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(4-Ethoxyphenyl)urea as a Fluorescence Probe in Sol−Gel Processes

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Measurement of the fluorescence of a sol−gel material during the transition permits monitoring of variations before and after the gelation point, periods for which other techniques show little signal variation. The excitation and emission spectra and the fluorescence lifetime of (4-ethoxyphenyl)urea (dulcin) were observed as a function of the time during the sol−gel−xerogel process of the tetraethyl orthosilicate system. The spectra were compared to those obtained in environments of different physical properties. The changes in lifetime of (4-ethoxyphenyl)urea provide a sensitive probe of the structural changes that occur during the sol−gel process.

Introduction

Sol−gel materials can be used in applications ranging from optical elements and integrated optical devices to antioxidant, anticorrosion coverings, and composite and biomedical materials.

Recent research has demonstrated that silicate glasses obtained by the sol−gel method can provide a host matrix useful in chemical and biochemical sensors.[1−6] Although the materials have been synthesized,[7,8] little is known about the structural, chemical, and physical properties of the sol−gel matrix surrounding the doped material on the molecular level.

The sol−gel−xerogel transition is continuous; the point where the sol changes from a viscous fluid to an elastic gel cannot be precisely defined. The gelation point is easy to observe qualitatively and easy to define in abstract terms but extremely difficult to measure quantitatively. The gelation of the sample is defined by the absence of flow under the gravitational field.[9−13]

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To understand and control the product, a detailed investigation of this process is required.

Viscosity and elasticity have a critical behavior near the gel point; however, measuring them is delicate since it is important not to disturb the transformation. Spectroscopic techniques can be used to visualize the evolution of different species. Photophysical probes were used for following the polymerization process.[14−23]

In this work, using steady-state and time-resolved fluorescence spectroscopy, the fluorescence spectra and the lifetime of (4-ethoxyphenyl)urea were used as a useful photophysical probe for studying the sol−gel−xerogel transition of the tetraethyl orthosilicate (TEOS) system at the molecular level because it permits monitoring the variations of viscosity before and after gelation. Such information will be valuable in assessing the use of such immobilized reagent systems in the development of optical chemical sensors.

Experimental Procedure

Sol−Gel Glass Preparation. Silica gel was prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in water−ethanol solutions, obtaining a suspension with colloidal particles (called sol). The starting mixture was 2.0 mL of TEOS, 1.2 mL of H_2O, 1.0 mL of ethanol, 2.0 mL of (4-ethoxyphenyl)-urea solution (5.56×10^{-3} M) in ethanol, and 30 μL of HCl 0.01 M. For the study of the KBr and NaOH effects, the water was replaced by solutions of 1 M KBr and 2 M NaOH. The gelation was carried out at room temperature, in a beaker glass or in a measurement cuvette, covered with aluminum foil. The solvents included in the sol were evaporated by punching small holes in the cover of the container.

Instruments. Excitation and emission spectra were obtained with a Perkin-Elmer LS-50 fluorescence spectrometer. An interchangeable device, front surface accessory Perkin-Elmer Part No. 52123100, permits reading the fluorescence of samples in gel and xerogel forms. Information is sent via the RS232C interface of the fluorescence instrument to an external computer. Instrumental parameters are controlled by Fluorescence Data Manager (FLDM) software.

Lifetimes were measured on an Aminco SLM 48000S spectrofluorimeter equipped with a 450 W xenon lamp source, a Hamamatsu R928 photomultiplier detector tube, and a Pockel cell electrooptic modulator. An IBM PC AT microcomputer was used for on-line data acquisition and processing. Fluorescence lifetimes were determined by using multifrequency-modulated excitation beams; a silica gel scattering solution was the reference. Phase and modulation measurements used the "100-average" mode, in which each measurement value is the average of 100 samplings, carried out automatically by the instrument circuitry in approximately 25 s. The slits were set at 16 nm, with an 8 nm band-pass entrance. To select emission wavelength, instead of a monochromator a band-pass interference filter (Oriel 333 nm) was placed in the sample emission receiving channel.

Multifrequency phase and modulation fluorescence provides information on the excited-state decay kinetics for a particular fluorescent center. A nonlinear squares analysis scheme, based on a χ^2 function, is used to extract the kinetic parameters. If the system is simple, the recovered decay law will be a single exponential; however, if the system is complex, the decay kinetics can follow multiexponential decay laws or continuous distributions.

Lifetimes are calculated usually in liquid samples by using glycogen aqueous solution as reference. Only phase data are reported in solid samples because of the difficulties associated with accurate modulation measurements from irregularly shaped solid samples when liquids are used as the reference lifetime standards.

Results

Sol−Gel Glasses and Measurements in Gel. Sol−gel glasses were doped with (4-ethoxyphenyl) urea in HCl and NaOH media and in acidic medium in the presence of KBr. As protons or hydroxide ions are required for catalysis in silicagel formation, the pH of the reaction medium is an important factor that affects the stoichiometry of the final gel. Acid catalysis tends to increase the rate of hydrolysis and disfavors condensation reactions, whereas basic hydrolysis produces rapid condensation. In basic media the gelification occurs in 1 or 2 min; the gel is a white powder that releases solvent continuously. In acidic media, gelification is slow; the gel is transparent and homogeneous. In presence of KBr, gelification is accelerated with respect to acid medium and shrinkage of the gel occurs. Acidic polymerization conditions were chosen because they provide a much slower reaction rate compared with basic conditions, thus enabling the gelation process to be followed.

The fluorescence spectra and the lifetime measurements of (4-ethoxyphenyl)urea immobilized in gel can be obtained with a device "front surface" or in cuvette; this depends on whether the transition sol−gel occurs in a crystal vial or directly in the measurement cuvette. The data obtained with these two measurement systems are not comparable.

Fluorescence in Different Environments of (4-Ethoxyphenyl)urea. The excitation and emission spectra of (4-ethoxyphenyl)urea in several organic solvents of different viscosities and polarities, β-cyclodextrine and filter paper have been obtained. Table 1 summarizes fluorescence data in the different environments. The excitation spectra of (4-ethoxyphenyl)urea shows two peaks, except for *N*,*N*-dimethylformamide. In solvents of small polarity (1,4-dioxane, ethyl acetate, and sol of TEOS) a slight red-shift in the excitation maxima was observed, and the long wavelength has the highest intensity. The spectra of (4-ethoxyphenyl)urea in solvents of mean and high polarity (ethanol and acetonitrile), adsorbed onto paper and included in β-cyclodextrin, show a slight blue-shift in the excitation maxima, and the short wavelength has the highest intensity. The hydrophobic character of the β-cyclodex-

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Table 1. Environment Effects on the Fluorescence of (4-Ethoxyphenyl)Urea 2.77×10^{-5} M

environment	ϵ_T	viscosity$_{25\,°C}$ (cP)	$\lambda_{ex(1)}$ (nm)	$\lambda_{ex(2)}$ (nm)	λ_{em} (nm)	$I_{ex(1)}/I_{ex(2)}$
1,4-dioxane	2.21	1.21	256	298	336	0.84
ethyl acetate	6.00	0.44	259	298	334	0.84
ethanol	24.3	$1.20^{20\,°C}$, $1.03^{30\,°C}$	247	290	333	2.84
acetonitrile	37.5	0.35	240	295	332	2.85
N,*N*-dimethylformamide	36.7	0.80	297		336	
β-cyclodextrin[a]	54.0	150	250	290	340	2.14
filter paper[a]			239	285	330	3.22
TEOS sol[a]	4.10		268	308	333	0.46

[a] Concentration 5.56×10^{-3} M.

Table 2. Effects of (4-Ethoxyphenyl)urea Concentration: Ethanol

(4-ethoxyphenyl)urea (M)	λ_{ex} (nm)	λ_{em} (nm)	lifetime (ns)
5.56×10^{-5}	295	329	1.21
1.11×10^{-4}	295	330	1.25
5.56×10^{-4}	301	328	1.21
1.11×10^{-3}	306	329	1.20
5.56×10^{-3}	313	330	1.22
1.00×10^{-2}	318	330	1.16

Table 3. Effects of (4-Ethoxyphenyl)urea Concentration: TEOS Sol

(4-ethoxyphenyl)urea (M)	λ_{ex} (nm)	λ_{em} (nm)	lifetime (ns)
5.56×10^{-5}	292	329	
1.11×10^{-4}	296	330	
5.56×10^{-4}	301	328	1.02
1.11×10^{-3}	306	329	1.00
5.56×10^{-3}	308	330	1.02
1.00×10^{-2}	314	330	1.00

trin[24] can explain the smaller blue-shift and intensity at short wavelength.

Effects of (4-Ethoxyphenyl)urea Concentration. Tables 2 and 3 show the data of excitation and emission wavelength and lifetime at different (4-ethoxyphenyl)-urea concentrations in two solvents, ethanol and sol of TEOS. Figure 1 shows the excitation and emission spectra at different concentrations of (4-ethoxyphenyl)-urea in sol of TEOS. We observed that wavelength emission and lifetime are not affected by concentration of (4-ethoxyphenyl)urea; however, a red-shift in the maximum excitation wavelength is observed with the increase of (4-ethoxyphenyl)urea concentration.

Fluorescence and Lifetime during the Sol−Gel Process. The changes of fluorescence of (4-ethoxyphenyl)urea during the sol−gel transition have been studied from a sol of initial concentration 1.78×10^{-3} M up to a gel state, obtaining fluorescence spectra and measuring lifetimes. Figure 2 shows the fluorescence spectra of two samples, with and without (4-ethoxyphenyl)urea at different times of the sol−gel process. The emission wavelength did not change, the excitation spectrum showed a band and a shoulder, and a slight red-shift of 3 nm in the excitation maximum occurred. However, sudden changes in two properties, the ratio of two excitation maxima intensity and the lifetime, occurred. Figure 3 shows the increase of the ratio of two excitation maxima intensity (I_{ex1}/I_{ex2}) during the sol−gel transition. This change is high between 120 and 122 h, when the sample reaches the gel state. Figure 4 shows the decrease of the lifetime during the gelification process. It is observed that the change is higher when the sample reaches the gel state.

Lifetime in Gel State. Values of (4-ethoxyphenyl)-urea lifetimes in gel state were obtained by using the phase-modulation approach. The excitation wavelength was set at $\lambda_{ex} = 310$ nm; at this value the absorption effects by the matrix are minimized. The phase date of (4-ethoxyphenyl)urea in gel state were fitted to an exponential single curve, which is a model applied to a single-component sample, obtaining a lifetime of 0.590 ns, and they were fitted to an exponential double curve, which is a model applied to a multicomponent sample, obtaining two lifetimes (1.320 and 0.404 ns, with fractions of 0.453 and 0.547, respectively). The errors are similar in both cases.

Mobility of the Doped Molecules. Mobility under harsh washing conditions was studied. (4-Ethoxyphenyl)urea (5.56×10^{-4} M) was trapped in gel structure, and this was incubated in distilled water for 3 days. The excitation and emission spectra of gel and water solution were obtained before and after incubation, obtaining a decrease of fluorescence intensity in the gel and the increase in water.

Discussion

Measurements in Gel. To compare the data obtained in gel and in solution, the sol−gel process must be carried out in the same measurement cuvette. Measuring with the device "front surface" produces distortions in the excitation spectra and in the intensity fluorescence that can attribute to the geometry of frontal lighting.[25] The geometry of frontal lighting means that a great light quantity comes to the emission monochromator, causing distortions and a smaller fluorescence intensity. When measuring in cuvette, the distortions do not occur, because the emission monochromator is perpendicular to excitation.

Fluorescence in Different Environments of (4-Ethoxyphenyl)urea. Gradual changes are observed in the fluorescence and the lifetime of (4-ethoxyphenyl)-urea in the different types of environment and during the progress of the sol−gel reaction of the TEOS system. The fluorescence data in the different types of environment show small emission wavelength displacements of (4-ethoxyphenyl)urea; this suggest small interactions of the dipole moment of the fluorophore in the excited state with the reactive fields induced in the surrounding solvent. Probably the symmetry of (4-ethoxyphenyl)-urea dictates a dipolar moment of zero or very small and so the spectroscopic displacements caused by dipolar moments are also small.[26] Furthermore, the small

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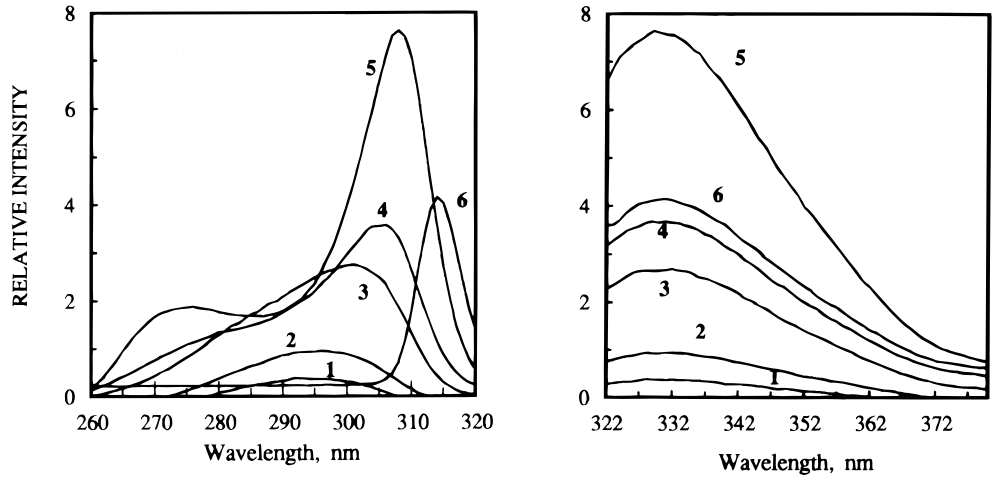

Figure 1. Excitation and emission spectra of (4-ethoxyphenyl) urea in sol of TEOS. Numbers 1−6 indicate increasing concentrations from 5.56×10^{-4} M (1) to 1.00×10^{-2} M (6).

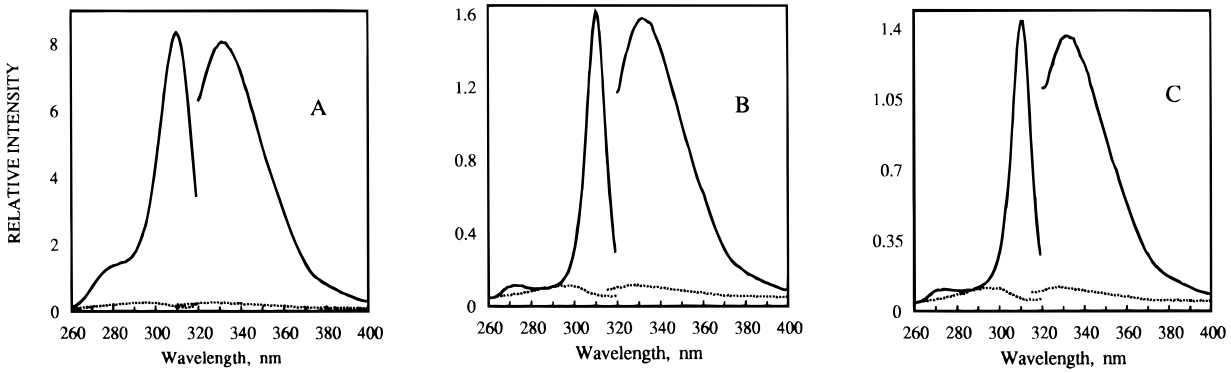

Figure 2. Excitation and emission spectra at different time of TEOS with (4-ethoxyphenyl)urea (solid line) and without (4-ethoxyphenyl)urea (dotted line): (A) initial sol; (B) sol at 76 h; (C) gel state.

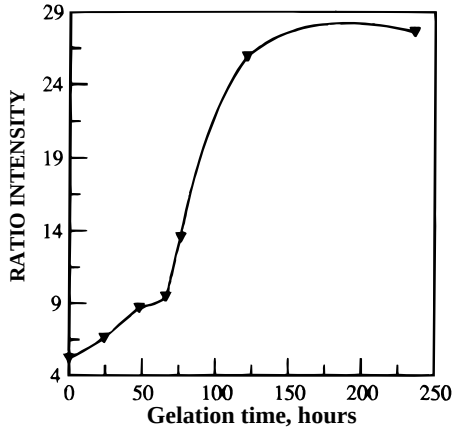

Figure 3. Changes in the ratio of excitation maxima intensity during the sol−gel transition in TEOS system (long wavelength, with high intensity, is $\lambda_2 = 310$ nm; and short-wavelength, with low intensity is $\lambda_1 = 274$ nm).

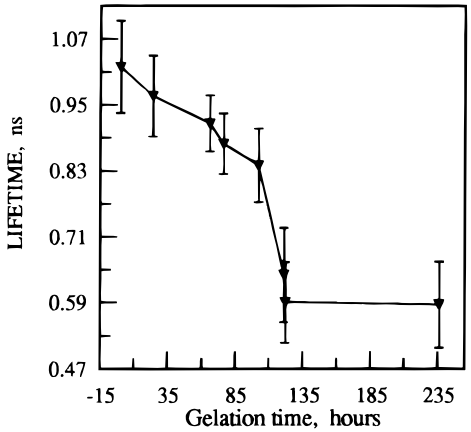

Figure 4. Changes in the lifetime of doped molecules of (4-ethoxyphenyl)urea during the sol−gel transition in TEOS system ($\lambda_{ex} = 310$ nm).

emission wavelength displacements of (4-ethoxyphenyl)-urea associated from the sol−gel−xerogel transition may be explained by the small dipolar interactions of the fluorophore with the surrounding medium.

The changes observed in the excitation spectra in different environments and during the sol−gel−xerogel transition cannot be associated with the formation of charged species in the ground state but to physical changes of the neutral molecular form. No effect of proton concentration on fluorescence of (4-ethoxyphenyl)urea is detected over the range 0−14.

In solvents of small polarity (1,4-dioxane, ethyl acetate, and TEOS sol) a red-shifted excitation spectra is observed (Table 1). On the other hand, the concentration increase of (4-ethoxyphenyl)urea in ethanol and sol of TEOS produces only a red-shift in the excitation maximum (Tables 2 and 3). However, the shift-red displacement with concentration cannot attribute to the dimer formations in the ground state, because the maxima absorbance wavelength is constant. Neither excimer formations can be attributed because in the emission

spectrum a band at largest wavelength that increases the intensity with the concentration does not appear. In conclusion, the red-shifted excitation spectra can be attributed to nonspecific intermolecular interactions.

The blue-shift in the excitation spectra that appears in solvents of mean and high polarity (ethanol and acetonitrile), with adsorption onto paper and inclusion in β-cyclodextrin suggest that in these media the possible electronic relaxation process is prevented.

Fluorescence and Lifetime During the Sol−Gel Process. Most silicate sol−gels absorb at wavelengths below about 300 nm. However, the doped matrix with (4-ethoxyphenyl)urea give an noticeable signal in the experimental and instrumental conditions used, as observed in the spectra of Figure 2.

The sol−gel−xerogel transition in TEOS system doped with (4-ethoxyphenyl)urea occurs with a slight red-shift of 3 nm in the excitation maximum, an increase of the ratio of excitation maxima intensity (I_{ex2}/I_{ex1}) and a decrease in the lifetime.

The slight red-shift of 3 nm observed during the sol−gel process can be attributed to the increase of (4-ethoxyphenyl)urea concentration due to solvent evaporation.

The increase of the ratio of excitation maxima intensity can be due to matrix absorption. When the condensation reactions occur, the absorption by the probe molecule at the short wavelength (λ_{ex} = 274 nm) decreases, the reason can be the filtering effect of the forming matrix.

The decay−relaxation lifetimes have been closely associated with viscosity-inhibited molecular motions.[27,28] In the absence of strong solute−solvent interactions, molecular reorientation time is a function of solution viscosity. An increase in the microviscosity of the matrix around the doped molecules is required for the prevention of the possible electronic relaxation process. The gelification occurs with an increase of macroscopic viscosity. However, the lifetime of (4-ethoxyphenyl)urea decreases during the sol−gel process (Figure 4), and this seems to indicate that the sol−gel process does not occur with a microviscosity increase in the pores with molecules of (4-ethoxyphenyl)urea and solvent. The two obtained lifetimes of (4-ethoxyphenyl)urea in gel state can be attributed to the presence of two emitting species. The short lifetime can be assigned to the molecules on the pores, and the long lifetime is assigned to the molecules with nonspecific molecular interactions. In this case, the decay−relaxation lifetimes are much long, in a manner similar to the highly viscosity environments (glycerol viscosity 2330 cp lifetime 1.55 ns).

The change in the lifetime suggest that the microenvironment surrounding the doped (4-ethoxyphenyl)urea molecules is directly related to the gelation time. Figure 4 show that the marked changes in this property of trapped (4-ethoxyphenyl)urea during the sol−gel process can be used as a measurement of the gelation time.

Mobility of the Doped Molecules. The decrease of fluorescence intensity in the gel and the increase in water after incubation indicate the transfer of (4-ethoxyphenyl)urea from gel to solution. These results are predictable because the water is hydrogen bonded to the silica cluster,[10] thus the silica ring without water is uniform. However, the ring with the water adsorbed is elongated along the axis with the water, and low molecular weight substances tended to leach out of the glass by diffusion through the pores.

Conclusions

From the study of the fluorescence and time-resolved fluorescence of (4-ethoxyphenyl)urea during the sol−gel transition of the TEOS system catalyzed by HCl, it is possible to elucidate physical changes of the system. The sudden changes in fluorescent properties near the gelation time are useful as a measuring gelation point. Thus it can be concluded that the lifetime of (4-ethoxyphenyl)urea molecules is a useful photophysical probe for determining the structural changes during the sol−gel−xerogel transition.

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