Role of the Comonomer GLYMO in ORMOSILs As Reflected by Nile Red Spectroscopy

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The spectroscopy of nile red (NR) was reported when incorporated in organically modified silicates (ORMOSILs), obtained by the copolymerization of (glycidoxypropyl)trimethoxysilane and tetramethoxysilane in various proportions. An increase of the fluorescence intensity, a gradual blue spectral shift by 43 nm in absorption and 45 nm in emission, and a change in the lifetime from 2.6 to 4.4 ns of the dye were observed as a response to the change of the polarity and the structure of the ORMOSILs caused by the addition of (glycidoxypropyl)t-rimethoxysilane. The decrease of the nonradiative H^+-NR form was observed as one of the consequence of addition of (glycidoxypropyl)trimethoxysilane. Absorption spectral shifts of the NR were used for the determination of a polarity empirical scale (E_{NR}) of the ORMOSIL. The value of $E_{NR}(r_{0/100}) = 48.70$ kcal/mol for NR in silica xerogels prepared from tetramethoxysilane and $E_{NR}(r_{100/0}) = 52.55$ kcal/mol for NR in ORMOSILs prepared from (glycidoxypropyl)trimethoxysilane showed the high polarity of the inorganic matrixes in contrast to ORMOSILs. A study in solution was performed in order to make a concluding comparison of the NR behavior in terms of the restricted environment around the NR molecule ORMOSILs.

Introduction

Pioneering studies about organically modified silicates (ORMOSILs) were reported by Schmidt in the early 1980s.[1] Organoalkoxysilanes have been widely used as the precursors in the preparation of ORMOSILs, in which organic and inorganic phases were chemically bonded. Organoalkoxysilanes could be used as comonomers to modify the structural properties of the hybrid material and to introduce new functionalities inside the hybrid network that are required for different applications[2−7] Those are of special importance for optical applications, where the incorporation of dyes in OR-MOSILs has a great scientific interest and has been extensively studied.[8−17] The optical properties and photostability of these dyes should be enhanced by knowledge of the nature of the local chemical environment around the trapped molecules. Usually, for a detailed comprehension of the trapped molecule behavior with the chemical environment, molecular probes for different characterizations of sol−gel materials have been widely used.[18]

Polarity probes have been extensively used in a variety of chemical and biophysical systems. In sol−gel materials the polarity reflects intermolecular interactions between the guest molecules and the host matrix. Satisfactory descriptions of medium effects have to take into account all nonspecific and specific solute/solvent, solvent/solvent, and, at higher concentrations, even solute/solute interactions. "Solvent polarity" is defined by Reichardt as the overall solvation capability of the solvent, which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding, however, those interactions leading to definite chemical alterations of the ions, or molecules of the solute (protonation, oxidation, etc.).[19]

Pyridinium *N*-phenoxide betaine (E_T-30) is one of the most solvatochromic probes known, and it has been also used as empirical scale of solvent polarity but is

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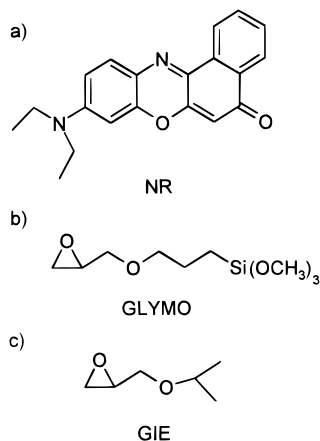(19) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

Figure 1. Structures of NR (a), (glicidoxypropyl)trimethoxysilane (b), and glycidyl isopropyl ether (c).

extremely sensitive to hydrogen-bonding solvents and proton donor/acceptor solvents; i.e., the E_T-30 dye is susceptible to a loss of molar absorptivity in the presence of acid. This molecule was used in hybrid silica matrixes to follow the variations in the cage interfacial polarities of ORMOSILs prepared by the sol−gel process from various proportions of methyltrimethoxysilane/tetramethoxysilane (TMOS)[20] and for characterization of the surface of the interfacial polarity of the polymer/solid interaction.[21] However the E_T-30 dye has very low molar absorbance in some silica matrixes made by the sol−gel process.[22] Fluorescence measurements can also reflect the polarity properties of the ORMOSILs cage,[23] but betaine dyes and their derivatives are not fluorescent. Recently flavins have been used for these studies.[24]

The phenoxazine dye 9-diethylamino-5*H*-benzo [α]-phenoxazin-5-one, NR (Figure 1), in contrast, is an efficient laser dye with high photochemical stability.[25] The synthesis of NR in acid solutions and its low basicity ($pk_a \sim 1$)[26] indicates stability toward an acid environment.[27] NR is an uncharged polarity probe and exhibits one of the largest known bathochromic shifts with increase in solvent polarity.[19,28] Absorbance maximum of NR does not appear to shift significantly when subjected to hydrogen bonding; however, the protonated form of NR can be formed in acidic environment, and the spectral behavior will be useful to complete the environment information. NR is soluble in a wide range of solvents and supercritical fluids, and it has been used as an empirical scale for solvent polarity.[28−30] Thus, the spectroscopic properties of NR are altered by the effective polarity of the environment and this may be

explained in terms of twisted intramolecular charge transfer (TICT). NR has been widely used in solvents,[28−34] lipids,[35−37] reverse micellar systems,[38,39] proteins,[40−42] enzymes,[43] polymers,[34,44] Langmuir−Blodgett films,[45] and zeolites.[46] Absorption measurements of NR have been reported by Lobnik and Wolfbeis[22] to obtain information about the polarity in ORMOSILs layers prepared with different proportions of TMOS and phenyltrimethoxysilane, octyltrimethoxysilane, or methyltrimethoxysilane. Matsui and Nozawa[47] used absorption and fluorescence measurements of NR to study ORMOSILs polarity of xerogels prepared from TMOS, tetraethoxysilane, triethoxysilane, and triethoxymethilsilane and established the hydrophobicity of different ORMOSILs.

In this work we determined, through NR spectroscopy, the role of the comonomer (glycidoxypropyl)trimethoxysilane (GLYMO), which was used in ORMOSILs preparations obtained from the copolymerization of GLYMO and TMOS in various proportions. We first focused on the NR protonation (H$^+$-NR) which can take place in a very acid environment and the effect of the organic groups on the NR spectroscopy. Then, the behavior of the absorption, the fluorescence steady state and the dynamic state spectroscopy of NR with the structural properties of the ORMOSILs were correlated. These studies have been complemented with different analytical techniques such as ^{29}Si NMR, FTIR, TEM, and BET. In this work, also it has been examined the restricted geometry from ORMOSIL cages on the TICT behavior of NR. Due to the fact that GLYMO is one of the most important comonomers in the preparation of hybrid materials,[2,48−52] the polarity of the ORMOSIL cages in terms of transition energies of NR (E_{NR}) was evaluated by semiquantitative means.

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Experimental Section

Materials and Sample Preparation. NR, alkoxides, and solvents were of the highest purity commercially available and were not further purified. NR, TMOS 99+%, GLYMO 96%, and GIE (glycidylisopropyl ether) 98% were from Aldrich and methanol (spectroscopic grade) was from Merck.

In this study different molar percentages ratios of GLYMO and TMOS were used to prepare hybrid sol−gel matrixes. Samples were named by $r_{G/T}$, i.e. for samples prepared without acid, and $r_{G/T}(ac)$, for samples prepared with acid, with G (G = 0, 20, 40, 60, 80, and 100) being the molar percent of GLYMO and T (T = 100, 80, 60, 40, 20, and 0) being the molar percentage of TMOS. A 13.5 mmol amount of alcoxide, 5 × 10^{-2} mmol of NR dissolved in 49.3 mmol of methanol, and 50.5 mmol of water were used the initial solution under stirring by several hours. The solution was poured in beakers, and after the gelation point the weight lost was controlled until a constant weigh was achieved. The concentration of NR used in solutions was 1.88×10^{-6} M, and the solvents were glycidyl isopropyl ether (GIE), methanol, and water in different percentages in volume.

Instrumentation. Steady-state and phase-modulation measurements were performed at 25 °C on a 48000 (T-Optics) spectrofluorometer from SLM-Aminco. The instrument is configured for software-controlled variable frequency light modulation from 100 Hz to 120 MHz. Samples were measured as powder in quartz cells with 1 mm path length, in front-face geometry in order to minimize light scattering form the excitation beam. Spectral modifications are not observed with different concentrations of NR, so the same unique concentration has been chosen for these studies.

Reflectance measurements of NR-doped xerogels were performed on a Varian 2300 UV−vis−NIR spectrophotometer. The samples were grounded in a fine powder and placed in a quartz cuvette.

The infrared studies were carried out in a Nicolet FT-IR spectrophotometer Model 20SXC for samples diluted in KBr at 2%.

The specific surface area (S_A) was obtained using a surface area analyzer Micromeritics ASAP 2010. The samples were degassed for 3 days without heat treatment. BET (Brunauer−Emmett−Teller) analysis was used to calculate surface areas on the basis of the N_2 adsorption isotherms.

The ^{29}Si NMR measurements were measured on a Bruker MSL 400 MHz (solids) spectrometer operating under a static magnetic field of 9.4 T. The radio frequency of 79.4 MHz was used for the detection of ^{29}Si resonance. The measurements were conducted by a magic angle spinning (MAS) method with a 5 s cycle time. The samples were spinning at 4000 c/s. The $\pi/2$ pulse used was 6 μs, and the spectra were accumulated at 1000 ac. A Gaussian function was chosen for deconvolution of NMR spectra, and then with application of a mathematic fit, the concentration of each species was obtained.

Results and Discussion

1. NR Absorption Spectral Behavior in OR-MOSILs. The behavior of the absorption spectra of NR in ORMOSILs prepared from different GLYMO (Figure 1) to TMOS molar ratios is shown in Figure 2a. The samples prepared from $r_{0/100}$ showed a single broad band around 587 nm; however, a shoulder around 650 nm can be observed when the sample was prepared from $r_{20/80}$. When the amount of GLYMO increases to $r_{50/50}$, the changes in the absorption spectra were related to a decrease of the intensity of the band around 650 nm and a blue shift of ∼30 nm for the 590 nm band. In samples prepared from $r_{60/40}$ the longer wavelength absorption band has disappeared almost completely and the blue shift was ∼50 nm. The 650 nm absorption band fully disappeared in the absorption spectra of the sample
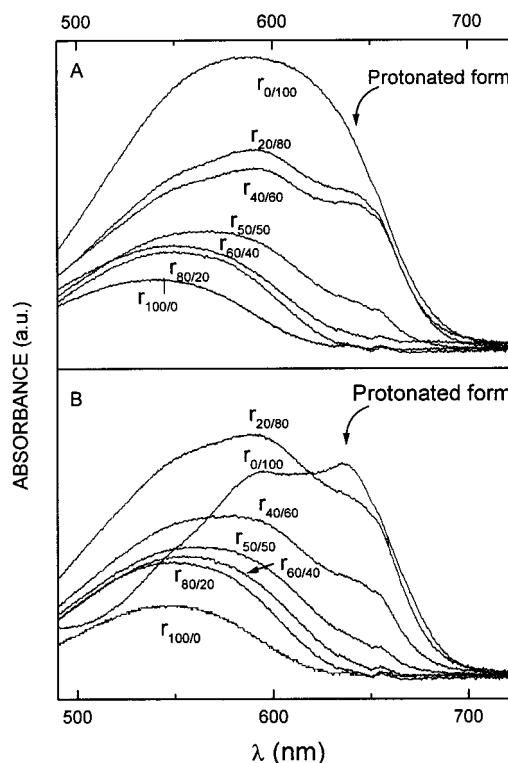

Figure 2. Reflectance spectra of NR in ORMOSILs xerogels with different $r_{G/T}$ values for nonacid (a) and acid (b).

$r_{80/20}$. When $r_{100/0}$ is achieved, a single band with low intensity in the spectra can be observed at 544 nm. The intensity decrease of the band at high wavelengths could be explained in terms of NR protonation (H$^+$-NR) which can take place in an acid environment.[27] Then, to identify the origin and the spectral behavior of this band in specific $r_{G/T}$ compositions shown in Figure 2a, the same batch of samples was prepared, but hydrochloric acid was also added into the initial solution of every $r_{G/T}(ac)$ composition.

The behavior of the absorption spectra of NR in ORMOSILs prepared from different $r_{G/T}(ac)$ in acid conditions is shown in Figure 2b. As compared to samples without acid, the samples prepared from $r_{0/100}(ac)$ showed two absorption bands at 650 nm and at 590 nm. By addition of GLYMO to the original preparation $r_{20/80}(ac)$, a decrease of the absorption intensity of the band at 650 nm was observed with respect to the significant increase of the band at 590 nm. The further increase of the amount of GLYMO to reach $r_{100/0}(ac)$ allows the decrease of the absorption intensity of the band at 650 nm as in samples without acid. However, the samples prepared from $r_{0/100}(ac)$ give rise to clear evidence that this band is certainly related to the protonation of NR, but this effect is completely hidden when GLYMO is added. These results indicated an active participation of GLYMO in the samples where NR is allocated in an acid environment.

The addition of GLYMO in xerogels allows for the decrease of the effective concentration of protons and silanol groups (weak acids p$k_a \approx$ 7.1),[53] through the chemical reactions of the epoxy groups[2,49,54,55] to the

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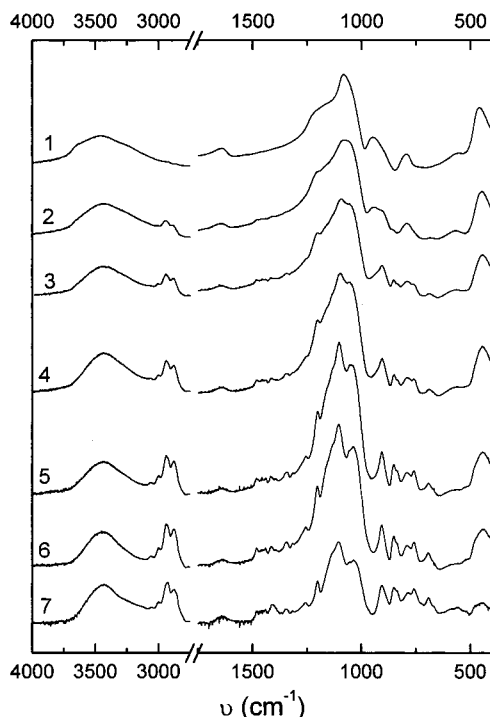(55) Xue, G. *Angew. Makromol. Chem.* **1986**, *140*, 127.

Figure 3. FTIR spectra of NR in hybrid matrixes with different $r_{G/T}$: $r_{0/100}$ (1); $r_{20/80}$ (2); $r_{40/60}$ (3); $r_{50/50}$ (4); $r_{60/40}$ (5); $r_{80/20}$ (6); $r_{100/0}$ (7).

Figure 4. Normalized and nonnormalized fluorescence spectra ($\lambda_{exc} = 530$ nm) of NR in ORMOSIL xerogels with different $r_{G/T}$ values.

Table 1. Spectral Properties of NR in ORMOSIL Xerogels with Different $r_{G/T}$

sample	λ_{ab} (nm)	λ_{em} (nm)^a	τ_1 (ns)	τ_2 (ns)	fi$_1$^{b}	χ_R^2
$r_{0/100}$	587	670	2.60	1.23	6.88	1.6
$r_{20/80}$	590	675/644	3.59		1.00	0.8
$r_{40/60}$	590	633/675	4.13		1.00	1.8
$r_{50/50}$	569	638+666 (shoulder)	4.43		1.00	0.5
$r_{60/40}$	550	633	4.40		1.00	0.2
$r_{20/80}$	550	634	4.46		1.00	0.3
$r_{100/0}$	544	625	4.40		1.00	0.9

^{a} $\lambda_{ex} = 530$ nm. ^{b} fi$_1$ + fi$_2$ = 1.

formation of diol units by hydrolytic ring opening, or it can undergo polyaddition. The chemical reactions of the epoxy group of GLYMO in aqueous solution were studied by FTIR spectra in samples prepared without acid (Figure 3). Neither indication about the formation of diol groups nor the characteristic absorption bands of the epoxy group reactions were observed. However the absorption bands ascribed to the epoxy group at 3060, 1250, and 910 cm^{-1} [2,56] are shown in Figure 3. Therefore, these results indicated that the effective concentration of protons was not decreased by chemical reactions of the epoxy groups. The changes derived from addition of GLYMO also showed a decrease of the Si–OH groups and the peaks of hydrogen-bonded SiO–H stretching vibration bands at 3640 and 950 cm^{-1} (Figure 3).

Thus, from the point of view of NR in ORMOSILs, the effect of addition of GLYMO on the decrease of the H$^+$-NR form is related to a strong effect of protection to protons from Si–OH or from the acid environments. By protection it is suggested that glycidoxypropyl groups would form an effective barrier like against protonation of NR molecules. FTIR results also showed that the decrease of the acidity of the environment by the decrease of silanol groups can also contribute to the decrease of H$^+$-NR forms.

2. NR Fluorescence and Lifetime Behavior in ORMOSILs. NR fluorescence and lifetime measurements were very helpful to clarify the properties of the ORMOSIL cage. The study of NR has been first performed in the starting sols (after 1 h of the preparation of the starting solution) and also in water/methanol solutions for comparison and second in different ORMOSIL ($r_{G/T}$) cages.
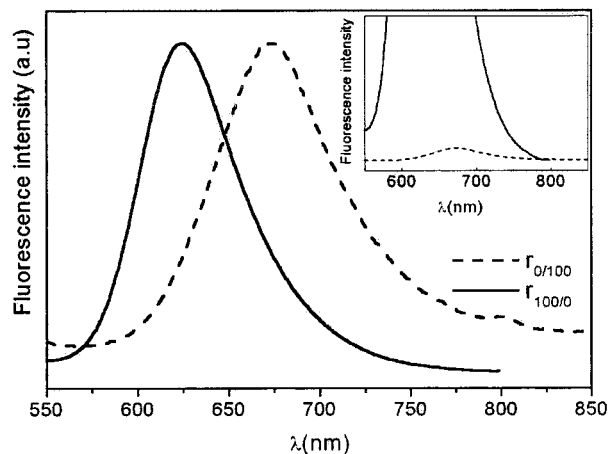
The fluorescence spectra and lifetimes for all starting sols have shown the same spectral results, i.e., the same fluorescence emission maximum around $\lambda_{em} = 640$ nm and a single lifetime around $\tau = 2.4$ ns. The NR behavior in sols with different $r_{G/T}$ indicated that NR was affected by water and methanol. The NR spectral behavior found in methanol and in water was $\lambda_{em(CH_3OH)} = 645$ nm, $\tau_{CH_3OH} = 3.06$ ns and $\lambda_{em(H_2O)} = 658$ nm, $\tau_{H_2O} = 1.45$ ns (12% of methanol was required for dissolution of NR). The NR behavior in a methanol/water solution (50% v/v) was $\lambda_{em} = 649$ nm and the $\tau = 2.4$ ns. Due to that the fluorescence and lifetime results of NR in these solutions were similar to the results obtained from NR in the sols, we can confirm that NR molecules were located, at the beginning of the process, in an environment in which water and methanol are neighboring the NR molecules.

Concerning the ORMOSILs, as previously shown in the absorption spectra in Figure 2a, the increase of $r_{G/T}$ causes a blue shift in the fluorescence emission maximum (Figure 4 and Table 1) from 670 nm in samples with $r_{0/100}$ to 625 nm in samples with $r_{100/0}$. The lifetime of samples prepared from $r_{100/0}$ was $\tau = 4.4$ ns; however, the lifetime from samples with $r_{0/100}$ showed two different values $\tau_1 = 2.60$ ns and $\tau_2 = 1.23$ ns. The two lifetimes may be attributed to the different locations of NR molecules inside the pores.[57] However, the blue shift and the increase of the fluorescence intensity can be interpreted in terms of the polarity influence of the environment inside the pores on the NR molecules. The photophysics of NR is characterized by two excited states: the nonpolar excited state with near planar geometry and dipolar moment similar to ground state

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($\mu \sim 8.9$ D) and the polar twisted intramolecular charge transfer (TICT) state with twist geometry and higher dipolar moment ($\mu \sim 14.4$ D).[58] Thus, changes in the excited-state dipole moment of the molecule cause geometrical distortion of the molecule in the excited state. The relaxation of the nonpolar state to TICT state is shown in a red shift in the emission and absorption spectra and a decrease of the lifetime. Energy transfers of an electron from NR flexible diethylamino end group (donor) to the rigid benzonitrile group (acceptor) bonded by a flexible single bond leads to the twist conformation of the NR molecules. When the conformation is near-planar, interaction between the donor and acceptor takes place and gives rise to a decrease of the dipole moments (nonpolar excited state).[59,60] When the π-systems are orthogonally and thus decoupled orbitals, a maximum for the dipole moment in the excited state TICT is produced, and then the twist activation barrier decreases linearly with the increase of the solvent polarity.[61] This suggests that the main cause for the spectral blue shift, as well for the increase of the fluorescence intensity (Figure 4, inset) and the increase of the lifetime, is the decrease of the polarity around NR molecules.

The results from the fluorescence spectra corroborated the explanations on the spectral shifts in the absorption spectra. Then, we can evaluate the ORMOSIL cage polarity from the absorption spectral shifts of the NR. E_{NR}, as a polarity empirical scale, designates transition energies of NR (from absorption maximum in Table 1). Deye presented NR transition energies for a large number of solvents.[28] The $E_{NR}(r_{0/100}) = 48.70$ kcal/mol (near water value $E_{NR}(H_2O) = 48.21$ kcal/mol[28]) calculated for xerogels prepared from $r_{0/100}$ shows the high polarity of the inorganic matrixes in contrast to OR-MOSILs prepared from $r_{100/0}$ with $E_{NR}(r_{100/0}) = 52.55$ kcal/mol, the same value of E_{NR} as for 1-octanol.[28]

Therefore, the absorption and fluorescence spectra and the lifetime behavior of NR are shown as satisfactory tools to examine the environment properties of ORMOSIL cages.

3. Structural Properties and Polarity of OR-MOSILs. Due to the influence of the structural properties of ORMOSILs on the steady-state and the dynamic response of NR, the correlation between the structural properties of ORMOSILs and their polarity was also investigated. ^{29}Si NMR was used as an analytical tool to analyze the structure of the ORMOSILs, since different chemical environments of the Si nucleus can be recognized. The notation of the ^{29}Si NMR lines is represented for T_i ($i = 0-3$) and Q_i ($i = 0-4$), if the precursors for the siloxanes bonds are trifunctional or tetrafunctional alkoxides, respectively. The spectra were deconvoluted and the concentration of Q_i and T_i species was obtained (Figure 5) for ORMOSILs with different $r_{G/T}$. The results obtained for the sample $r_{0/100}$ showed
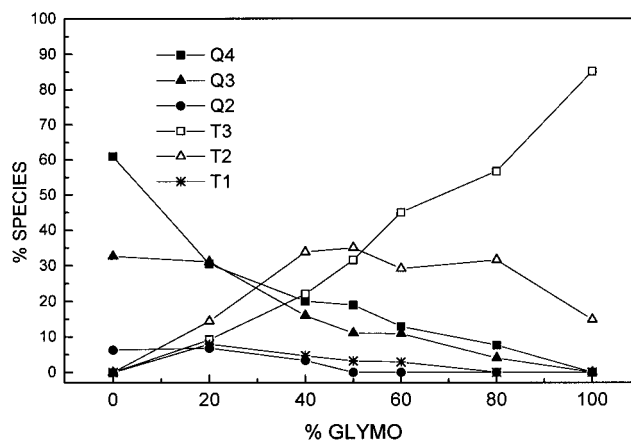
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Figure 5. Relative amounts (%) of Q_n and T_n from NMR [29]Si spectra of ORMOSIL xerogels with different $r_{G/T}$ values as a function of the different G values.
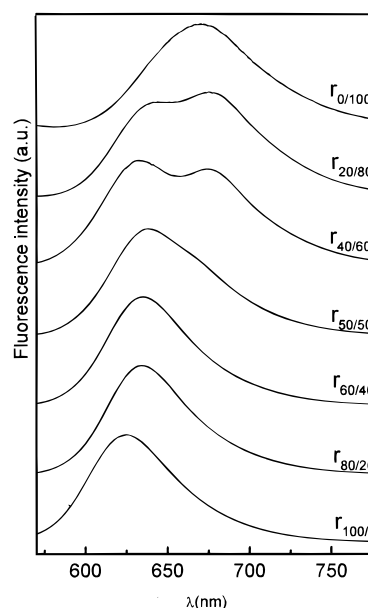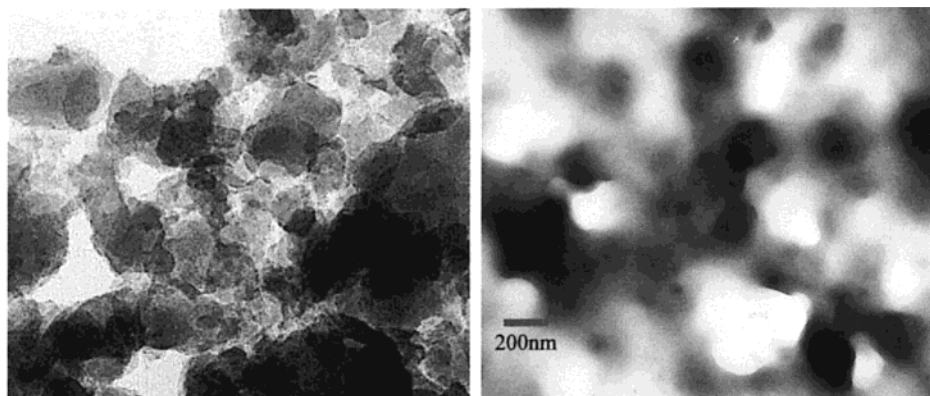

Figure 6. Fluorescence spectra of NR in ORMOSIL xerogels with different $r_{G/T}$ values. The excitation wavelength was $\lambda_{exc} = 530$ nm for all spectra.

high percentages of Q_4 (61%) and a low percentage of Q_3 (32%) and Q_2 (6%). The fluorescence and lifetime behavior (Figure 6, Table 1) showed an emission band at 670 nm and two lifetimes $\tau_1 = 2.6$ ns and $\tau_2 = 1.23$ ns, which correspond to NR molecules in twist conformation nearest a cage polar environment formed by Si–OH and Si–OCH$_3$ groups as reflected by Q_3 and Q_2.

The emission spectrum for the sample $r_{20/80}$ results in a red shift from 670 to 675 nm of the TICT emission band and the formation of a shoulder at 642 nm. The red-shift arises from the partial contributions of the emission of near-planar molecules in the nonpolar excited state, which appeared as a shoulder (Figure 6). This shoulder is related to the contributions of NR molecules near T_2 (14.43%), T_3 (9.24%), and T_1 (7.94%) oligomers, which indicate that pores are formed also by nonhydrolyzed and less polar glycidoxypropyl groups. By the addition of GLYMO, a decrease in the electron-transfer processes (higher energy barrier) induced an increase of the emission from the nonpolar state. Concerning the polar band at 675 nm, the TICT excited states are located nearest to Q_4 (30.47%) and Q_3

Figure 7. TEM images for ORMOSIL xerogels with $r_{G/T}$: $r_{0/100}$ (a); $r_{100/0}$ (b).

(31.10%). In regard to the effect of the environment on the lifetime, a single lifetime can be observed for these samples. The shorter lifetime ($\tau_2 = 1.23$ ns in samples with $r_{0/100}$) was not found in these samples, but an increase of the lifetime from $\tau_1 = 2.60$ ns (samples with $r_{0/100}$) to $\tau = 3.59$ ns (samples with $r_{20/80}$) was obtained (decrease of the nonradiative emission of molecules to TICT excited state). Then, we can assume that, with this composition, the NR environment begins to be less polar.

When the percentage of GLYMO is further increased to $r_{40/60}$ (Figure 5), the proportion of T_3 (22%) and T_2 (34%) with regard to Q_4 (20%) and Q_3 (16%) accordingly showed the higher proportion of glycidoxypropyl groups, which correspond to the decrease of silanol and methoxy groups. The changes in the fluorescence spectra of these samples showed to some extent how the contribution of the hydrophobic and the hydrophilic groups can affect the fluorescence behavior (Figure 6). As a consequence of an increase of the T_3 and T_2, an increase of the nonpolar emission band at 633 nm can be observed, while the decrease of the Q_4 and Q_3 is accompanied by the decrease of the polar emission band at 675 nm. Accordingly with the decrease of the environment polarity, the lifetime increases to $\tau = 4.13$ ns. In samples prepared from $r_{50/50}$, the emission maximum gradually shifted to the nonpolar emission band (Figure 6). Under this situation, the energy barrier toward a TICT state is higher due the decrease of the polarity of the environment, and therefore, there is a decrease of the TICT emission.

In samples prepared with higher amounts of GLYMO, from $r_{60/40}$ to $r_{100/0}$, T_3 species (>45%; Q_4 and Q_3 < 10%) were practically governing the surface composition. The presence of hydrophobic groups linked to the silicon atoms seems to favor the elimination of residual alkoxy and hydroxyl groups, allowing a high degree of condensation, although the cross-linking degree from matrixes prepared from trialkoxysilanes is lower. Under this situation, a blue spectral shift is observed, the twist emission was not shown, and the lifetime obtained ($\tau = 4.40$ ns) was not affected. This behavior is reasonably expected due to 4.40 ns is the higher lifetime value obtained by NR in a GIE solution (Figure 1), where the dye is surrounded only by groups very similar to glycidoxypropyl groups. Only the fraction of NR molecules bound to glycidoxypropyl groups contributes effectively to the total emission. Battachayya and Chowdhury observed a similar effect in a fluorescent

molecule with TICT properties as TNS in reverse micelles.[62] However, when the lowest polar degree in ORMOSILs prepared from GLYMO was reached, a blue spectral shift from 633 to 625 nm was observed for the nonpolar band, showing that fluorescence spectroscopy is a very sensible technique to analyze the changes in ORMOSILs.

4. Restricted Environment and the Spectral Behavior of NR in ORMOSILs. The spectral behavior of the NR-doped molecules in ORMOSILs was explained in terms of polarity; nevertheless a gel cage could affect the intramolecular motion and, therefore, a restricted environment (in terms of rigidity and amount of free volume around the NR molecule) could impede the formation of the TICT state.[63–65] Al-Hassan et al.[63,64] have shown the role of free volume in TICT emission of dimethylaminobenzonitrile in rigid polymers. The increase of the free volume was shown by the increase of the TICT band.

Through the fluorescence study, we observed that in samples prepared from $r_{0/100}$ there is enough free volume to allow the torsion required by the NR molecules to adopt a twist motion in the excited state. However, in $r_{100/0}$ matrixes where the fluorescence results showed the NR as a near planar molecule, a clarification of the question on the origin of the spectral results was related either to the environment polarity or to the restricted environment is necessary.

Concerning the restricted environment, we have complemented the spectral analysis with other analytical tools such as TEM and BET. BET measurements for the sample $r_{0/100}$ showed a $S_A = 494.5$ m^2/g, while the other matrixes showed the same S_A < 20 m^2/g. The S_A of the sample $r_{0/100}$ and the isotherm behavior (data not shown) were typical of a porous material, while for the ORMOSIL $r_{100/0}$ corresponded to a nonporous material. However, the examination of the samples by TEM (Figure 7) showed a porous microstructure in both cases. From the S_A and isotherms results, it is thus appropriate to assign the ORMOSIL pores as the most feasible allocation of the glycidoxypropil groups. The TEM image showed an inorganic network filled with an organic material (Figure 7b). Therefore, the glycidoxypropyl groups inside the pores could be avoiding the twist

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motion by a decrease of the free volume around the NR molecule.

Finally, GIE and GIE/MeOH were used in order to make a concluding comparison of the NR behavior between a restricted and a nonrestricted environment, in which similar groups are surrounding the NR molecules. $E_{NR} = 53.84$ kcal, $\tau = 4.4$ ns and $E_{NR} = 52.46$ kcal, $\tau = 3.92$ ns were obtained for NR in GIE and in GIE/methanol (33% v/v), respectively. When comparing to ORMOSILs prepared from $r_{100/0}$ ($E_{NR} = 52.55$ kcal, $\tau = 4.4$ ns), we found that they are in agreement with the behavior of NR in solution. Therefore, it seems that the main parameter governing the NR spectral behavior is the polarity environment rather than the restricted environment.

Conclusions

We conclude that the absorption, fluorescence, and lifetime measurements of NR are shown as satisfactory tools to examine the environment properties of ORMO-SIL cages. We found that the effect of addition of GLYMO on the decrease of the nonradiative H^+-NR form is related to a strong effect of "protection" to protons from Si–OH or from the acid environments. Glycidoxypropyl groups form an effective barrier like against protonation of NR molecules. Concerning the ORMOSIL cage polarity, we determined the $E_{NR}(r_{0/100})$

$= 48.70$ kcal/mol and $E_{NR}(r_{100/0}) = 52.55$ kcal/mol that showed the high polarity of the inorganic matrixes in contrast to ORMOSILs. The main cause for the spectral blue shift, as well for the increase of the fluorescence intensity and the increase of lifetime, is the decrease of the polarity around NR molecules with increase of the amount of glycidoxypropyl groups. When the lowest polar degree was reached, only the nonpolar band is observed, showing that fluorescence spectroscopy is a very sensible technique to analyze these changes in ORMOSILs.

The study on the behavior of NR in solution concluded that it seems that the main parameter governing the NR spectroscopy is the environment polarity rather than the restricted environment imposed by the ORMOSIL cages.

The knowledge, through NR spectroscopy, of the GLYMO–TMOS ORMOSIL behavior will be very useful to achieve environmental conditions and cage properties that should be required in sol–gel preparations for certain applications.

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