Probing the Microenvironment of Polymer-Impregnated Composite Glass Using Solvatochromic Dye

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Poly(methyl methacrylate) (PMMA)-impregnated silica composite glasses are hosts for organics in advanced optics applications. The advantages of composite glasses are their high optical quality and mechanical strength. Composite glasses are composed of a silica skeleton which contains narrow channels. Organic polymeric chains such as longitudinal PMMA chains fill these channels to form an inorganic:organic composite glass. Using 6-propionyl-2-(dimethylamino)naphthalene (PRODAN), a solvent-sensitive dye, we probed the local microenvironment in these PMMA/silica composite glasses using steady-state and time-resolved fluorescence. The steady-state fluorescence results clearly demonstrate that the Stokes shifts ($\Delta\tilde{\nu}$) obtained for PRODAN in solid matrices (composite glass, pure PMMA, and pure silica-gel glass) are in good agreement with the expected dependence in orientational polarizability (Δf) obtained for liquid solvents. These results also demonstrate that the dye molecules are primarily surrounded by a PMMA-like environment, but there is a distinct influence of the silica skeleton and the hydrogen bonds which connect the silica matrix and PMMA. The time-resolved fluorescence results also suggest a multidomain microenvironment for the PRODAN molecules within the composite glass.

Introduction

The realization of photonics technology rests on the development of novel materials which simultaneously satisfy many functional requirements.[1] A promising class of material is the sol–gel-derived inorganic:organic hybrid composite glasses which combine the merits of an inorganic glass and an organic polymer. A novel way to prepare high optical quality nanocomposite monoliths with the desired mechanical properties is to form a template gel, by the sol–gel process, diffuse an organic monomer into the open gel pores, and polymerize therein.[2–4] This method has been used previously to prepare silica:poly(methyl methacrylate) (PMMA) composite glass for photonics applications such as lasing,[5–7] optical power limiters,[8,9] optical switches,[10] and optical storage devices.

Although promise of these organic polymer:inorganic composites is evident, it is also clear that achieving good optical performance from an active organic molecule doped within a composite glass requires an understanding of how the evolving composite matrix affects the active molecule entrapped within the composite glass. One of the most convenient methods to investigate the physicochemical properties within such a composite is to use a solvent sensitive probe doped into the glass matrix.[11–21] 6-Propionyl-2-(dimethylamino)naphthalene (PRODAN), whose molecular structure shown in Figure 1, is a solvent-sensitive probe[22] and has been previously used to investigate the cybotactic region in tetramethylorthosilicate-derived sol–gels (TMOS sol–gels).[14] In

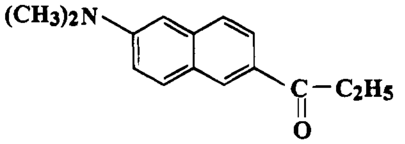

Figure 1. Molecular structure of 6-propionyl-2-(dimethylamino)naphthalene (PRODAN).

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this paper, we report on the photophysics of PRODAN entrapped within a PMMA:silica composite glass.

The influence of the solvent on the spectroscopy of dyes is usually determined in a qualitative and comparative method.[23-26] A relative scale of *solvent polarity* has been previously used[23-26] based on the shift of the absorption maxima relative to a standard solvent. This scale depends on the nature of the dye and the solvent surrounding the dye molecules. A more quantitative scale for *solvent polarity* is based on measuring the orientational polarizability (Δf) of the medium surrounding the dye.[27] The orientational polarizability (Δf) is defined as[27]

$$\Delta f = f(\epsilon) - f(n) \tag{1}$$

where $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$; $f(n) = (n^2 - 1)(2n^2 + 1)$; ϵ is the low-frequency relative dielectric constant, and n is the optical refractive index in the visible.[28]

The interaction between the (host liquid solvent or solid matrix) and the dye molecules, affects the ground and the excited state energies (i.e., the absorption and emission maxima, as well as the Stokes shift $\Delta\tilde{\nu}$) of the dye molecules. To a first approximation, the Stokes shift is a function of the orientational polarizability and is given by the Lippert expression:[27]

$$\Delta\tilde{\nu} \equiv (\tilde{\nu}_a - \tilde{\nu}_e) = (\tilde{\nu}_a - \tilde{\nu}_e)_v + 2(\mu^* - \mu)^2 \Delta f/hca^3 \tag{2}$$

where $\tilde{\nu}_a$ is the wavenumber of the absorption peak, $\tilde{\nu}_e$ is the wavenumber of the emission peak, $(\Delta\tilde{\nu})_v = (\tilde{\nu}_a - \tilde{\nu}_e)_v$ is the Stokes shift of the molecule in the vapor state, μ and μ^* are the ground and excited-state dipole moments, respectively, h is Planck's constant, c is the speed of light, and a is the characteristic dimension of the molecule probe.

More detailed information regarding the microenvironment of the entrapped molecule within a composite glass can be achieved by time-resolved fluorescence spectroscopy. Previously, Narang et al.[14] studied PRODAN-doped TMOS-derived sol–gel microenvironment using frequency-domain fluorescence spectroscopy.[14] They reported that a unimodal Gaussian distribution best describes the experimental intensity decay thus demonstrating that the microenvironment around the PRODAN molecules within a sol–gel matrix is heterogeneous. In another report, using the same technique as Narang et al., Monte and Levy investigated the microenvironment of TMOS sol–gels doped with hexamethylindotrycarbocyanine iodide (HITC) and oxazine-1.[29] They also report a heterogeneous microenvironment for the TMOS sol–gels and suggest a two-domain model.

In this report, we investigated the Stokes shift as a function of the orientational polarizability of PRODAN in various liquid solvents and solid matrices. To get more insight into this system, we studied the fluorescence excited-state decay kinetics using multifrequency phase and modulation fluorometry. These methods allow one to probe the microenvironment around the doped dye molecules within a solid matrix. The solid matrices investigated are PMMA:silica composite glass, pure PMMA, and pure sol–gel glass.

Experimental Section

Sample Preparation. Solutions of PRODAN (1 μM) in various solvents were prepared as follows: First the dye was dissolved in ethanol to obtain a 100 μM solution. This solution (20 μL) was pipetted into fused silica cuvettes. The cuvettes were then kept in an oven (60 °C) for 5–10 min to evaporate the ethanol followed by the addition of 2 mL of the desired solvent to obtain a 1 μM PRODAN solution.

The preparation of dye-doped composite glasses followed the method described by Gvishi et al.[30] Highly porous silica gel bulk glasses were prepared by a two step hydrolysis sol–gel process.[31] We started from a precursor solution which contained tetraethoxysilane (TEOS) and ethanol in the molar ratio 1:4. After 1 h of prehydrolysis, water (molar ratio 4), and HNO_3 (molar ratio 0.06) were added to complete the hydrolysis. This was followed by the addition of HF (molar ratio 0.8) to achieve fast gelation. The solution was then covered with a lid having small orifices to allow the solvents to escape for aging at 40 °C for 1–3 weeks. The bulk gels were then dried by slow heating (60 °C/h) from room temperature to 500 °C. These glasses had an initial surface area of about 850 m^2/g, pore volume of 68%, and an average pore size of 46 Å (measured using nitrogen adsorption isotherms and calculated by the BET method).[32] These bulk glasses (dimensions 10 mm × 5 mm × 1–5 mm) were immersed in the methyl methacrylate (MMA) monomer solution containing PRODAN (1 or 100 μM) for 10–15 min. The MMA–dye solution diffused into the sol–gel-derived glass pores and were polymerized therein using benzoyl peroxide (2%) as the catalyst. The MMA-dye-doped bulks were reimmersed in a MMA–dye solution, which at this stage was catalyzed for full polymerization with benzoyl peroxide (0.5%), and kept in a sealed container at 40 °C until the polymerization process was completed (few days). After the completion of the polymerization process, the samples were withdrawn, cleaned with chloroform, and polished to obtain parallelepiped slabs with clear smooth surfaces. The polishing method consisted of the following stages: prepolishing on a SiC paper (300 and 600 grit in gradual steps) using deionized water as the lubricant, followed by fine polishing on cloth using 1 and 0.25 μm grade diamond pastes as abrasives. A commercial water-based fluid (Buehler) was used as the lubricant. The polishing procedures were performed manually on a Buehler polishing wheel. Good optical quality samples of 1 and 100 μM PRODAN-doped composite glasses were prepared using the method described above. The composite glasses were totally inactive for adsorbing nitrogen.[32]

Solid samples of dye-doped PMMA were also prepared from a MMA–dye solution which were polymerized using 0.5% benzoyl peroxide, and kept in a sealed container at 40 °C until the polymerization process was complete (few days). The polishing method was the same as detailed above. In this way, good optical quality of 100 μM PRODAN-doped PMMA bulk samples were prepared.

Fluorescence Measurements. The bulk of the instrumentation used for this work has been described in detail elsewhere.[33-35] All steady-state fluorescence measurements were performed (90° geometry) with an SLM 48000 MHF spectrofluorimeter using a xenon arc lamp as the excitation

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Table 1. Spectral Properties of PRODAN in Various Solvents and Solid Matrixes

no.	solvent	ex. max (nm)	em. max (nm)	$\Delta\tilde{\nu}$ (cm^{-1})	Δf^a	n	ϵ
1	cyclohexane	344	404	4317	0.000	1.424^b	2.015^b
2	chloroform	355	443	5596	0.148	1.446^c	4.806^c
3	acetone	350	450	6349	0.285	1.357^b	20.7^b
4	DMF	353	456	6399	0.276	1.427^b	37.57^b
5	acetonitrile	349	462	7008	0.304	1.342^b	33.59^b
6	ethanol	355	490	7761	0.289	1.359^b	24.30^b
7	water	351	527	9515	0.320	1.332^b	78.54^b
8	PMMA	365	425	3868	0.020	1.496^d	2.45^d
9	composite glass	354	448	5927	0.191	1.472^d	7.8^d
10	TMOS sol–gel	358	512	8401	~0.277	1.444^d	~55^e

[a] Orientational polarizability (Δf) is defined by eq 1 in the text. [b] Data for refractive index (n) and dielectric constant (e) are taken from ref 40 at 25 °C. [c] Data for refractive index (n) and dielectric constant (e) are taken from ref 40 at 20 °C. [d] Data for refractive index (n) and dielectric constant (e) are taken from refs 5 and 32. [e] Data are estimated following refs 13 and 41.

source. Excitation and emission spectra were background-subtracted and corrected for detector and monochromator transmission nonlinearities. Absorption measurements were done on a Shimadzu UV3101 spectrophotometer.

All fluorescence lifetime measurements were performed in frequency domain using a SLM 48000 MHF spectrofluorimeter with the use of a modified version of the instrument described by Bright.[35] In the frequency domain, the sample under study is excited with high-frequency (MHz–GHz) sinusoidal modulated light, and one measures the frequency-dependent phase shift ($\theta(\omega)$) and modulation ($M(\omega)$) of the resulting emitted light. From the data, one can extract the corresponding excited-state decay kinetics using appropriate decay models.[36–38] A more detailed discussion of the theory of this method and the various decay models for extracting the kinetic parameters were presented in a previous report.[14]

An argon-ion laser (Coherent, INNOVA 400) was used as the excitation source. The 363.8 nm line was used for the time-resolved experiments and the fluorescence was collected through a 435 nm longpass filter (Oriel). 1,4-Bis(4-methyl-5-phenyloxazol-2-yl)benzene (Me_2POPOP) in ethanol (τ = 1.45 ns) was used as the reference fluorophore.[39] For all time-resolved experiments, data were acquired for 60 s from 5 to 150 MHz (30 frequencies). The frequency domain data were analyzed using the software from Globals Unlimited (Urbana, IL).

Results and Discussion

Steady-State Fluorescence. Following Weber and Farris,[22] we plotted the excitation and emission spectra of PRODAN (1 μM) in various solvents. The excitation maxima for PRODAN in all the solvents were found to be similar to the respective absorption maxima within the experimental error. The observed values of the excitation and emission maxima are summarized in Table 1. In Figure 2A, a series of emission spectra shows remarkable shifts in its maxima with the solvent polarity for cyclohexane, chloroform, acetonitrile, ethanol, and water. The emission maximum varies from 404 nm in cyclohexane to 527 nm in water. In Figure 2B, three additional emission spectra for PRODAN in the solid matrixes (PMMA, composite glass, and TMOS sol–gel, respectively) are shown, demonstrating the solvent sensitivity of PRODAN in the solid environments. The emission spectrum for PRODAN in TMOS sol–gel (pure sol–gel hereafter) is taken from a previous study by Narang et al.[14] Several features in Figure 2 merit additional discussion. First, the full width at half-maximum (fwhm) of the emission spectra for PRODAN is the highest in the composite glass (4942 cm^{-1}) compared to pure PMMA (4040 cm^{-1}) and pure sol–gel (2838 cm^{-1}). Second, the emission maximum of PRODAN in the composite glass (448 nm) is red shifted compared to that in pure PMMA (425 nm) and blue shifted compared to that in pure sol–gel (512 nm). Third, the magnitude of the blue shift (composite glass vs sol–gel) is approximately 3 times the red shift (composite glass vs PMMA) in the emission maxima. These results clearly demonstrate that PRODAN, within the composite glass, experiences a more PMMA-like environment but is substantially influenced by the silica skeleton of the sol–gel matrix.

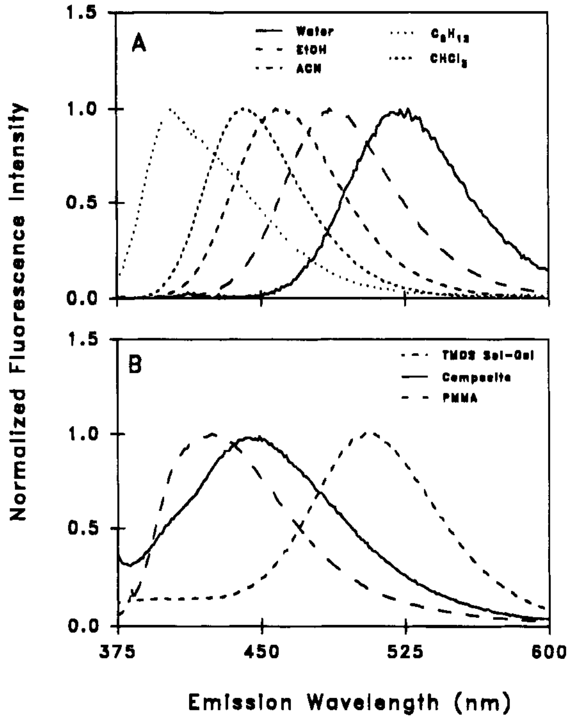

Figure 2. Normalized fluorescence spectra of PRODAN in liquid solvents and solid matrices upon excitation (350 nm). Normalized emission spectra of PRODAN in cyclohexane, chloroform, acetonitrile, ethanol, water (panel A, left to right); PMMA, composite glass, and TMOS-derived sol–gel (panel B, left to right).

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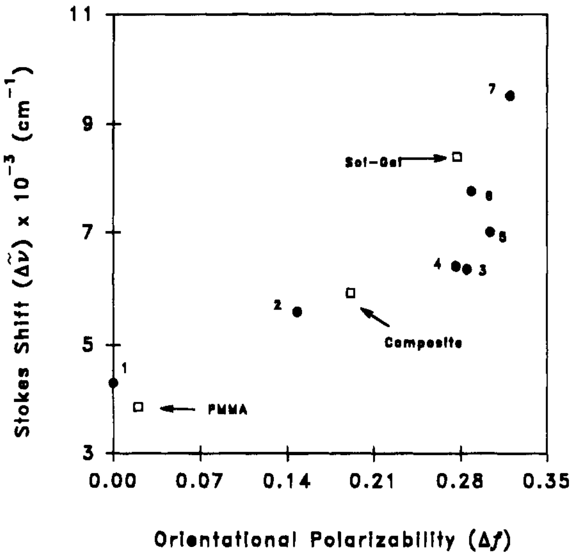

Figure 3. Lippert plot (Stokes shifts (cm^{-1}) vs orientational polarizability (Δf) for PRODAN. The numbers next to (●) correspond to the number in Table 1 identifying the solvent used. (□) The solid matrix.

Using the data obtained for the excitation and emission maxima of PRODAN in various solvents and solid matrices, we prepared a Lippert plot. The values of the refractive indices and the dielectric constants of the various solvents (for calculating Δf) were taken from the literature.[40] The values of the refractive indices and the dielectric constants of the solid matrices have been measured previously[5,32] and are summarized in Table 1. The values of the dielectric constants of the composite glass and the PMMA were calculated by measuring their capacitance and that for TMOS-derived sol–gel bulk, the value was estimated as higher than that of methanol and less than that of water following previous studies.[13,41] The Lippert plot (Figure 3) for PRODAN in liquid solvents was similar to that obtained by Weber and Farris.[22]

In the dye-doped composite glass, one would expect that the observed Stokes shift will be the same as in PMMA, since the dye was impregnated in the glass via methyl methacrylate monomers. From the emission plots of PRODAN in composite glass, PMMA, and sol–gel glass (Figure 2B), it is clear that the dye molecules experience an environment which is intermediate of pure PMMA and pure sol–gel. It is further demonstrated by the Lippert plot (Figure 3) that the microenvironment experienced by PRODAN is a combination of PMMA and sol–gel-like environments. In addition, the Stokes shifts in the solid matrices obey a similar dependence on Δf as observed in the liquid solvents. Therefore, in the composite glass, (which is a two phase matrix), we observe a microenvironment similar to the one expected due to the physicochemical properties of the macroenvironment (Δf). The nonlinearity in the Lippert plot is known to be due to specific interactions (for example, hydrogen bonding, electron donation) between the dopant and the solvent that can influence the Stokes shift.[27] The effect of hydrogen bond to increase the Stokes shift by acting as proton donors has been reported for PRODAN in liquid solvents.[22] The effect of an electron-donor solvent to decrease the Stokes shift was reported for red perylimide dye (RPD).[42] It is clear from our study that PRODAN-doped PMMA and PRODAN-doped composite glass lie in the linear region of the Lippert plot (Figure 3) hence do not apparently exhibit any specific interactions. The effect of hydrogen bonds to increase the Stokes shift is most pronounced in the PRODAN-doped pure sol–gel (Figure 3). This result is not surprising due to a large number of free silanol (–Si–OH) groups known to be present in the pure sol–gel matrix,[3,14] which could be in the immediate vicinity of PRODAN.

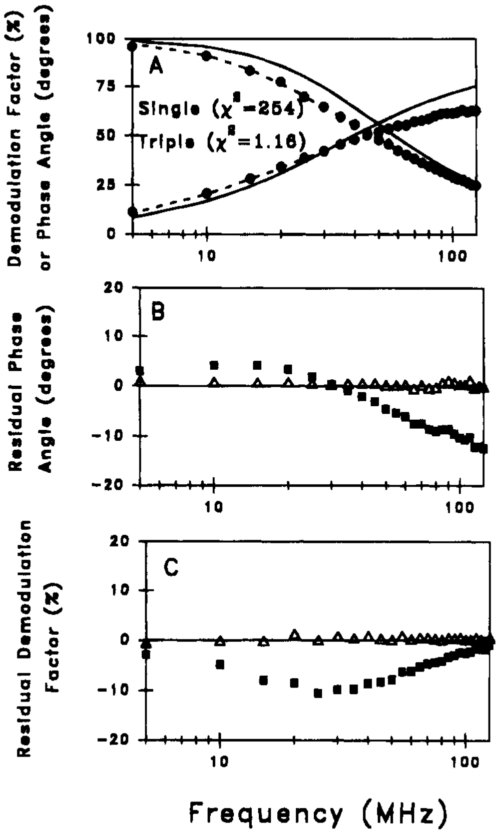

Figure 4. Typical multifrequency phase and modulation data for PRODAN-doped composite glass. (Panel A) Phase angle and demodulation factor (points) and fits (lines) to various decay models (single exponential (–) and a triple exponential (- - -) decay laws). (Panel B) Residual phase angle for fits to a single exponential (■) and triple exponential (△). (Panel C) Residual demodulation factor for fits to a single exponential (■) and triple exponential (tuo).

Time-Resolved Fluorescence. Multifrequency phase and modulation fluorescence is a powerful technique for determining the excited-state decay kinetics of a fluorescent molecule. Figure 4 presents a typical multifrequency data set for PRODAN-doped composite glass and their fits to various decay models. In panel A, we present the experimental data points (●) along with the best fits to a single exponential (–) and a triple exponential (- - -) decay laws. The single-exponential fit is clearly poor and is confirmed by the residual plots (panel B, residual phase angle; panel C, residual demodulation factor; single-exponential (■) and triple-

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Table 2. Recovered Excited-State Decay Parameters for PRODAN-Doped Composite Glass (A) and PRODAN-Doped PMMA (B) Using a 435 nm Longpass Filter to Collect the Emission

decay model	$\langle\tau\rangle^a$	$\tau_1{}^b$	$\tau_2{}^b$	$\tau_3{}^b$	$F_1{}^c$	$F_2{}^c$	W^d	χ^2
				A				
single		4.77						254
double		6.86	1.21		0.84			3.47
triple		8.46	3.51	0.46	0.55	0.36		1.16
Gaussian	5.96						3.86	2.07
				B				
single		3.6						613
double		6.78	1.12		0.68			10.08
triple		13.37	3.86	0.65	0.36	0.56		0.97
Gaussian	1.00						6.32	1.30

[a] Central or mean value for the continuous distribution (ns). [b] Discrete lifetime (ns). [c] Fraction intensities. [d] Width term: "σ" for the Gaussian.

exponential (△) decay models). Table 2 collects the recovered lifetime(s) and the associated fractional intensities from the various decay models for PRODAN-doped composite glass (data shown in Figure 4) and for PRODAN-doped PMMA (data not shown). The quality of the fit of the various decay models can be compared to the recovered chi-squared value (χ^2). A χ^2 closer to unity indicates a good fit. In both cases (Table 2), a triple-exponential decay law is clearly a superior model describing the experimental data. These results indicate that PRODAN is not in a homogeneous environment, both in pure PMMA and in the composite glass.

For the PRODAN-doped composite glass, a high contribution is due to a longer-lived component ($\tau = 8.5$ ns, 55%) with an additional shorter lifetime ($\tau = 3.5$ ns, 36%) resolved. In contrast, for the PRODAN-doped PMMA, there is high contribution due to a shorter-lived component ($\tau = 3.9$ ns, 56%) with an additional longer-lived component ($\tau = 13.4$ ns, 36%) resolved. In both cases, the third component is extremely short-lived with similar minimal contributions.

In previous work by Narang et al.,[14] the recovered experimental phase and modulation data for PRODAN-doped TMOS sol–gels exhibit a best fit to a unimodal Gaussian distribution, indicating that the PRODAN molecules are trapped in a heterogeneous microenvironment. By using a triple exponential decay law, they observed high contribution from a longer-lived component ($\tau = 4.2$ ns) and an additional shorter-lived component ($\tau = 2.2$ ns). The third component was extremely short-lived (0.002 ns). In addition, Monte and Levy observed two discrete lifetimes for HITC- and oxazine-1-doped TMOS-derived sol–gel.[29] They proposed a two-domain model. The short-lived component is similar to that obtained in solution, indicating that the dye molecules are solvated in the residual solvent present in the porous matrix (domain 1). The longer-lived component was attributed to dye molecules trapped in rigid cages and deactivated by the silica skeleton of the sol–gel matrix (domain 2).

Our results for PRODAN-doped PMMA suggest that there are two major contributing domains. One of the domains has the dye molecules which are dispersed/solvated between the polymer chains with lifetime similar to the one resolved in ethanol solution[22] ($\tau = 3.7$ ns). The other domain consists of dye molecules trapped/strongly interacting with the polymer chain which exhibit a longer lifetime.

Table 3. Recovered Excited-State Decay Parameters for PRODAN-Doped Solid Matrix Using Triple-Exponential Decay Law

matrix	$\tau_1{}^a$	$\tau_2{}^a$	$\tau_3{}^a$	$F_1{}^b$	$F_2{}^b$
composite glass	8.65	3.67	0.48	0.55	0.48
PMMA	13.4	3.85	0.65	0.36	0.56
TMOS sol–gels[c]	4.16	2.14	0.002	0.39	0.57

[a] Discrete lifetime (ns). [b] Fractional intensities. [c] Data from ref 14.

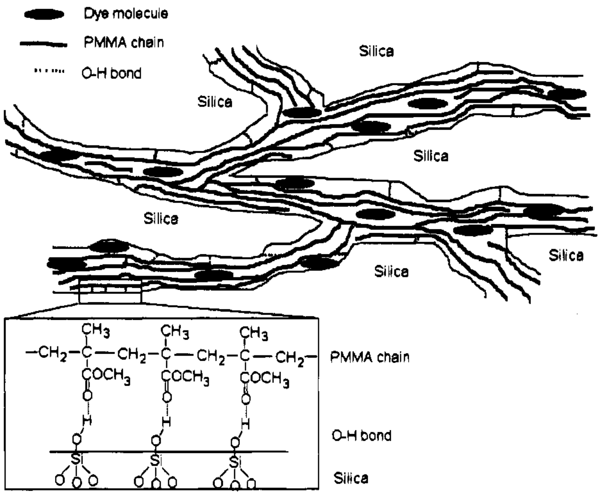

Figure 5. Model representing the dispersion of the dye molecules in a composite glass.

The case of the PRODAN-doped composite glass is much more complex because the overall matrix contains both PMMA and silica. To get more insight into this system, we compared the recovered excited-state lifetimes for PRODAN doped in PMMA, composite glass, and pure sol–gel (Table 3). These results merit additional discussion. First, PRODAN experiences a heterogeneous microenvironment in the composite glass, PMMA and pure sol–gel. Second, the recovered excited-state lifetimes for PRODAN-doped in a composite glass are intermediate between that observed for pure PMMA and pure sol–gel but more similar to those observed in pure PMMA. These results support the steady-state results that PRODAN experience a more PMMA-like environment in the composite glass. PRODAN molecules which are located primarily in the PMMA are also influenced by the silica skeleton.

Conclusions

From the steady-state and time-resolved fluorescence results, we observed that the microenvironment experienced by PRODAN in the composite glass is a combination of PMMA- and sol–gel-like environments. Figure 5 presents a simple model consistent with the microenvironment sensed by PRODAN in the composite glass and results of some previous studies.[4,14] The key points are (1) the longitudinal PMMA chains fill the sol–gel pores (channels), (2) PRODAN is primarily present in the PMMA region, and (3) the hydrogen bonds and the silica surface of the sol–gel matrix appear to distinctly influence the photophysics of PRODAN.

It is important to recall that doping of dyes in a composite glass prevent the formation of aggregates.[30] For PRODAN and RPD, the maximum fluorescence efficiency was found to be in solvents of medium polarity.[22,42] It was also observed that there was a high fluorescence efficiency in the composite glass[30] (medium polarity). Thus, the composite glasses are potential hosts for laser dyes. There are some preliminary reports on the lasing of laser-dye-doped composite glasses.[5-7] Composite glasses exhibit extremely high photostability under lasing conditions compared to other host matrices such as PMMA and (organically modified silans) ORMOSILS.[7] These findings make composite glasses a good candidate as host matrixes for organics in advanced optics applications. Recently, we reported a novel approach of preparing useful materials for photonics based on composite glasses.[43] This approach produces a composite glass which consists of many phases, but the phase separation is on a nanometer scale. The concept of a multiphasic nanostructured composite can be used to prepare a wide variety of optical materials. Using a previously described method,[43] we are able to dope two (or more) different optically responsive materials, each of which will be in different phases of the matrix (silica phase, PMMA phase, or interfacial phase), to make multifunctional bulk materials for photonics.

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