl chromophore. These solutions were then vigorously mixed for 1−2 min with a touch mixer (Fisher Scientific Model 231). We then added 160 μL of 0.1 M phosphate buffer (pH 6.9) to each cuvette to initiate the gelation process. Each cuvette was then sealed with a cap, mixed for 10−15 s with the touch mixer, and maintained in the dark at room temperature (24 ± 2 °C). After aging for 300 h, all samples and blanks were completely unsealed and they continued to age in the dark at room temperature. The relative humidity during aging was 15−25%.

There was no evidence of significant fluorophore leaching from fully aged class I or II xerogels, even after we soaked the monoliths in EtOH for several hours.

All xerogels and blanks were prepared in triplicate. Results are reported as the average for measurements on each sample. Error bars denote one standard deviation.

Fluorescence Measurements. The instrumentation used to perform the steady-state and time-resolved fluorescence experiments has been described in detail elsewhere.[51] For the steady-state experiments, the excitation wavelength was adjusted to 351 nm and the excitation and emission spectral band-passes were set to 4 nm. All spectra were background corrected by using appropriate blanks. The blank contribution to the total integrated fluorescence was always less than 1%. Time-resolved fluorescence intensity decay data were acquired by exciting at 351.1 nm with an argon-ion laser. The emission was monitored in the typical L-format through a 455-nm long-pass filter and magic angle polarization conditions.[52] The Pockels cell modulator was operated at a 5-MHz repetition rate. Data were acquired at 5-MHz intervals up to 105 MHz. We typically acquired 10−20 complete data sets/samples. Our reference lifetime standard was Me_2POPOP dissolved in EtOH; its lifetime was assigned a value of 1.45 ns.[53]

Results and Discussion

Initially, we investigated the static excitation and emission spectra and excited-state fluorescence intensity decay kinetics of dansylamide and Dan-TriEOS dissolved in liquid acetonitrile, cyclohexane, EtOH, and water. The results of these experiments (not shown) demonstrated that the spectra and time-resolved fluorescence intensity decay kinetics of dansylamide and Dan-TriEOS were statistically equivalent to one another. These results demonstrate that the covalent tether does not affect the dansyl residue behavior in solution.

Steady-State Fluorescence. Dansyl derivatives exhibit spectra that shift in a predictable manner depending on the dipolarity of the surrounding medium.[47] To explore this issue in more detail, we measured the dansyl residue excitation and emission spectra over the course of 1 year as our samples evolved from liquids to aged xerogels. Figure 1 summarizes the effects

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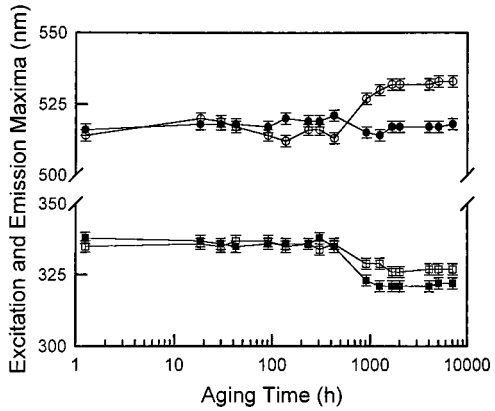

Figure 1. Effects of aging time on the dansyl steady-state excitation and emission maxima for class I (○,□) and II (●,■) xerogels.

Table 1. Recovered Average Global χ^2 Values[a] for Fits of the Dansyl Fluorescence Intensity Decay Data at All Aging Times to Various Decay Models

model	number of floating parameters	global χ^2 for class I xerogels	global χ^2 for class II xerogels
single (eq 1, $m = 1$)	1	312	429
double (eq 1, $m = 2$)	3	2.17	3.35
triple (eq 1, $m = 3$)	5	1.27	1.86
unimodal uniform (eq 3)	2	8.41	7.73
unimodal Gaussian (eq 4)	2	1.49	2.11
unimodal Lorentzian (eq 5)	2	1.16	1.07

[a] The reported χ^2 values are the average χ^2 values for the analysis of 48 independent phase-modulation traces (3 replicates of each xerogel at 16 discrete aging times).

of aging time on the steady-state dansyl excitation and emission maxima for the class I (open symbols) and class II (closed symbols) xerogels. The general trend is for the excitation maxima to remain constant up to ≈400 h and to then blue shift as the xerogels age up to 1−2000 h. After the xerogels age for 1−2000 h, the excitation spectra remain constant (up to our longest aging time of 8500 h, 354 days). The same trend is seen for the class II xerogel; however, the dansyl excitation spectra appear to blue shift more relative to the those of the class I xerogel. The dansyl emission spectra for the class I xerogel remain constant up to ≈400 h and then shifts to the red as the xerogel ages between ≈400 and 1−2000 h. As the xerogel age beyond 1−2000 h, the dansyl emission spectra remain constant. The dansyl emission spectra for the class II xerogel do not shift significantly as the xerogel ages. These results argue that there are differences in the local microenvironment surrounding the dansyl reporter group within the class I and II xerogels.[54] Specifically, the steady-state spectra suggest that the dansyl probe in an aged class I xerogel encounters, on average, a more dipolar and/or more dynamical environment relative to the dansyl residue within a class II xerogel.

Time-Resolved Fluorescence. Table 1 reports the average reduced global χ^2 for fits between several test models and the experimental phase-modulation data for the dansyl reporter group within class I and II xerogels across all aging times. Taken together with previous work on the behavior of fluorescent probes sequestered within xerogels,[46] these results argue that a continuous unimodal Lorentzian lifetime distribution describes the

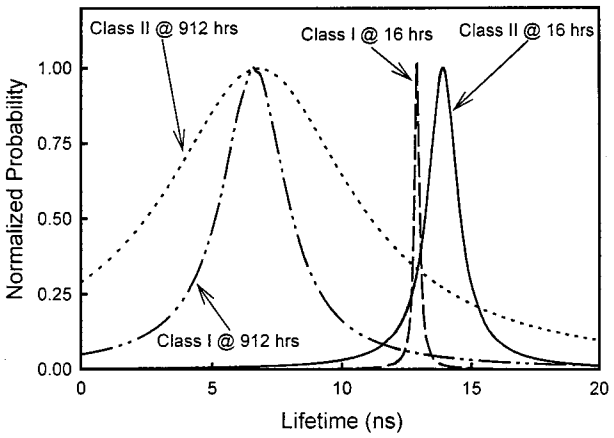

Figure 2. Recovered unimodal Lorentzian lifetime distributions for dansyl sequestered within in class I and II xerogels after they aged for 16 and 912 h.

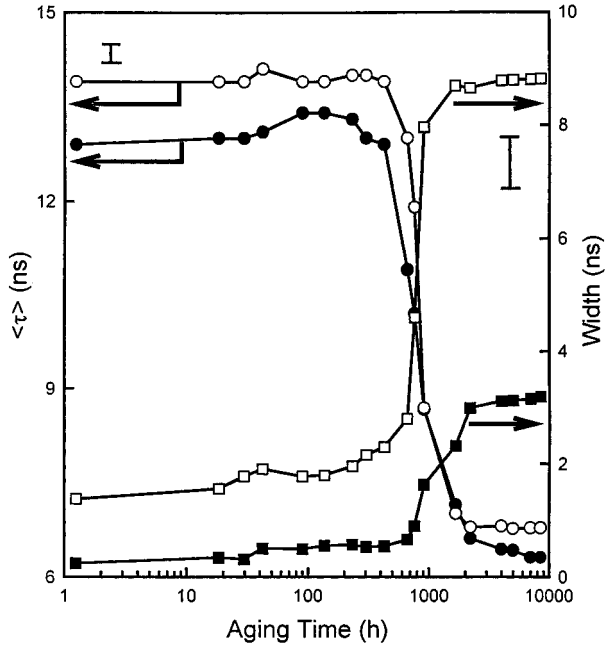

Figure 3. Effects of aging time on the dansyl fluorescence intensity decay kinetics. Center lifetime of class I (●) and II (○) xerogels. Distribution width for class I (■) and II (□) xerogels.

observed time-resolved fluorescence intensity decay of these dansyl-doped xerogels well.

Figure 2 presents typical excited-state fluorescence lifetime distributions for the class I and II xerogels that have aged for 16 and 912 h. Figure 3 summarizes the effects of aging time on the dansyl time-resolved fluorescence intensity decay kinetics within the class I and II xerogels. Several aspects of these data merit additional discussion. For example, after aging for only 16 h, the average microenvironment surrounding dansyl within the class I xerogel is *less* dipolar in comparison to dansyl sequestered within a class II xerogel (i.e., $\langle\tau\rangle_{\text{classI}} < \langle\tau\rangle_{\text{classII}}$), and the microenvironment surrounding the dansyl residue within the class II xerogel is *more* heterogeneous in comparison to that of dansyl within the class I xerogel ($W_{\text{classII}} > W_{\text{classI}}$). Given that the intensity decay kinetics for dansylamide and Dan-TriEOS dissolved in homogeneous liquids are equivalent, this result demonstrates that there are quantifiable differences in the local environment surrounding

the dansyl dopant within class I and II xerogels at the onset of xerogel formation.

As the xerogels age, the average local dipolarity surrounding the dansyl dopant increases ($\langle\tau\rangle$ decreases), and the heterogeneity increases (W and $W/\langle\tau\rangle$ increase). The increase in dipolarity is fully consistent with the literature[46,55,56] on xerogel evolution. The greatest change in the local microenvironment surrounding the dansyl dopant in either xerogel occurs after the samples have aged between ≈300 and 2000 h. After 2000 h, the microenvironment surrounding the dansyl within the xerogels changes more slowly. The average microenvironment that surrounds the dansyl dopant within an aged xerogel (>2000 h) is *less* dipolar in a class I xerogel relative to a class II xerogel. Finally, the microenvironment surrounding the dansyl dopant within a class II xerogel is significantly (∼3-fold) *more* heterogeneous in comparison to that of a class I xerogel that has aged for a similar time.

Model. For an aged xerogel, we interpret the static and time-resolved results in terms of the model presented in Figure 4. In a class I xerogel we envision the dansyl locating primarily near or at the pore interface such that the Si−OH groups dominate the local dansyl microenvironment relative to the SiO_2 that makes up the pore wall proper. Under these conditions, dansyl at or near the pore surface would encounter a more dipolar (Si−OH vs SiO_2) and more dynamic microenvironment relative to a dansyl sequestered within the pore wall SiO_2. In a class II xerogel, we suggest that the dansyl distributes preferentially into the SiO_2 region over the Si−OH region and the "SiO_2" microenvironment is more heterogeneous relative to the Si−OH microenvironment. One possible driving force for the dansyl residue redistribution within the class I and II xerogels may arise from the hydrophobicity of the tether within the class II xerogel relative to that within the class I xerogel.

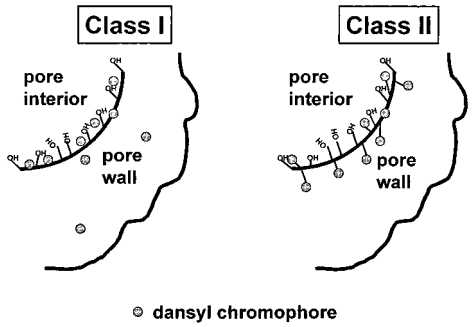

Figure 4. Model to describe the selective partitioning of dansyl within Si−OH- and SiO_2-rich regions of fully aged class I and II xerogels, respectively.

Conclusions

The local microenvironment surrounding an organic dopant within class I and II xerogels can be different. From the perspective of a dansyl fluorophore, the local microenvironment within a class II xerogel is always more heterogeneous in comparison to a class I xerogel, and the local dipolarity surrounding the dansyl dopant is greater for the class I xerogel than for the class II xerogel. These results may be a manifestation of the dansyl probe locating preferentially near the Si−OH-rich region (pore surface) within the class I xerogel and more within the SiO_2-rich pore wall for the class II xerogel. These results have ramifications in areas ranging from materials design to chemical sensor development based on sol−gel-derived xerogels.

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