Probes of Pore Environment and Molecule−Matrix Interactions in Sol−Gel Materials

Bruce Dunn*,† and Jeffrey I. Zink*,‡

Departments of Materials Science and Engineering and Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095

Received April 30, 1997. Revised Manuscript Received September 2, 1997⊗

The use of molecular probes to study the nature of the local environment around dopants in silicate sol−gel materials is reviewed. The review selectively focuses on probes of pore solvent composition and molecule−matrix interactions using electronic spectroscopy. The sol−gel environment is complex; to systematize the discussion, four regions are defined. The most commonly probed region is the free liquid region where the surroundings of a dopant molecule are similar to those of an equivalent solution. The molecular composition of the mixed solvent, its polarity, and its pH are discussed. The three regions that are most important in affecting the dopant via molecule−matrix interactions are the interfacial region within a few molecular diameters of the pore wall, the pore wall itself, and the constraining regions where the distances between opposite sides of the pores are about the same as the size of the probe molecule. The aspects of molecular mobility that are reviewed are probe molecule rotation, solvent molecule motion, intramolecular motion (conformational changes), and local intermolecular mobility. Finally, a probe of matrix pore shaping is discussed. In all of the examples that are reviewed, the subject is presented from the operational and experimental measurement point of view, i.e., in terms of specific measured properties. The measured quantities are interpreted on the basis of the location of the probe molecule in the various regions of the sol−gel material and as a function of the stage of processing of the material.

1. Introduction

The sol−gel process is a chemical synthesis technique for preparing oxide gels, glasses, and ceramics at far lower temperatures than is possible by conventional methods.[1−5] The approach is based on the hydrolysis and condensation of molecular precursors such as metal alkoxides, and by controlling the chemistry of the process, one can prepare oxide powders, thin films, fibers, and bulk materials at ambient temperatures. Ambient processing conditions also enable one to encapsulate numerous organic, organometallic, and biological molecules within these sol−gel derived inorganic matrixes. The resulting properties of the material are determined by the nature of the dopant molecule. This synthetic approach is well recognized as an important direction for the design and synthesis of a wide range of novel materials, especially in the areas of photonics and chemical sensors.[6−9]

The nature of the local environment around the dopant molecule is frequently a critical consideration in achieving the desired property. To design and optimize a material whose optical behavior is based on properties induced by molecules, it is necessary to understand the local environment of the active molecule. Many powerful methods have been used to study the state of the bulk sol−gel material (e.g., NMR, IR, and Raman spectroscopies), but these methods may not be able to provide detailed information about the local conditions around low-concentration dopants. Methods of monitoring the microenvironments on the molecular dimension scale that are sensitive to the low dopant concentrations used in these materials are needed. Electronic spectroscopy of specific probe molecules, especially emission spectroscopy, offers sensitive methods of reporting the local environment of the probe molecule.[10,11]

The purpose of this paper is to review the field of spectroscopic probes of sol−gel materials, specifically optical probes of the microenvironment of the molecule. The probe molecule is added during the sol stage in the same manner as the dopant molecules that induce a desired property for a specific application. In some cases, the desired dopant molecule may itself act as a probe. The use of luminescent molecules as optical probes of the sol−gel process has been reported for over 10 years, but it is only within the past few years that studies involving more than steady-state luminescence measurements have appeared. The result is that certain dynamic optical properties have been characterized which enhance our understanding of the nature of the interactions between the matrix and the probe molecule.

The emphasis of this paper is to review our present understanding of two aspects of molecule microenvironment: the chemistry of solvent-filled pores and the properties of molecule−matrix interactions. The former considers issues of solvent composition, polarity, and pH during the various stages of the sol−gel process. The second part of this review emphasizes how the sol−gel environment affects certain dynamic properties of optical probe molecules. The latter is of central importance to the development of the optical properties of dye-doped sol−gel materials because such processes as molecular rotations and conformation changes determine the nature of the optical behavior of the final solid-state material.

† Department of Materials Science and Engineering.
‡ Department of Chemistry and Biochemistry.
⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

S0897-4756(97)00270-6 CCC: $14.00

2. Preparation of Inorganic Glasses by the Sol−Gel Method

The synthesis of materials by the sol−gel process generally involves the use of metal alkoxides which undergo hydrolysis and condensation polymerization reactions to give gels and has been the subject of several books and reviews.[1−5] The sol−gel process can ordinarily be divided into the following steps: forming a solution, gelation, aging, drying, and densification. In the preparation of a silica glass, one starts with an appropriate alkoxide (e.g. $Si(OC_2H_5)_4$, tetraethyl orthosilicate or TEOS, or $Si(OCH_3)_4$, tetramethyl orthosilicate or TMOS) which is mixed with water and a mutual solvent, such as ethanol or methanol, to form a solution. Hydrolysis leads to the formation of silanol groups Si−OH. These species are only intermediates as they react further to form siloxane Si−O−Si groups. The overall reactions leading to the formation of a silica gel are

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad (1)$$

$$nSi(OH)_4 \rightarrow nSiO_2 + 2nH_2O \quad (2)$$

There are several parameters which influence the hydrolysis and condensation polymerization reactions, including the temperature, solution pH, particular alkoxide precursor and solvent, and relative concentrations of the alkoxide precursor, water, and solvent. Another consideration is that catalysts are frequently added to help control the rate and the extent of hydrolysis.

As the hydrolysis and condensation polymerization reactions continue, viscosity increases until the solution ceases to flow. This sol−gel transition is irreversible, and at this stage the one-phase liquid is transformed to a two-phase system. The gel consists of amorphous primary particles of variable size (5−10 nm or smaller) with an interstitial liquid phase. At this stage the pores have yet to shrink and the liquid phase fills the pores. After gelation, gels are generally subjected to an aging process during which the gels are sealed and very little solvent loss or shrinkage occurs. Condensation reactions continue, increasing the degree of cross-linking in the network.

The drying process involves the removal of the liquid phase. Ambient temperature evaporation is frequently employed, and there is considerable weight loss and shrinkage. It is at this stage that pore collapse occurs, decreasing pore size and thus decreasing the solvent volume. The combination of these effects causes an increase in the interaction between added probe molecules and the matrix. The drying stage is critical as the ability to dry without cracking serves to limit the sizes of monolithic pieces. The final stage of the sol−gel process is that of densification. It is at this point that the gel-to-glass conversion occurs and the gel achieves the properties of the glass. The high temperatures required for densification generally will destroy any incorporated probe molecules, and thus this stage of the sol−gel process is not considered in this review.

3. Spectroscopic Probes of the Sol−Gel Process

In the use of spectroscopic probes of the sol−gel process, a critical question to be considered is the location of the dopant molecule as this determines the environment to which the dye molecule is exposed. Four very general locations of the sol−gel matrix can be differentiated: the interiors of pores (often filled with liquids), the interface between the liquids and the solid pore wall, the pore wall itself, and the constraining region where the distance between opposite sides of the pores is the same as the probe molecule itself. These four different locations are shown in Figure 1. The latter three regions are discussed in section B.

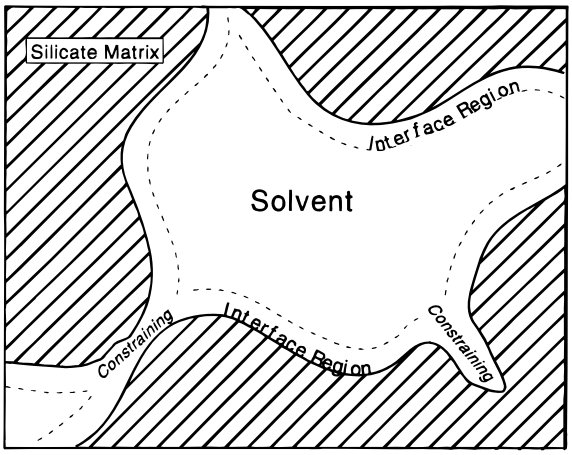


Figure 1. Sketch of four important regions of sol−gel materials discussed in the text. The regions are the solvent region in the interior of a pore, the interface region between the solvent and the pore well, the pore wall, and the constraining region where the distance between the pore walls is about the same as the diameter of a probe molecule.

The most common environment, based on many studies, is the solvent-filled pore interior. The molecule can be thought of as existing in a solution contained in a very small test tube that is interconnected with other small test tubes by tiny channels. If the molecule is in such an environment, then crucial properties that need to be assessed include the identity or composition of the solvent, the pH of the solvent (if it includes water), and the rates of chemical reactions. Other important properties are a function of the solvent composition, including the polarity or dielectric constant of the liquid and the viscosity of the liquid.

The influence of the pore walls may also be very important, even when the molecule is dissolved in a solvent contained in the pore. Thus, interactions of the molecule with the pore walls must always be considered. These molecule−matrix interactions may include frequent collisions with the pore walls, effects from the constraining region, and adhesion via electrostatic, covalent, and/or hydrogen-bonding interactions. Furthermore, the solvent itself may be perturbed by the pore walls; the first several molecules near the wall may be partially ordered. Finally, the pore may become partially dry and the molecule may be in the gas phase (if it is highly volatile) or more likely simply to adhere to the wall because of one of the interactions given above.

The molecule may be incorporated into a tiny constraining region and thus be surrounded by the relatively rigid inorganic structure. In such a case, the environment will be far different from the solvated or solvent−solid interface discussed above, and the molecule will be effectively confined in the solid state. Molecules are generally introduced to the sol−gel material at the sol stage, and thus they are usually dissolved and remain in the liquid phase of the gel.

A. Probes of Solvent-Filled Pores. This section reviews studies of photoprobes which provide insight

concerning solvent chemistry changes during the sol−gel process. The probes monitor a significant part of the sol−gel process, including that of sol formation, gelation, aging, and the early stages of drying. The probes are sensitive to various aspects of sol−gel reaction chemistry, synthesis conditions, the processes of hydrolysis and condensation, and changes in the physical and chemical properties of the solvent. Yet the probe properties are not exclusively determined by the solvent because such features as pore walls and the size of the inorganic cage will exert some influence.

The addition of low concentrations of organic molecules to sol−gel systems has very little effect on network formation. The concentration of molecules represents a very small volume fraction; typical concentrations are 10^{-3}−10^{-5} M while a typical xerogel matrix is some 50% porous by volume. Moreover the size of the organic dopant molecule is much less than the average pore diameter. From the inception of the work on encapsulated molecules in sol−gel matrixes,[12] it has been well accepted that the molecules are located in the pores of the network rather than being part of the network itself. Subsequent papers involving the incorporation of many organic molecules attributed the optical properties of the material to the molecule being confined within a silicate pore or cage.[10,11]

Photoprobe studies of solvent chemistry during the sol−gel process are designed to establish the nature of the chemical environment and how it changes during the processes of sol formation, gelation, and aging. In the studies described below, one must take some care in the interpretation of these results because the information is highly localized and reflects the immediate environment of the probe molecule. Thus, there is the question of whether the probe is solvated in the pore or attached/adsorbed to the inorganic polymer.

Water and alcohol content changes during the sol−gel process provide some insight concerning the nature of the hydrolysis and condensation reactions of the precursors. In silicate systems based on TEOS or TMOS, hydrolysis leads to the production of ROH groups while condensation releases both ROH and H_2O. Thus, associating specific spectral changes with hydrolysis and condensation reactions may be ambiguous for silicate systems which have received the most attention for photoprobe studies. From a broader perspective, the spectral changes do establish whether these reactions are continuing to occur or if they have reached a certain equilibrium solvent composition. This, in turn, provides insight as to the rates at which hydrolysis and condensation occur. Once an equilibrium is established, there is then the prospect of perturbing the equilibrium, as would occur during drying. In this way information may be obtained regarding the solvent composition changes during the drying process.

Solvent Composition. The fluorescence properties of pyranine (8-hydroxy-1,3,6-trisulfonated pyrene) are sensitive to proton-transfer phenomena and have been used successfully to detect solvent chemistry changes. The fluorescence response to a series of water/alcohol compositions is shown in Figure 2. The water content can be quantified by measuring the ratio of the luminescence intensities of the protonated and deprotonated forms of pyranine. The first studies with this probe were carried out in TMOS-derived gels, and the chemical changes were characterized during sol formation and gelation.[13] These studies are quite consistent with the description of solvent chemistry given above. In general, the results reflect a combination of both hydrolysis and condensation processes which advance toward an equilibrium value representative of the final solvent composition. An interesting observation in this study is the influence of pH and how this influences the rate at which equilibrium is achieved. Moreover, by investigating low pH conditions (pH 2.5) which have very rapid hydrolysis and slow condensation, it is possible to track the condensation process over time. These studies also indicate that condensation reactions continue to occur long past the gelation point.

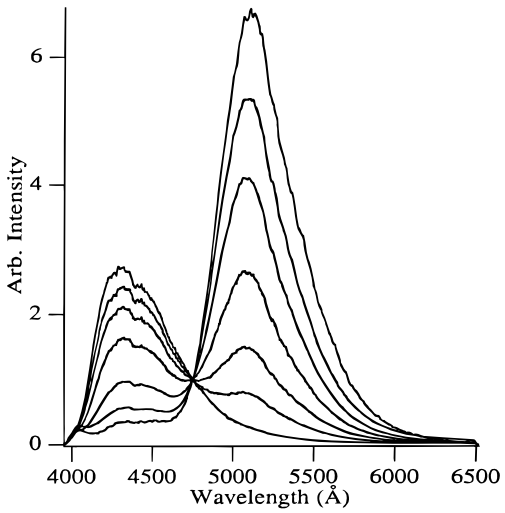


Figure 2. Emission spectra of pyranine in ethanol−water mixtures. The 515 nm band dominates in pure water and the 438 nm band dominates in pure ethanol (from ref 20).

Studies of pyranine doped in an aluminosilicate sol−gel matrix offer a very different response because the probe molecules become part of the colloidal particles formed from partial condensation of Al−OH groups.[14] The results are substantially different from those based on TMOS because the molecules monitor the chemical modifications occurring in the adsorbed layers on the inorganic polymer surface. These layers are initially well hydrated and become substantially less water-rich during gelation and aging, but here, too, the system ultimately reaches an equilibrium composition representative of the initial sol composition. This behavior is shown in Figure 3. These experiments also demonstrate that changes in gel chemistry occur well beyond the gelation stage.

An important result from this study was the recognition that the pore network was interconnected and the probe molecules responded to external solvent composition.[14] This result has had enormous implications for sol−gel sensor applications. Because the pyranine was effectively trapped within the polymer, it could not be leached by any washing treatment. However, the molecule responded to the external solvent composition. This sensitivity to external solvents and their dissolved species has been exploited in a wide range of optical sensor applications in transparent sol−gel matrixes.[15−19]

The use of pyranine as a probe molecule has also been extended to thin films.[20] The sol−gel dynamics here are considerably different from that of bulk monoliths as gelation, aging, and drying processes typically occur within 30 s for dip coating or spin coating of sol−gel thin films with the drying overlapping both of the other

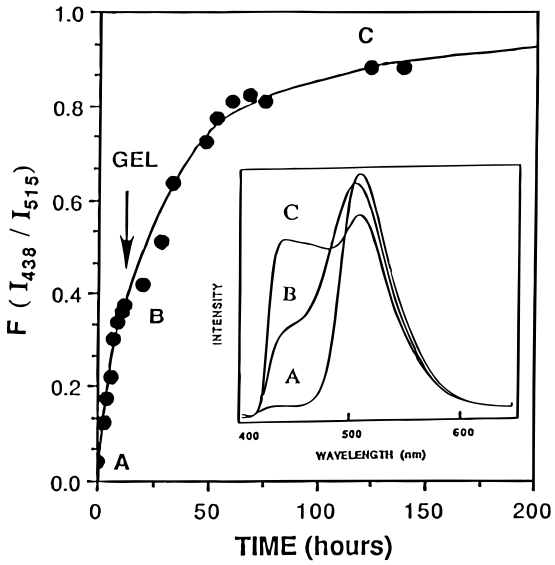


Figure 3. Change in the ratio of the intensities of the blue (438 nm) and green (515 nm) emission intensities of pyranine during processing of aluminosilicate sol−gel materials (from ref 14).

processes.[21] In contrast, for bulk monoliths the same processes are separated in time and occur over days or weeks. The measurements emphasized the changes occurring in the water/alcohol ratio during film deposition and their kinetics. The spatially resolved results established quantitatively that preferential evaporation of alcohol occurs during deposition, leaving the film increasingly enriched in water content with increasing distance from the sol reservoir. This is a potentially important feature since the water content in the pores influences the capillary forces which affect densification. In addition, changes in solvent composition were correlated with film thickness. This type of in situ, noncontact measurement demonstrates the utility of optical probes for automated process control of sol−gel thin films.

Eu^{3+} was one of the first optical probes investigated for sol−gel systems.[22] The well-understood energy level structure of the Eu^{3+} ion makes interpretation of spectra quite direct, and as a result it has been used to study local structure and bonding in a variety of systems. As a probe of the solvent chemistry in sol−gel systems, however, Eu^{3+} provides relatively little information. In aged gels and in xerogels (unheated), fluorescence from Eu^{3+} resembles that of Eu^{3+} in aqueous solution.[22,23] The low fluorescence intensity and short fluorescence lifetime are attributed to electron−phonon coupling with C−H and O−H groups. There is some influence of the counterion on the optical properties;[24] however, it is only upon heating that Eu^{3+} begins to interact with the silica matrix and display rich spectroscopic features which may then be used to consider issues of local structure and bonding.

Solvent Polarity. Another area where photoprobes provide unique information is that of solvent polarity. In the sol and aged gel, the pore solvent should reflect that of an aqueous alcohol environment. Subsequent drying processes will lead to enrichment in the water content of the pore liquid. In the final stages of drying when the residual solvent evaporates and the pore collapses around the dopant molecule, a more polar environment than that of the aged gel should develop, especially in the case of TMOS or TEOS systems where hydrated surfaces of the pore come in contact with the probe molecule. Organically modified sol−gel systems should exhibit a less polar environment than that of the inorganic silica matrixes.

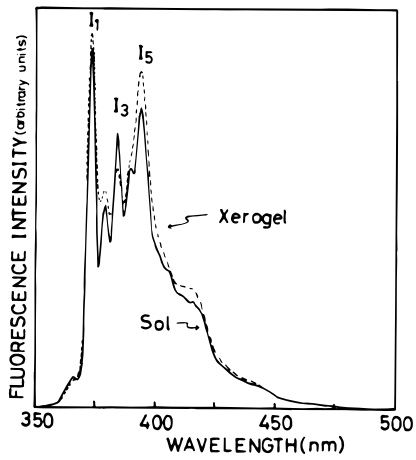


Figure 4. Fluorescence spectra of pyrene in TEOS-derived materials during the sol−gel process. The ratio of the vibronic peak intensities I_1/I_5 or I_1/I_3 are correlated with solvent polarity (from ref 26).

Pyrene has been used as a photoprobe for a number of studies.[25−28] The sensitivity of the vibronic structure of its luminescence spectrum to polarity is most relevant to this review and is discussed below. The ability of pyrene to form excimers has been used to study the sol−gel−xerogel transformation in a variety of systems. This research has been able to provide insights concerning the processes of dopant aggregation and isolation during the sol−gel process,[25,28] an interesting topic, but one beyond the scope of this review.

As a polarity probe, the relative intensities of pyrene vibronic peaks, I_1 and I_5 or I_1 and I_3, have been correlated with local solvent polarity.[28−30] Initial studies ascribed the polarity changes in TMOS and TEOS systems to pyrene aggregation.[25] Later studies showed that polarity in TEOS systems changed relatively little during gelation but did exhibit increasing polarity upon drying.[26,27,31] The changes in the I_1 and I_5 ratios between the sol and the xerogel are shown in Figure 4. These changes were attributed to evaporation of ethanol, effectively increasing the polarity of the silica cage. The highly polar environment of the probe in TEOS xerogels is comparable to that of water, but this may be representative of a water rich layer at the pore surface.

Studies which extended the use of pyrene to organically modified silicate systems showed that the introduction of organic groups into the matrix decreased the polarity of the xerogel matrix and that increasing the alkyl chain length led to a more nonpolar environment.[28,31] The polarity of pyrene doped into phenyltrimethoxysilane is comparable to its polarity in an aromatic solvent such as toluene, suggesting that the pyrene is solvated by the aromatic substituent of the silane precursor.

Another method of determining polarity in sol−gel systems uses an empirical parameter of solvent polarity, the $E_T(30)$ scale.[32,33] It is possible to obtain a semiquantitative measure of the polarity of sol−gel systems using solvatochromic photoprobes. $E_T(30)$ is defined as

$$E_T(30) = 28591/\lambda_m \qquad (3)$$

where $E_T(30)$ is in kcal/mol and λ_m (in nm) is the wavelength maximum of the longest absorption band of pyridinium *N*-phenolate betaine. The data can be normalized (E_T^N) to values between 0 and 1:

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} \quad (4)$$

In this way, E_T^N values range from 0 for tetramethylsilane (TMS) to 1.00 for water.

Nozawa and Matsui used the absorption and luminescence properties of Nile Red to determine the polarity of several sol−gel systems including TMOS, TEOS, methyltriethoxysilane (MTES), and triethoxysilane (HTES).[34] The solvatochromic properties of Nile Red were extremely effective in this study. Sols composed of the precursor, EtOH, and water exhibited E_T^N values of approximately 0.75 which are representative of a solvent−water mixture, i.e., slightly higher than that of ethanol ($E_T^N = 0.65$) and comparable to that of a binary ethanol−aqueous solvent. Upon drying, the resulting xerogels exhibited substantial blue shifts or red shifts depending upon whether the dried material was less polar or more polar, respectively, as compared to the sol. TMOS and TEOS xerogels were highly polar, and values of E_T^N were 0.9−1.0, depending upon synthesis conditions. Adsorbed water on pore surfaces undoubtedly contributes to this high value. In contrast, MTES ($E_T^N = 0.27-0.40$) and HTES ($E_T^N = 0.13$) were less polar. Introduction of $SiCH_3$ or SiH groups makes these xerogels hydrophobic.

Rottman et al. showed that it is possible to span the range between the polar and nonpolar xerogels.[32] Mixtures of TMOS and methyltrimethoxysilane (MeTMOS) exhibited values in which $E_T(30)$ decreased as the MeTMOS concentration increased. The experimental results also suggest that small amounts of MeTMOS have a significant effect on polarity. The addition of 10 mol % MeTMOS produced gels with a polarity comparable to that of methanol.

pH in Pores. The measurement of the pH of solvent-filled pores and the interface region is of obvious importance for pH sensors as well as other devices based on the encapsulation of proteins or organometallics which are sensitive to pH environment. Despite the interest in sol−gel-based pH sensors, surprisingly few studies have been reported. Sol−gel materials containing coumarins reveal the presence of protonated species even though these species were not observed in reference solutions of the same pH.[11] In pH sensors prepared from sol−gel materials doped with bromophenyl blue, the broad shape of the titration curve was attributed to the entrapment of the probe in a distribution of chemically inequivalent microenvironments.[35] For a series of acid base indicators spanning a pH range from 3 to 10, titrations indicated that the pH in the pore could be up to 1 pH unit lower than that in the aqueous buffer solution.[36]

It is evident that the matrix plays a significant role; the dye molecule is not simply sampling the solvent present in the pore. The fact that protonation affects spectral changes far more in the xerogel stage suggests that dye−matrix interactions become stronger as the solvent evaporates and the pore network collapses.[11] It also seems that new approaches are necessary to understand the protonation effects. When the medium contains acidic species other than protons, it may not be adequate to determine the protonating ability by simply measuring pH. Other acidity functions (H_o, H_g, H_a, etc.) may be needed to assess the acidity of the system.

B. Dynamics of Molecule−Matrix Interactions. This section reviews optical studies that have the common theme of dynamic properties of optical probes in sol−gel matrixes. First, we review the local environments of the sol−gel matrix and the expected effects of the environments on molecules. Second, we discuss how the sol−gel environments influence the rotations of the probe, the rotations of the solvent, intramolecular reactions, and intermolecular changes. Finally, we discuss specific results of studies on the dynamic properties of optical probes in sol−gel matrixes.

The concept of mobility of dopant molecules in sol−gel matrixes is a complex issue and subject to a wide variety of interpretations. In this section we will review molecular mobility from the operational point of view, i.e., in terms of specific molecular properties. For example, rotational mobility will be characterized by direct measures of rotation such as fluorescence depolarization rather than from an interpretive point of view based on the microviscosity of the surrounding medium. Although bulk concepts such as viscosity and dielectric constant can sometimes be applied to sol−gel materials, the effects of the small pores can dramatically complicate such interpretations.[37] Mobility is a very important aspect of doped sol−gel materials because many applications require that the dopant molecule be able to perform its desired function unconstrained by the matrix. Examples include the ability of a molecule to undergo conformational changes such as photochromism or enzyme activity, and the ability of analyte molecules to move to and interact with a probe molecule as is required for chemical sensor applications.

To systematize the discussion of molecular mobility in sol−gel materials, we divide the material into four regions as shown in Figure 1. The first of these regions (which figured prominently in section A) is the free liquid region where the surroundings of a dopant molecule are similar to those of an equivalent solution. The second region is the interfacial solvent region, the portion of the gel within a few molecular diameters from the pore wall. The third region is the pore wall itself where the probe molecule interacts on one side with functional groups of the silicate and on the other side with solvent molecules in the interfacial region. Finally, there may exist constraining regions where the distance between opposite sides of the pores is the same order of magnitude as the probe molecule itself and both physical constraint and constraint by ordered solvent molecules can occur. The high surface area of sol−gel materials causes a high percentage of the solute or solvent molecules to interact with a surface. The large number of such interactions creates a gradient that extends from the interface to tens of angstroms into the bulk and may partition the molecular populations into distinct regions, each with its own dynamical features.[37]

Most of the luminescence studies on probe molecules reported to date measure the site-weighted average of the four regions. Thus, fluorescence studies of a probe molecule in a solvent-filled pore (such as in a freshly gelled sample or a xerogel that has been back-filled with solvent) will generally observe the molecules in the

interior of the solvent-filled pore and not detect the small fraction of the molecules in the other regions.

Another complicating factor in interpreting optical studies of probes is the effect of the site on the photophysical properties of the probe itself. Quantum yields for emission may be very different in the different sites; intensities of luminescence cannot be reliably used to interpret populations of molecules in the various sites. On the other hand, emission lifetimes of the same molecule may be different; multiexponential decay may reveal the presence of more than one type of site.[38,39]

The rotational and translational mobility of a probe molecule in the free liquid region will be very similar to that in a solvent-filled beaker. The pore walls are far away from the majority of the probe molecules and have only small perturbing effects. Spectroscopic methods that measure rotations and translations will give results virtually indistinguishable from those in solution. Probe molecules in the interfacial solvent region may have quite different mobilities because the solvent molecules are themselves partially or completely ordered by interactions with the walls.[37] Rotations and translations will be slower and may be anisotropic. If the probe molecules interact directly with the pore walls (via hydrogen bonding or ionic interactions), rotational and translational mobility may be dominated by the binding/debinding rate constants. When such interactions are strong and the rate of release of the probe is small, the molecule may appear to be completely immobile on the time scale of the spectroscopic study. Finally, when the probe molecule is actually constrained because the pore is about the same size as the probe, the molecule may only librate. Fluorescence polarization directly measures the mobility of the probe as discussed in the following section.

The mobility of the solvent molecules will be affected by the regions of the sol−gel material in a manner similar to that discussed above. An important consideration is the relative strength of the solvent−probe interaction as compared to the solvent−solvent or solvent−wall interaction. If the solvent shell strongly interacts with the probe but solvent−pore wall interactions are relatively weak, then the probe molecule will behave as it would in solution. If, however, the solvent shell strongly interacts with the probe and solvent−pore wall interactions are also strong, then constraint of the solvent by the pore wall will also constrain the probe. The rigidochromic effect discussed below provides a method by which solvent mobility can be differentiated from probe mobility.

Frequently the mobility of interest is intramolecular, e.g. cis−trans isomerization. In such cases, measures of the mobility and the physical interactions affecting it take on different meanings. In the cis−trans isomerization reactions, for example, one end of the molecule could be covalently attached to the pore wall, totally inhibiting rotation. However, the isomerization mobility could be essentially unchanged from that in the solution. Rates of isomerization reactions that probe the intramolecular mobility are discussed in the following section.

The final type of mobility discussed in this review is intermolecular (diffusional) mobility. Two extremes can be recognized: long-range transport through the matrix and local diffusion within a pore. The former is of profound importance in the design and activity of sol−gel chemical sensors, but it is affected by many factors such as selective adherence of the molecule being transported to the sol−gel matrix, porosity and tortuosity. More locally, the mobility *within* a pore is of importance to the reactivity of a probe molecule. This local mobility can be studied by generating two reactive fragments from a single precursor and measuring the rate of recombination. This local mobility is the subject of our review.

Molecular Rotation in the Gel. The most important optically based method of measuring the rotation of a molecule in a sol−gel matrix is fluorescence polarization. It is a direct method because it actually monitors the reorientational movements of molecules. On the basis of the movement, it is possible to define local viscosities or "microviscosities". After a brief review of fluorescence polarization techniques, we discuss the results of studies of molecular motions and the relevance of these measurements to the locations of the molecules in the matrix.

Fluorescence polarization measurements are based on the degree to which the orientation of polarized light is maintained after emission from a fluorescent chromophore.[40,41] It is defined in terms of either the polarization anisotropy, r, or the polarization, p,

$$r = (I_{||} - I_{\perp})/(I_{||} + 2I_{\perp}) \quad (5a)$$

$$p = (I_{||} - I_{\perp})/(I_{||} + I_{\perp}) \quad (5b)$$

where $I_{||}$ and $I_{\perp}$ are, respectively, the relative intensities emitted by the fluorescent chromophore parallel and perpendicular to the direction of the illumination. The viscosity of the medium, η, is related to the polarization anisotropy by

$$r_o/r = 1 + (kT\tau/\eta V) \quad (6)$$

where k is the Boltzmann constant, T is the absolute temperature, τ is the emission lifetime of the chromophore, r_o is the experimentally determined limiting anisotropy of the chromophore in a rigid matrix, and V is the molar volume of the chromophore. Viscosity calculated in this manner has been called the microviscosity.[41] These measurements have been applied extensively to biological membranes in order to determine the fluidity and the microviscosity of lipids.

Time-dependent fluorescence anisotropy provides an even more powerful method for studying orientational dynamics of probe molecules.[42,43] The time-dependent fluorescence anisotropy $r(t)$ is defined as

$$r(t) = [I_{||}(t) - I_{\perp}(t)]/[I_{||}(t) + 2I_{\perp}(t)] \quad (7)$$

where $I_{||}(t)$ and $I_{\perp}(t)$ are now the *time-resolved* intensities of emission polarized parallel and perpendicular to the polarization of the excitation pulse. Following a polarized excitation pulse, the time-resolved fluorescence anisotropy decay for a spherical molecule is single exponential, $r(t) = r_o \exp(-t/\Phi)$ where $r_o = 0.4$ for an isotropic medium with parallel absorption and emission dipoles and Φ is the rotational correlation time of the chromophore. The magnitude of Φ can be calculated by using the Debye−Stokes−Einstein hydrodynamic theory, which for a spherical molecule yields

$$\Phi = \eta V/kT \quad (8)$$

This theory can be modified for ellipsoidal molecules by

including shape and friction factors as well as an inertial correlation time, but such modifications have rarely been incorporated in studies of sol−gel materials.

In one of the earliest fluorescence depolarization studies of sol−gels, four different probe molecules of varying sizes (including the most popular depolarization probe molecule, Rhodamine 6G) were studied.[44] The depolarization of the smallest probe molecule, 1,6-diphenyl-1,3,5-hexatriene, was essentially invariant during and after gelation. In contrast, (2,3-diphenylhexatrienyl)propanoyl-3-palmitoyl-L-α-phosphatidylcholine, a much larger molecule, detected the onset of gelation by a small increase in polarization. Two charged probes exhibited changes of the polarization during processing, but all of the changes were small ($p < 0.06$).

A more detailed study of R6G used both static and dynamic measurements.[45] One of the most important results of that study is the interpretation of sol−gel "domains" of "constant", "low", "intermediate", and "high" microviscosities. The "constant" domain corresponds to the pore solvent region in which the molecule has a reorientation time similar to that in a solution in a beaker. During sol−gel aging, a fraction of the probe molecule population remains in this region while others are found in the variable microviscosity domains as evidenced by a second measured reorientation time. The results were interpreted as R6G reporting simultaneously from distinct domains and not a result of anisotropic rotational reorientation from a single molecule. The microviscosity domains probably correspond to the interface, pore wall, and constraining regions.

Similar studies were carried out using 6-propionyl-2-(dimethylamino)naphthalene. Once again, microviscosity domains were identified.[46] The apparent change was minimal until the removal of solvent.

Time-resolved studies on the nanosecond time scale of the reorientation of quinizarin (1,4-dihydroxy-9,10-anthraquinone) were carried out on silicate and aluminosilicate sol−gel matrixes.[47−49] Very different rotational dynamics were found in the aluminosilicate because the probe binds to the aluminum. In wet silica gels, the probe is completely in the solvent region and is unaffected by the matrix, but in xerogels the rotational motion ceases on the time scale of the fluorescence.

Solvent Motion. The mobility of the solvent molecules is the second important mobility property in sol−gel pores. Most frequently it will be closely related to the mobility of the probe molecule; highly mobile solvent molecules will allow the probe molecule to rotate whereas immobile solvent molecules will slow or inhibit the rotation of the probe. Thus, the fluorescence depolarization measurements described above not only provide a direct measure of the motion of the probe but also provide an indirect indication of the mobility of the solvent. Rigidochromism is a relatively new probe technique that measures the reorientation of solvent dipoles around the probe. The combination of this technique and fluorescence depolarization can distinguish between rotation of the solvent molecules and rotation of the probe itself. It has recently been observed that in TMOS gels the molecular motion of the probe on the microsecond time scale is stopped but the solvent motion is large.

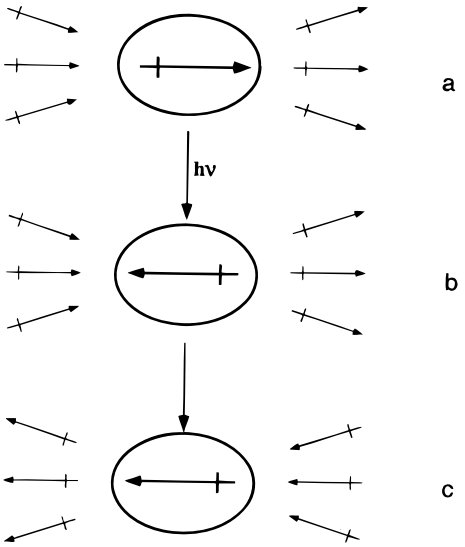


Figure 5. Orientations of the dipole moments of solvent molecules (arrows) and a probe molecule (ellipse). (a) Orientations in the ground electronic state. (b) Orientations after photoexcitation but before solvent molecule reorientation. The dipole moment of the probe molecule reverses direction upon excitation. (c) Orientations after photoexcitation and after solvent molecule reorientation. The emission band maximum from the probe molecule in orientation b is higher in energy than that in orientation c.

Wrighton et al. demonstrated and defined the property of luminescence rigidochromism in $ClRe(CO)_3L$ [L = 1,10-phenanthroline and related ligands] over twenty years ago.[50,51] Rigidochromism is defined as a blue shift in the energy of an emission band with increasing rigidity of the local environment. The origin of the effect is the reorientation of solvent molecule dipole moments. If reorientation occurs before the luminescence (in nonrigid media), there is a red shift of the band maximum. In rigid media, reorientation is suppressed, leading to a higher energy emission.[52] These orientations are shown in Figure 5.

The luminescence rigidochromism of (2,2′-bipyridine)-tris(carbonyl)chlororhenium(I), $ClRe(CO)_3$-2,2′-bipyridine, was used to probe structural changes which occur during the sol−gel−xerogel processes of TEOS silicates and aluminosilicates.[53] In a viscous medium the maximum of the luminescence band of this molecule occurs at higher energy (blue shifted) than that found in fluid solutions. In the silicate sol−gel system formed from TEOS, the solvent molecules remain unconstrained in an interstitial liquid phase until the final stages of drying. In contrast, in the aluminosilicate system formed from (diisobutoxyaluminoxy)triethoxysilane, the emission maximum of the probe showed that the solvent molecules become partially constrained during aging and more constrained during the drying of the gel. The mobility of the same probe molecule was studied in TEOS and aluminosilicate sol−gel systems using fluorescence polarization. In both cases the polarization ratio followed the same general trends observed in the shifts in the luminescence spectra. In methacrylate-modified silicates, the emission from the encapsulated probe molecule remains unchanged throughout aging, similar to the behavior in TEOS gels.[54] At the conclusion of the drying stage, the emission properties are consistent with a molecule encapsulated in a site of intermediate rigidity. The rigidity is reversibly increased by cooling of the material. This behavior is

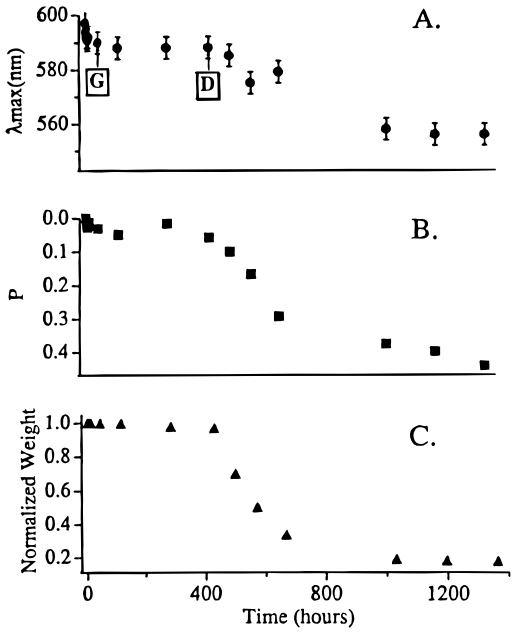


Figure 6. Spectroscopic properties of $ClRe(CO)_3$bipyridine in TMOS sol−gel materials as a function of processing time. The three plots show (a) the emission maximum, (b) the degree of polarization, and (c) the normalized weight of the sample.

consistent with recent studies that show that the methacrylate was not fully polymerized.[55]

The ability to distinguish between solvent and probe mobility was demonstrated in a recent study of TMOS silicates doped with $ClRe(CO)_3$bpy.[56] The key feature in this study was the observation that in air-dried xerogels the probe was not rotating as evidenced by the polarization ratio of 0.45, whereas the solvent molecules were still mobile as shown by the rigidochromic shift to 545 nm (instead of 530 nm). The results are shown in Figure 6. Oven drying of the xerogels to drive off residual solvent induced a fully rigid state as detected by the 530 nm emission. The results suggest that while the probe molecule is trapped in a constraining region and is unable to rotate, not all of the solvent surrounding it is constrained.

Intramolecular Motion and Conformation. Intramolecular mobility of molecules in sol−gel matrixes is important for two reasons. First, the rates of conformational changes can be used as the probe. The rate of a cis−trans isomerization reaction, for example, may be unaffected by the gel matrix even though a part of the molecule remote from the site of the rearrangement is chemically bonded to the matrix. This example illustrates an important difference between fluorescence depolarization studies of molecular rotation (which would be inhibited) and intramolecular motions (which would be unaffected). Second, matrixes can be designed to control the rates in order to achieve specific optical processes. For example, a reversible intramolecular reaction may be the basis for photochromism, a reversible color change caused by the absorption of light. Optical data storage applications require long-lived intermediates (slow rates) whereas optical switching applications require short lifetimes (fast rates). Sol−gel matrixes may be designed to control the reaction rates.

The most thorough studies of the effects of the medium on intramolecular reactions are those of cis−trans photoisomerizations, especially of stilbene and substituted stilbenes.[57] In these studies, the rate of the reactions can be correlated with microviscosity (instead of the macroscopic shear viscosity) and interpreted in terms of the friction caused by the solvent as the molecule undergoes its large amplitude motion. The detailed quantitative studies were carried out in nonpolar solvents; the microviscosity model does not account for solvation effects other than the viscosity changes.[57] In the more polar environments in sol−gel matrixes, many other interactions including hydrogen bonding and ionic effects may play a role and interpretations of the matrix effects in terms of viscosity may be misleading.

We begin our discussion with intramolecular photoisomerization reactions. We continue with a second type of intramolecular rearrangement where excimer formation occurs between two parts of a molecule connected by a flexible chain. Finally, we discuss photochromism based on intramolecular rearrangements.

Azobenzene Derivatives. Photoinduced trans−cis isomerization and thermal cis−trans isomerization of azobenzene derivatives have been used to study the microenvironment of the probe molecules. These reactions have also been well studied in organic polymers as a photoreactive probe to estimate the free volume and rigidity of solid polymers. The experimental observation is that the cis fraction of a photostationary state in a sol−gel matrix was much smaller than in poly(methyl methacrylate).[58,59] On the basis of this observation, it was concluded that the free volume in sol−gel silica films is smaller than in PMMA films. In a second series of experiments, azobenzene chromophores were covalently attached to the silica precursor and prepared as a film. The attachment of the chromophore to silica through a single covalent bond had only a slight effect on the isomerization, whereas it was markedly suppressed when an azobenzene was fixed to the silica matrix at both ends of the chromophore.[60] The mobility of the single covalent bonded species suggests that the interface layer is very similar to the liquid region because the molecule "feels" no constraining effect.

Azobenzene derivatives were further studied in bulk sol−gels, films of sol−gels, and PMMA.[60] First-order kinetics of the thermal isomerization of the photoinduced cis isomer was interpreted in terms of steric restrictions, and the restrictions follow the order sol−gel bulk < PMMA < sol−gel films. In this study the authors emphasized that cis to trans thermal isomerization obeys first-order kinetics even though the probe compound is trapped in solid bulk material. This behavior indicates the existence of large free volumes in the sol−gel bulk silica matrix so that the isomerizations of the azo chromophore take place as readily as in solution. It is likely that the interface region of the xerogels still contained sufficient solvent that the probe molecules retained their mobility. It is important to remember that it is the reactive molecules being observed; unreactive molecules in other regions would not contribute to the optical response.

Intramolecular Excimers. Spectroscopic studies of excimer formation in sol−gel matrixes have played an important role in probing intermolecular interactions. Excimers (excited state dimers) are formed when a molecule in an excited state interacts with a second (ground state) molecule. Excimer emission is detected

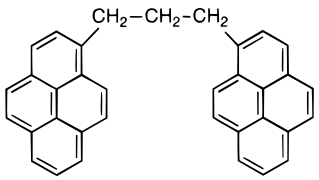


Figure 7. Structure of 1,3-bis(11-pyrenyl)propane, a probe of intramolecular mobility.

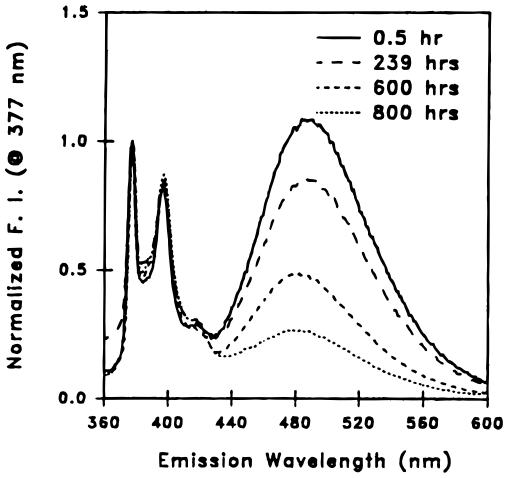


Figure 8. Normalized fluorescence spectra of 1,3-bis(11-pyrenyl)propane in a TMOS-derived sol−gel material during various stages of processing from ref 61. The decreased excimer emission at about 490 nm is associated with matrix structural changes and/or solvent loss.

at longer wavelengths than the emission of the monomers. Pyrene has been used to probe excimer formation.[25] Excimer emission was observed in a fresh sol−gel, but the intensity diminished in the xerogel. These observations were interpreted in terms of trapping of individual pyrene molecules within isolated pores which prevented excited state dimerization from occurring. These types of studies provide information about diffusional mobility between pores but do not directly probe the mobilities of individual molecules.

An innovative type of study that uses excimer formation but does not require transport between pores involves isolated molecules that consist of incipient excimer-forming moieties covalently connected by a flexible chain. When the molecule is completely mobile and one end is excited, it can form an excimer with the other end. If the molecule is immobile and the ends are spatially separated, only monomer emission is observed. Thus the effect of the matrix on the conformational flexibility of a single molecule can be studied.

Several recent studies have been reported. The probe 1,3 bis(1-pyrenyl)propane (Figure 7) was doped in TMOS sol−gel materials.[61] In solution, the two ends of the probe molecule do not interact in the ground state, but on photoexcitation the molecule reorients to form an intramolecular excimer as shown in Figure 8. The excimer emission was followed using both steady state and time-resolved fluorescence spectroscopy. It was observed that in a fresh gel the flexibility is similar to that in solution. Thus, these probe molecules are in the liquid region of the gel. In the xerogel (air-dried at room temperature) the flexibility is restricted but not completely stopped as evidenced by decreased but nonzero excimer formation (Figure 8). The time-dependence was interpreted using three exponentials. These results may reflect either (or both) inhibition of the intramolecular motion by more ordered solvents in the interface region or increasing population in the constraining region.

In a related study, molecules containing two anthracene groups connected by three-membered chains were investigated.[62] In aerated solution, the bichromophoric anthracenes undergo both reversible photodimerization and photooxidation. The photodimerization reaction is not excimer formation because the dimer persists in the ground electronic state. However the process is similar because the two ends of the probe molecule must come into proximity. In sol−gel glasses, they undergo photooxidation in preference to intramolecular dimerization. This result was interpreted in terms of the steric constraint of the matrix. However, the nature of the constraint was not determined.

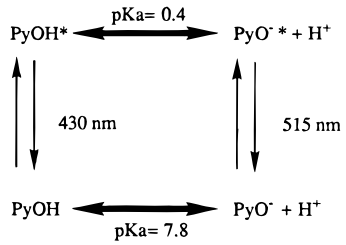
Photochromism. The activity of photochromic molecules in sol−gel matrixes was studied intensively with the prospect of developing photochromic glass for practical applications. Because of the advantages of low-temperature processing from solution, it is possible to explore the many photochromic molecules that have been studied in solution. The potential applications include photochromic glass for energy conservation, for optical data storage, and for optical switching. It is also hoped that photochromic properties could be tuned by the properties of the matrix.

The use of photochromic molecules as probes is usually an indirect result of the investigations of photochromism for applications. In general, it has been observed that the rates of the intramolecular changes that lead to the reversible color changes become slower as the matrix ages and dries. Thus, applications for practical devices have had limited success. The decreases in the reaction rates are generally attibuted to increasing constraints by the matrix as it ages and dries, but the nature of the constraints is usually not determined. On the basis of the fluorescence depolarization results in the xerogel state, it is likely that reduced molecular motion causes the decrease in the reaction rates.

A popular class of photochromic molecules are the spiropyrans.[63−65] A large number of photochromic derivatives are known from solution studies, and the colors of the systems at thermal equilibrium and in their photostationary states can be changed by changing the substituents. In silicate and aluminosilicate glasses, the photochromism only occurs in the aged, solvent-filled gels and stops at the xerogel stage. The nature of the matrix can influence the photochromism; when the sol−gel material is changed to poly(dimethylsiloxane), the color of the system at thermal equilibrium is the same as that of the photostationary state in solution.

Other photochromic molecules including 2,3-diphenylindenone oxide[66] and spirooxazines[67] have been studied. The former system also exhibited photochromism when the pores were filled with solvent, but lost activity upon drying. Rate measurements showed that the forward (light driven) reaction slowed continuously during aging. The disappearance of photochromism was attributed to matrix-constraining effects, but the details were not elucidated. In the latter system the effects of different chemical environments were observed in organically modified silicate matrixes. Both normal and reverse photochromism were found and attributed to the

Scheme 1



effects of the organic and inorganic regions of the material.

Photochromism in the fluorescence spectra of 1,2-bis-(9-acetoxy-10-anthryl)ethane in silicate glass was recently reported.[68] Four different conformers (including two that involve intramolecular excimer emission) were observed. The relative abundances and the relative fluorescence intensities changed when irradiated at 358 nm and then relaxed back to the equilibrium values. These changes persisted over a period of almost 2 months. The changes in the relative concentrations at thermal equilibrium as a function of gel aging time were attributed to the shrinkage of the pores caused by the escape of ethanol and water molecules.

Local Intermolecular Mobility. The final aspect of mobility in the pores of sol−gel materials to be reviewed is local intermolecular mobility. Very few dynamic studies of this type of mobility have been carried out. The best method of studying local intermolecular mobility is to use a perturbation method; an external source provides a sudden perturbation to the system, and a detection method measures the rate of return of the system to equilibrium. Because the mobilities of interest are rapid and occur on the time scale of diffusion, the perturbation must be fast on that time scale and the detection methods must be correspondingly fast.

Ionic Mobility. A convenient way of perturbing molecules in sol−gel materials is by using a laser pulse. Pulses that are short on the diffusional time scale are easily generated, and recombination times on the order of tens of nanoseconds can be monitored optically. In this study a 10 ns laser pulse perturbs an organic molecule and produces a proton and a cation with a distinctive absorption band different from that of the original molecule. The decrease of the absorbance as a function of time (on the microsecond time scale) enables the mobility of the two species to be measured as the cation and anion recombine. Both the rate constant of the recombination reaction and the activation energy are used to interpret the influence of the sol−gel matrix on the local mobilities of the ions.

The pyranine molecule is employed as a proton generator.[69,70] The acid dissociation constant, pK_a, of the protonated molecule (PyOH) in the ground state is about 7.8. This value can be compared to the acid dissociation constant of the first excited singlet state, pK_a*, which is about 0.4. This difference is used to create a sudden increase in the concentration of protons, [H^+], by irradiation with a laser pulse. The overall process is summarized in Scheme 1. The back-protonation reaction is studied by following the variation of the concentration of the deprotonated form with time by measuring its transient absorption after the excitation pulse. The deprotonated form has a broad, strong absorption band centered at about 460 nm.

A series of measurements at room temperature were performed on samples at different stages of the sol−gel process.[71] The initial sol, the aged gel, and the air-dried xerogel were examined. The effect of temperature on the recombination rates was studied on air-dried xerogels at temperatures between −6 and +20 °C. The quantitative results were expressed in terms of rate constants. The small difference between the values of the rate constant in the xerogel (4.6×10^{10} M^{-1} s^{-1}) and in water 8.5×10^{10} M^{-1} s^{-1}) suggests that proton transport along the interface region is similar to that in solution.

The activation energy of the back-reaction is calculated from the temperature dependence of the rate constant. The activation energy is 8.4 kcal/mol, about 2.4 times larger than that measured in aqueous solution (3.5 kcal/mol).[70] The measured activation energy, assuming a diffusion-controlled mechanism, includes contributions from three sources. Two of these, the contributions from the dielectric constant and the ionic strength, are small. The activation energy due to the mobility of the proton is the principal contribution to the activation energy, accounting for almost 80% of the total. The activation energy therefore reflects the process of proton transport through the medium.

The activation energy for proton motion is much closer to that observed for water than for solid materials. Activation energies for ionic diffusion through solids are much higher, and this is inconsistent with the experimental value of the activation energy for the diffusion of protons obtained here. It is likely, therefore, that the mobile species are in the interface region and are not moving through the solid silica network.

Photoinduced Electron Transfer Reactions. Several studies of photoinduced electron transfer in sol−gel materials have been reported.[72−75] These studies differ from the pH jump studies in several important ways: steady state irradiation is used to perturb the system, slower rates of back reaction are measured, and a third compound not perturbed by the light acts as a mobile charge carrier. For example the irradiation of pyrene in the presence of methylviologen (MV^{2+}) produces an excited state that transfers an electron and reduces methylviologen:

$$\text{pyrene} + h\nu \rightarrow \text{pyrene}^* \quad (9)$$

$$\text{pyrene}^* + MV^{2+} \rightarrow \text{pyrene}^+ + MV^+ \quad (10)$$

The radical pair is very reactive and in solution rapidly reacts back to the starting materials. In the sol−gel matrix, pyrene* transfers an electron to *N*,*N*′-tetramethylene-2,2′-bipyridium, which is mobile in the porous network. In this system, the lifetime of the pyrene^+ and MV^+ is on the order of hours. Other donor and acceptor species including ruthenium and iridium complexes were also studied. The long lifetimes (implying slow reaction rates) were attributed to the constraining effects of the matrix.

Pore Shaping. An extremely active area of research in sol−gel materials containing dopants is the engineering of porosity.[76] The goal is to tailor-make pores with desired sizes and shapes. Applications include molecular recognition, shape-selective catalysis, chemical sensing, and selective adsorption. The first report of success in this area involved molecular imprinting to control pore shape and size by using methyl orange.[12]

This molecule was encapsulated in the xerogel and then leached out with methanol. Adsorption studies showed that methyl orange was preferentially adsorbed over ethyl, *n*-propyl, and *n*-butyl orange. The field of template-based approaches to the preparation of nanoporous silicas has been recently reviewed.[76]

Spectroscopic probes that reveal the existence of selective interactions have not yet been developed. Such probes would need to show a selective response to pores that had been previously templated for selective interaction of the probe. However, as a first step toward probing pore-shaping, a large molecule with a charged surface and/or a surface containing many hydrogen bonding sites might reveal selective interactions with pores. One such study that suggests the existence of pore shaping has been reported. The probe molecule is the large biomolecule, cytochrome *c*.[77]

Cytochrome *c* (cyt *c*) is a heme-containing electron-transfer protein with a molecular weight of ~12 400. The optical absorption properties of the protein (an intense Soret band at ~400 nm and a Q-band in the 550 nm region) provide useful information about the state of the protein in the confined environment of TMOS gels.[78] The characteristic absorption spectral pattern of the cyt *c* in the solution phase and the aged silica gel sample is similar, but the solution spectrum shows the Soret band centered at 406-nm, and the aged gel spectrum shows a slight blue shift to 404 nm. The blue shift may be caused by interactions with the silica cage. Upon ambient drying of the samples (to 20% of the original weight of the aged gel), the blue shift continues during the aged gel to xerogel structural transformation. A total shift of 9 nm (404−395 nm) can be attributed to drying effects. These effects, shown in Figure 9, must arise due either to pore collapse or to loss of solvent from the aged gel samples that accompanies drying.

To determine the exact cause of the blue shifts, absorption spectra were obtained on rehydrated xerogel samples. Absorption spectra of xerogels immersed in 0.1 M acetate buffer (pH 4.5) show a distinctly red-shifted Soret transition centered at 404 nm, exactly the same as that observed for aged gel samples. The 9 nm shift in the Soret transition is thus caused by drying/rehydration of the gel samples. The reversibility of these shifts indicates that physical constraints do not contribute to this effect.

Pore shrinkage of the silica gel upon drying is an irreversible process. If pore collapse due to drying were to cause the blue shifts upon dehydration, the original spectrum of the aged gel would not be recovered upon rehydration. Therefore, one can interpret the absorption spectroscopic changes as caused by loss of intervening solvent phase upon drying. The dimensions of the pore containing the protein are greater than or equal to those of the biomolecule throughout the drying process. The absorption spectroscopic data only pertain to the pores that contain the protein and do not apply to the free pores which undergo the usual shrinkage as evidenced by the overall volume shrinkage of the gels by ~70%.

The above results suggest that the pores that contain the protein behave differently from the free pores and the presence of the protein dopant alters the behavior of the silicate porous structure. The gel network shows a wide distribution of pore sizes, but it appears that the protein is trapped within pores which meet its dimensional requirements. Since the protein is added to the sol and is encapsulated in the growing gel polymeric network, the spectroscopic results suggest that the pore forms around the protein. The silicate fragments formed as part of the initial hydrolysis reactions are charged as well as being capable of H-bonding, and the complementary properties of the protein may allow it to interact with the silica polymer. If such interactions are sufficiently attractive, the protein is likely to act as a structural template around which the gel network can form.

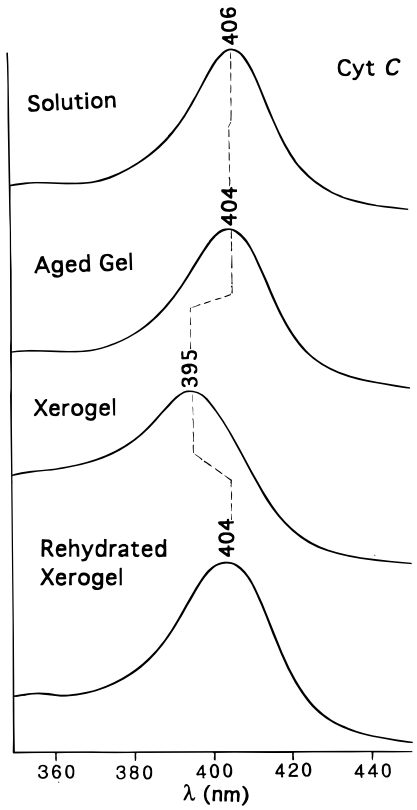


Figure 9. Absorption spectra of cytochrome *c* in aqueous solution, aged gel, xerogel, and rehydrated xerogel. The recovery of the aged gel spectrum after rehydration indicates that solvent loss rather than pore collapse is responsible for the shift in the xerogel spectrum.

4. Conclusions

This review has focused on questions concerning the nature of the microenvironment experienced by probe molecules during the sol−gel process. One area of emphasis has been the use of optical probes to identify the chemistry of solvent-filled pores. The results of these studies are consistent with long-held hypotheses of how solvent composition changes from hydrolysis and condensation reactions, and during the aging and drying stages. One area where there is a need for improved understanding is the protonating behavior of the sol−gel matrix, a topic of considerable significance for pH sensors as well as for future applications based on encapsulated molecules.

A second emphasis in this review was that of the dynamic properties of optical probes in sol−gel matrixes. These studies provide insights into the properties of the novel materials based on the encapsulation of organic and biological molecules in sol−gel matrixes. One general result is the measurement of the extent to which

molecule−matrix interactions suppress both the intramolecular and the intermolecular mobility of the probe molecule. The general observation is that the constraining effects of pore collapse reduce molecular motion. However, detailed understanding of the specific interactions and the matrix sites leading to the suppression is generally lacking. This molecule−matrix feature must be more thoroughly understood if it ultimately can be controlled for development of specific optical materials. In view of the emerging importance of molecule-doped sol−gel materials in fields ranging from photonics to chemical sensors, it is likely that carefully and imaginatively chosen spectroscopic probes will play an increasingly important role in the design and optimization of these sol−gel-derived materials.

Acknowledgment. This work was made possible by a grant from the National Science Foundation (DMR94-08780). The authors gratefully thank Michael Huang, Hermes Soyez, and Dr. Jing Wang for their assistance.

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CM970270P