Photophysical, photochemical and laser behavior of some diolefinic laser dyes in sol–gel and methyl methacrylate/2-hydroxyethyl methacrylate copolymer matrices

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ABSTRACT

The photophysical properties such as singlet absorption, molar absorptivity, fluorescence spectra, dipole moment, fluorescence quantum yields, fluorescence lifetimes and laser activity of 1,4-bis (β-Pyridyl-2-Vinyl) Benzene (P_2VB), 2,5-distyryl-pyrazine (DSP) and 1,4-bis(2-methylstyryl)benzene(MSB) diolefineic laser dyes have been measured in different restricted hosts. (P_2VB), (DSP) and (MSB) are embedded in transparent sol–gel glass and a copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) media. The absorption and fluorescence properties of these laser dyes in sol–gel glass matrices are compared with their respective properties in copolymer host. The photostability of these laser dyes in sol–gel glass and (MMA/HEMA) copolymer samples are measured in terms of half-life method (using nitrogen laser 337.1 nm in pumping), as the number of pulses necessary to reduce the dye laser intensity to 50% of its original value. The gel laser materials show improved photostability upon pumping by nitrogen laser compared with those in organic polymeric host matrix.

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1. Introduction

Liquid solutions of organic laser dye molecules have been widely used as good laser gain media from the near UV to the near IR regions of the spectrum [1]. There are several disadvantages in using liquid dye lasers like poor thermal stability of dye solutions, requirement of large volume of solutions and need of significant maintenance, etc [2–5]. These difficulties can be overcome by doping stable laser dye molecules into restricted host matrices like polymers, silica gels, xerogels and sol–gel glasses [4–8]. Solid-state dye laser presents some advantages, e.g. they do not contain volatile solvents, they are non-flammable, nontoxic, compact in size and mechanically and thermally more stable [2,3]. The possibility and applications of incorporating a dye in a gel was first illustrated by Avnir and coworkers in 1984 [2]. The effect of drying control chemical additives (DCCA) on the optical and lasing properties of pyrromethene (PM) dye-doped sol–gel and organically-modified silicates (ormosils) has been reported [9]. Moreover, DCCA can control the hydrolysis and the condensation rate that strongly influences the dye molecule in sol–gel matrix [10]. In this sense,

silica xerogel matrix would be a good host for these dyes due to its transparency, chemical inertness and the possibility to disperse the dye at molecular level [2,11,12]. However, polymeric host materials have been shown to be inherently lacking in mechanical and thermal properties and photostability [13,14].

The sol–gel method is a method for incorporation of organic dye molecules into an inorganic silica host [15]. Incorporation of the laser dyes into sol–gel matrices by doping method was reported by several authors [2,4,5]. A simple classification, based on the nature of the links and interactions that the organic and inorganic components exchange, has been proposed for hybrid materials. Two main classes have been defined. Class I corresponds to all the systems where there are no covalent or iono-covalent bonds between the organic and the inorganic components. In such materials, the various components only exchange interactions such as van der Waals forces, hydrogen bonding or electrostatic forces. On the contrary, in class II materials, at least parts of the organic and inorganic components are linked through strong chemical bonds (covalent or iono-covalent) [16]. In dope method, dyes are mixed at the sol stage and drying is carried out afterward. Sol–gel shows some advantages, e.g. its reaction can be controlled easily by chemical methods. It allows introducing permanent organic groups to form inorganic–organic hybrid materials [17] and the process takes place at low temperature [18]. High porous

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material was prepared in which the matrix is chemically inert and possesses low poisoning [19]. It has exultant optical low intrinsic fluorescence. The higher thermal conductivity of silica in comparison with that of polymer materials allows heat dissipation and minimizes both photo degradation and thermal lensing effect which causes laser beam divergence [20]. The process provides good flexibility during polymerization steps [21] with ability to be functionalized before or after polymerization. Hence sol–gel host provides a more suitable surrounding for the dye molecules compared to polymeric hosts.

In the past, we reported a number of studies on 1,4-Bis (β-Pyridyl-2-Vinyl) Benzene (P₂VB) [22–27], 2,5-distyryl-pyrazine (DSP) [22–27] and 1,4-bis(2-methylstyryl)benzene (MSB) [28–30], as new laser dyes having the advantage of laser emission in the UV- blue spectral region. In the present paper, we report the behavior of these diolefinic laser dyes in silica sol–gel solid as well as in a copolymer of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) media in a trial to improve the quality of laser action. The plasticity of the material was internally increased by copolymerization of methyl methacrylate (MMA) with 2-hydroxyethyl methacrylate (HEMA). The presence of HEMA increases the plasticity of the material while maintaining its transparency. It also ensures a good solubility of dyes such as Rh6G due to the polar character of HEMA [31].

It is necessary to know and understand the effect of various host matrices on the various properties including photostability, photophysical properties as well as laser efficiency. Photophysical properties provide basic information about the lasing behavior of the material [1]. With this objective, sol–gel host samples were prepared by HCl acid catalyzed hydrolysis of tetraethylorthosilicate (TEOS). The absorption and emission properties of these laser dyes in sol–gel glass matrices are compared with their respective properties in copolymer host matrices. The data are also compared with those in free solutions.

Laser dye life-time is a key performance parameter which limits a laser dye application. Intensive research efforts have been made to

photostability of the dye molecules doped in the solid host is improved as compared with the dye molecules in a liquid solvent [32].

The improved photostability of the dye within solid hosts has been attributed to caging and immobilizing the dye molecules, thereby minimizing excited-state interaction with other species including molecular oxygen. So in a solid host, the photodegradation of the laser dye depends on the nature of dye molecule, the composition and structure of the host, and the impurities present in the host. In order to further improve the photostability and decrease photodegradation of the laser dye, control of the surroundings of the dye molecules becomes the most critical issue for the solid-state dye laser.

Sol–gel derived glasses have many advantages e. g. thermally stability much beyond the range of temperatures which are of relevance for polymeric matrices, they do not photodegrade and, in the case of SiO₂ matrices, are not involved in light induced reactions with the matrix. Sol–gel matrices are transparent well into the UV region down to ∼250 nm for SiO₂ and are thus highly suitable for optical applications. These are major advantages of silicate matrices compared with organic polymeric ones.

Another possible factor that may explain the reduced rate of degradation in the more rigid matrices may be that the dye molecules are more tightly confined within the pores of the matrix, limiting rotational and translational freedom. A mobile molecule, as in solution, will be more likely to encounter an oxygen molecule and undergo degradation. Less freedom, as defined by the restrictive pores of the matrix, may make the dye molecule less likely to interact with molecular oxygen leading to photodegradation or fluorescence quenching. Molecular oxygen is a well-known fluorescence quencher due to its paramagnetic nature [32].
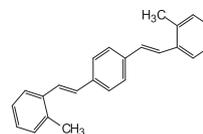
In the present communication we report lasing, photostability, and a number of photophysical characteristics of three UV-blue diolefinic laser dyes in sol–gel and polymeric matrices. A number of advantages of sol–gel matrix over the copolymer are highlighted.
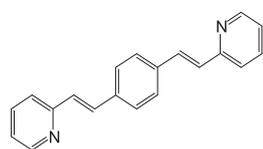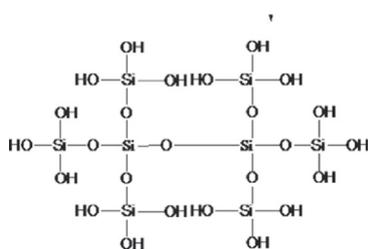

1, 4-bis (β-pyridyl-2-vinyl) benzene (P₂VB)
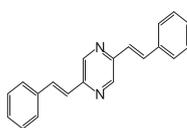
2, 5 distyrylpyrazine (DSP)

1, 4bis (2-methylstyryl) benzene (MSB)

Sol-gel network

explore the mechanism of photodegradation of laser dyes. It has been demonstrated that the mechanism of photodegradation occurs by the interaction of the dye molecules in the excited state with other species such as impurities, other dye molecules and singlet oxygen. Through the process of doping laser dyes into a solid medium, the photochemical pathways including bimolecular reactions can be suppressed by caging or trapping the dyes within a solid host, and the

2. Experimental

Sol–gel materials were prepared by the hydrolysis of silicon alkoxide followed by polycondensation. Dye is incorporated into the matrix by doping method. The sol–gel matrix was prepared using HCl as a catalyst and glycerol as DCCA to reduce the cracking of monoliths during drying [33]. This method involves the

additions of (TEOS) (Aldrich, 98%) 11.2 mL, methanol (MeOH) (Aldrich) 6 mL, distilled water (H_2O) 9 mL, HCl (Merck, about 35% pure, sp. gr. 1.18 g mL^{-1}) 1 mL (0.1 N) and 8 mL glycerol (Merck, IP for analysis) as DCCA. The sol thus prepared was subjected to ultrasonic stirring for 14.5 h. Approximately 1 mL of laser dye methanol solution and 2.5 mL sol were poured into rectangular polystyrene cuvettes and then sealed with Teflon tape. Drying and aging were carried out in controlled clean oven at 60 °C. After 3 weeks from the date of preparation, the samples get dried so that it can be handled and can be subjected to various measurements [33].

2.1. Preparation of laser dyes-doped copolymer (MMA/HEMA)

MMA/HEMA copolymer was prepared as follows: [34–40] 3 g/L of azobisisobutyronitrile (AIBN) as initiator was dissolved in freshly purified MMA and HEMA (volume ratio 1.5:1) monomers. The solution was placed in an ultrasonic bath for a period of about 15 min until the initiator was completely dissolved. Then the laser dye was added to obtain the desired concentration and allowed to dissolve in the ultrasonic bath for up to 20 min. Drying and aging were carried out in controlled clean oven at a proper temperature of 60 °C, above which the specimen possesses low quality physical appearance and transparency. After one week from the date of preparation, the samples got dried so they could be handled and subjected to various measurements.

Absorption and transmission spectra of the prepared samples were recorded on a UV–vis spectrophotometer (Perkin Elmer, Lambda 35). The absorption spectra of the dye-embedded solids were recorded with the undoped host as the reference. The fluorescence spectra were recorded on assembled fluorometer (PF-6300 Spectrofluoro-photometer) in front surface excitation-emission geometry. The excitation wavelengths were adjusted at maximum absorption wavelengths for each fluorescence measurement of each dye. The oscillator strengths (f) show the effective number of electrons whose transition from ground to excited state gives the absorption area in the electronic spectrum [41]. The values of oscillator strength were calculated from [42,43]:

$$f = 4.32 \times 10^{-9} \int \varepsilon(\tilde{\nu}) d\tilde{\nu} \qquad (1)$$

where $\tilde{\nu}$ is the wavenumber and ε is the molar extinction coefficient. The value of (f) is dependent on the molecular structure. The atte-nuation length $\Lambda(\lambda)$ (the distance at which the original light intensity I_0 is reduced to $I=I_0/e$, is given by [44]:

$$\Lambda(\lambda) = \frac{1}{\varepsilon(\lambda) c \ln(10)} \qquad (2)$$

where $\varepsilon(\lambda)$ is the molar extinction coefficient at a specified wave-length and c is the molar concentration. The Λ values are markedly dependent on the wavelength. The transition dipole moment μ_{12} from ground to excited state was calculated by using [45]:

$$\mu_{12}^2 = \frac{f}{4.72 \times 10^{-7} E_{max}} \qquad (3)$$

where E_{max} is the maximum energy absorption.

The radiative decay rate constant (k_r) (or fluorescence rate constant) of a fluorophore can be theoretically predicted from the Strickler–Berg equation, which has its foundations on Einstein's spontaneous emission rate and Planck's black body radiation law as given by [46,47]:

$$k_r = \frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \frac{\int F(\tilde{\nu}) d\nu}{\int F(\tilde{\nu}) \tilde{\nu}^{-3} d\nu} \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} \qquad (4)$$

where $F(\tilde{\nu})$ is the fluorescence intensity, $\tilde{\nu}$ is the wavenumber and $\varepsilon(\tilde{\nu})$ is the molar extinction coefficient at a particular wavenumber ($\tilde{\nu}$), n is the refractive index of the solid host. The absorption cross-section σ_a is given by [48–50]:

$$\sigma_a = 0.385 \times 10^{-20} \varepsilon(\lambda). \qquad (5)$$

Rhodamine-6G (R6G)/MeOH solution in quartz cuvette ($1 \times 1 \times 4.5$ cm^3) with a quantum yield (ϕ_f) of 0.96 [51] was used as a reference to determine the fluorescence quantum yield (ϕ_f) of the dye-containing solids. The emission spectra were corrected for the monochromator and photomultiplier responses at different wave-lengths. The fluorescence intensity of the dye-embedded solid was normalized. To determine the quantum yield of a compound relative to a standard material, the following relationship was applied [52,53]:

$$\phi_u = \phi_s \times \frac{I_u}{I_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2}. \qquad (6)$$

where ϕ, I and A are the fluorescence quantum yields, the areas under emission curves and absorbances respectively. The subscripts u and s denote unknown and standard respectively. n_s and n_i are the refractive indices of solvents used.

Fluorescence lifetimes (τ_f) were calculated by using :

$$\tau_f = \tau_0 \phi_f \qquad (7)$$

where (τ_0) is the natural lifetime ($\tau_0 = 1/k_r$). The intersystem crossing rate constant (k_{isc}) is related to the quantum fluorescence yield ϕ_f for ($\phi_f \approx 1$) by the approximate relationship [54,55]:

$$k_{isc} = (1 - \phi_f)/t_f. \qquad (8)$$

The energy yield of fluorescence (E_f) was calculated by [56]:

$$E_f = \phi_f \frac{\lambda_A}{\lambda_f} \qquad (9)$$

where ϕ_f is the fluorescence quantum yield, λ_A and λ_f are the maximum absorption and fluorescence wavelengths respectively. The emission cross-section σ_e was calculated according to [47–49]:

$$\sigma_e = \frac{\lambda^4 F(\lambda) \phi_f}{8\pi c n^2 \tau_f} \qquad (10)$$

where λ is the emission wavelength, n the refractive index of the host, ε is the extinction coefficient, c the velocity of light, $F(\lambda)$ is the normalized fluorescence spectrum where $\int F(\lambda) d\lambda = 1$ and ϕ_f is the fluorescence quantum yield.

The laser dyes/sol–gel glass and laser dyes/copolymer samples were pumped by nitrogen pulsed laser ($\lambda_{ex} = 337.1$ nm) of 800 ps duration and 1.48 mJ pulse energy. The output energy of laser dyes was mea-sured as a function of wavelength to determine the lasing range in different solid hosts. The maximum gain coefficient (α) was calculated at the maximum laser emission by measuring the intensity I_L of laser emission from the entire cell length L and the intensity $I_{L/2}$ from the cell half-length. The laser gain was then evaluated from [54,57]:

$$\alpha(\lambda) = \frac{2}{L} \ln \left[\frac{I_L}{I_{L/2}} - 1 \right]. \qquad (11)$$

The normalized photostability is defined as the accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls to one-half of its initial value using relation [58–62]:

$$\text{Normalized photostability (MJ/mol)} = \frac{E_{pulse} N_{1/2}}{\pi \times r^2 \times l \times c \times 10^6} \qquad (12)$$

where E_{pulse} is the pulse energy (in Joules), $N_{1/2}$ is the number of pulses to get half the initial emission intensity, r is the radius of the laser beam on the surface of the sample and l is the sample thickness (in centimeters) and c is the dye concentration (mol/L).

3. Results and discussion

In the synthesis of laser dye-doped silica matrix host, TEOS was used because it gets easily hydrolyzed and becomes condensed in the presence of an acid catalyst giving rise to transparent and homogeneous alcogel within 3 weeks. The transparency and monolithicity of the silica xerogels were not affected much by doping laser dye molecules but a color change was observed [63].

The undoped sol–gel glass showed a good transmission in the spectral range from 300 to 800 nm compared with copolymer host matrix due to the presence of absorbing carbonyl chromophores in the copolymer. This condensation process is also associated with the loss of water/alcohol from the pores of the solids prepared by sol–gel technique as the time of condensation proceeds. The UV–vis. spectra of undoped sol–gel glass and copolymer host matrices are shown in Fig. 1. The sol–gel glass shows higher optical transparency in the UV region compared with copolymer matrix.

Figs. 2–4 show the UV–vis absorption and fluorescence spectra of P_2VB, DSP and MSB laser dyes respectively both in sol–gel and in copolymer matrices. The strong absorption of the copolymer in the spectral range 300–400 nm strongly modifies the absorption maxima of the three dyes. This is not the case upon using sol–gel matrix that is nearly transparent in this spectral region. Accordingly, there is no overlap between absorption and emission spectra of the three laser dyes in sol–gel matrix. This is critically important as far as reabsorption of emitted photons is concerned. There is a minimum reabsorption of laser dyes emitted photons in sol–gel matrices compared with copolymer ones.

Comparison between spectral data of P_2VB, DSP and MSB laser dyes in sol–gel and in copolymer matrices is shown in Tables 1 and 2. Sol-gel media are characterized by higher fluorescence quantum yields (ϕ_f) values compared with copolymer matrices.

Inspection of Table 2 shows that the fluorescence emission wavelengths are red shifted in copolymer matrix compared with sol–gel glass, indicating a more relaxed excited state due to dye-copolymer interaction within excited state lifetime. Fluorescence quantum yield (ϕ_f) values are generally lower in copolymer matrix compared with those in sol–gel, indicating more interaction between dye molecules and copolymer matrices. The carbonyl chromophore in copolymer matrices possesses (n,π^*) electronic states that are characterized by low singlet – triplet splitting energies ($\Delta E_{S,T}$) leading to triplet state population, with subsequent fluorescence quenching [64]. It is known that the ($T_1 \rightarrow T_n$) transition is a spin-allowed one that can quench fluorescence by
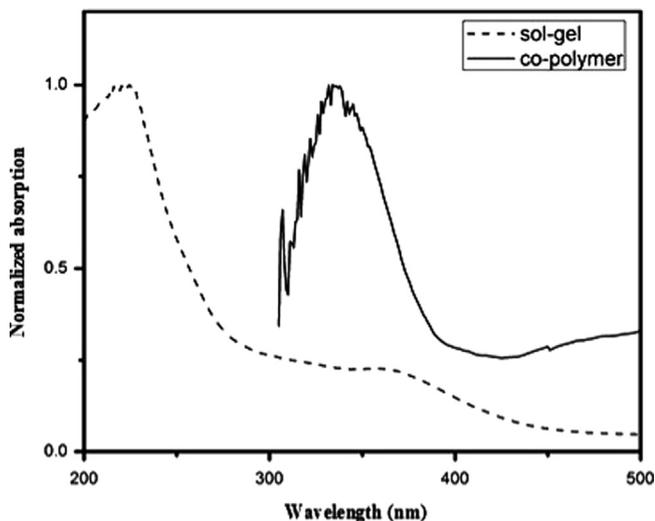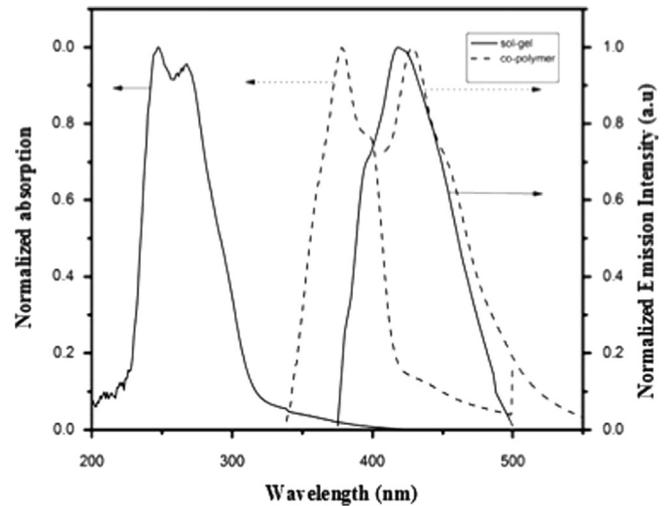

Fig. 2. Normalized absorption (short wavelengths) and emission (long wavelengths) spectra of 4×10^{-5} mol dm^{-3} P_2VB in sol–gel and 1×10^{-5} mol dm^{-3} in copolymer.
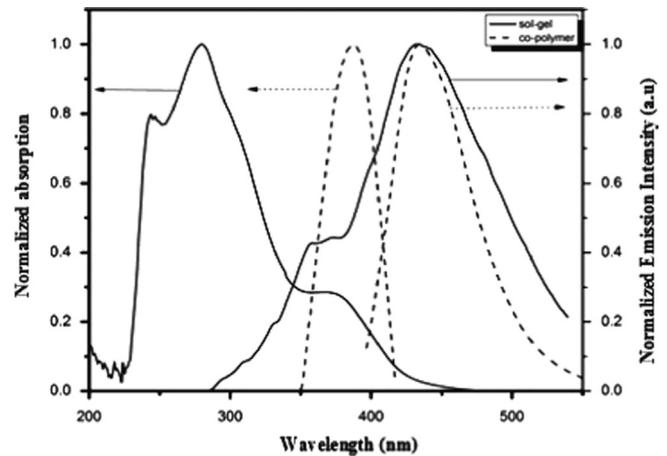

Fig. 3. Normalized absorption and emission spectra of 4×10^{-5} mol dm^{-3} of DSP in sol–gel and 1×10^{-5} mol dm^{-3} in copolymer.
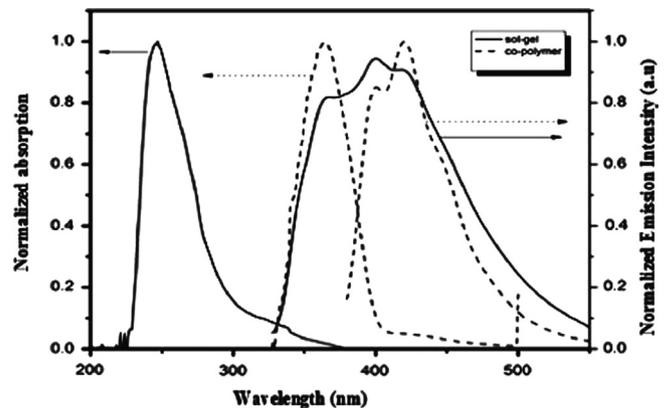
Fig. 4. Normalized absorption and emission spectra of 4×10^{-5} mol dm^{-3} of MSB in sol–gel and 1×10^{-5} mol dm^{-3} in copolymer.

photon reabsorption. The lower energy level of (n,π^*) states also allows for exciton trapping [64] adding to factors causing fluorescence quenching. These factors give a privilege of sol–gel glasses over copolymer matrices. Further confirmation of the role of copolymer matrices in fluorescence quenching comes from the

Fig. 1. Normalized UV–vis absorption spectra of un-doped sol–gel and copolymer matrices.

Table 1
Absorbance properties of P$_2$VB, DSP and MSB in different restricted hosts.

Solid host	Dyes	λ_{abs} (nm)	$\varepsilon \times 10^4$ M^{-1}cm^{-1}	f	$\Lambda_{(cm)}$	$k_r \times 10^8$ s^{-1}	$\sigma_a \times 10^{(-16)}$cm^2	μ(D)
Sol–gel glass	P$_2$VB	247	2.8	0.75	0.38	3.0	1.08	6.27
	DSP	280	2.2	0.87	0.49	3.9	0.84	7.20
	MSB	247	1.5	0.04	0.72	2.9	0.58	1.48
Copolymer	P$_2$VB	378	6.5	0.64	0.66	5.7	2.50	7.17
	DSP	388	3.9	0.42	1.11	3.5	1.50	5.87
	MSB	364	4.9	0.36	0.88	36.7	1.88	5.28

Table 2
Fluorescence properties of P$_2$VB, DSP and MSB in different restricted media.

Solid host	dyes	λ_f (nm)	ϕ_f	τ_f (ns)	$\sigma_e \times 10^{-16}$ cm^2	E_f	$k_{isc} \times 10^8$ s^{-1}
Sol–gel glass	P$_2$VB	418	0.75	2.5	1.08	0.44	1.00
	DSP	433	0.78	1.9	1.06	0.69	1.15
	MSB	400	0.75	2.5	4.60	0.46	1.00
Copolymer	P$_2$VB	428	0.36	0.6	1.20	0.31	10.15
	DSP	434	0.42	1.2	7.80	0.29	4.83
	MSB	420	0.53	0.14	1.11	0.46	32.60

higher intersystem crossing rate constants (k_{isc}) values in copolymer matrices compared with sol–gel glass.

Another factor leading to higher fluorescence efficiencies in sol–gel compared with copolymer matrix is the replenishment of dye molecules in lasing regions in a sol–gel matrix. The sol–gel glass samples contain glycerol that may help in the mobility of the embedded dye molecules available for lasing action [21]. This happens very efficiently in liquid state as the self-repair in liquid is natural because of Brownian motion. In solid state as well, the resultant intensity depends on the number of dye molecules getting excited by pump radiation in the front surface. When degraded molecules are replaced by fresh molecules quickly, high fluorescence efficiencies are observed. This is not the case in copolymer matrix where the place of degraded molecules may not be taken by other fresh molecules. This is because in copolymer samples, the laser dye molecules are surrounded by only (PMMA, HEMA) matrix with negligibly small solvent around it.

Excited state lifetime (τ_f) values in copolymer matrices are lower than those in sol–gel glass. This indicates a dynamic quenching process in which the copolymer matrix interacts with the excited state dye molecules. This leads to shortening of τ_f values in copolymer matrices compared with sol–gel glass.

Fluorescence energy yields for P$_2$VB and DSP in sol–gel are higher than in copolymer, but fluorescence energy yields for MSB in sol–gel and in copolymer are the same.

Both absorption and emission cross-sections were calculated for the three laser dyes in sol–gel and copolymer host matrices (Tables 1 and 2). The values of absorption and emission cross sections are in agreement with values reported for other efficient laser dyes [65].

The photostability of laser dyes in solid host samples can be expressed in terms of the half-life of lasing materials defined as the number of pulses needed to reduce the laser output intensity to half of its initial value [33]. Fig. 5 shows the photostability of DSP, MSB and P$_2$VB diolefinic laser dyes in sol–gel glass and in copolymer matrices. This was studied by monitoring the output laser intensity as a function of the number of nitrogen laser pump pulses. Fig. 5 shows a two-step decline, which appears to be somewhat linear. However the difference between the two decrease rates is not huge.

The oscillator strength values of electronic transitions were calculated for laser dyes in sol–gel and in copolymer hosts. For both P$_2$VB and DSP laser dyes, the oscillator strength values in sol–gel matrix are higher than those in copolymer matrix. Hence,
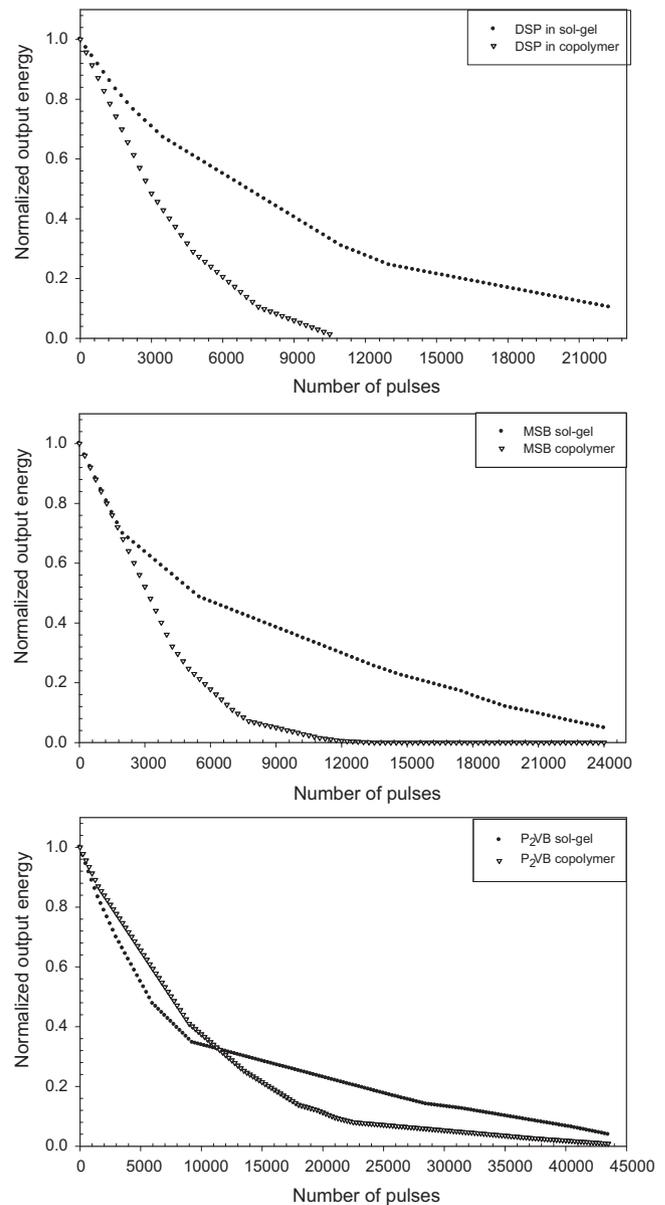

Fig. 5. The output energy as a function of the number of pump pulses for P$_2$VB, DSP and MSB in different restricted hosts using nitrogen pulsed laser (λ=337.1 nm).

the effective number of electrons transferred from the ground to excited states in sol–gel is higher than in copolymer. The attenuation lengths for P$_2$VB, DSP and MSB dyes embedded sol–gel are lower than in copolymer.

For P$_2$VB and MSB dyes, the radiative decay rate constants (k_r) for dyes embedded in sol–gel are lower than those in copolymer

Table 3
Laser parameters of P_2VB, DSP and MSB in different restricted media.

Host	Dyes	Lasing range (nm)	λ_{max} (nm)	α (cm^{-1})	Normalized photostability (J/mol)	No. of pulses for 50% reduction
Sol–gel glass	P_2VB	394–410	418	0.20	0.00521	5670
	DSP	417–456	434	4.85	0.00649	7056
	MSB	394–409	400	0.43	0.00486	5285
Copolymer	P_2VB	412–430	428	2.03	0.00693	7532
	DSP	424–453	434	2.35	0.00268	2922
	MSB	410–430	420	2.04	0.00289	3142

matrices. For DSP laser dye, the radiative decay rate constant in sol–gel and in copolymer is nearly the same.

Table 3 lists the lasing range, the maximum wavelength of laser spectrum, the normalized photostability (in J/mol) and the number of pumping pulses giving a 50% reduction in the intensity of the material for laser dyes in different solid hosts. The half-life of P_2VB, DSP and MSB laser dyes/sol–gel glass samples are 5670, 7056 and 5285 pulses respectively compared to 7532, 2922 and 3142 pulses in copolymer respectively. So the half-lives of DSP and MSB in sol–gel are higher than in copolymer. However, the half-life of P_2VB in sol–gel is lower than in copolymer.

The laser emission and gain coefficient (α) as well as half-life energy of photostability ($E_{1/2}$ in Jmol^{-1}) are also determined for different dyes in solid hosts and are given in (Table 3).

The gain coefficient (α) values for both P_2VB and MSB dyes are higher in copolymer compared with sol–gel matrices. This is not the case in DSP where (α) values in sol–gel is higher than polymer matrices. The gain coefficient (α) is given by the relation [64]:

$$\alpha = B_{mn}\frac{h\nu}{c}(\rho_m - \rho_n)$$

Where ρ_m and ρ_n are the population densities of the two states involved in the transition and represent the populations (N_m, N_n) per unit volume, h is Planck's constant, c is the velocity of light, ν is the frequency of light and B_{mn} is constant. The population densities of dyes differ from one matrix to another and this is reflected on (α) value.

Laser gain maxima show that the three studied dyes lase in the important UV-violet-blue spectral regions. Both DSP and MSB laser dyes show increased photostability in sol–gel compared with copolymer matrices but P_2VB shows an opposite behavior showing more photostability in copolymer matrix. This is explained in terms of differences in ground and excited state electron charge distributions in different dyes with subsequent differences in interactions with matrix and molecular oxygen. The photostability of the copolymer matrix can also further improved by co-doping with singlet oxygen quenchers including Tinuvin770 and coumarin 500, or small molecules e.g. methanol and ethanol [66].

4. Conclusion

The three studied diolefinic laser dyes give emission in the UV-blue region which is important in many fields. In earlier studies, we reported the lasing characteristics of these dyes as new liquid laser dyes. Doping laser dye molecules into restricted host matrices like silica gel and copolymers presents some advantages. The lasing properties and photostability of these laser dyes in sol–gel are studied and compared to copolymer matrices. From these studies, we conclude that the undoped sol–gel glass shows better transmission in the spectral range from 300 to 800 nm compared with copolymer host. Intersystem crossing rate constants (k_{isc}) are high in copolymer matrices compared with sol–gel glass leading to fluorescence quenching. The carbonyl chromophore in copolymer matrix is expected to play a

role in copolymer host characteristics due to its low singlet – triplet splitting energies ($\Delta E_{S,T}$) which leads to triplet state population.

Improved photostability of laser dyes within sol–gel derived hosts has been the focus of this study. Photo degradation rates in sol–gel are generally lower than in copolymer under N_2 laser pumping with sol–gel presenting a more inert matrix compared with copolymer.

Reference

[1] Schafer FP. Dye Lasers. New York: Springer; 1990.
[2] Avnir D, Levy D, Reisfeld R. J Phys Chem 1984;88:5956.
[3] Avnir D, Kaufman VR, Reisfeld R. J Non-Cryst Solids 1985;74:395.
[4] Deshpande AV, Panhalkar RR. J Lumin 2002;96:185.
[5] Deshpande AV, Kumar U. J Non-Cryst Solids 2002;306:149.
[6] Sastre R, Costela A. J Adv Mater 1995;7:198.
[7] Rahn MD, King TA. J Appl Opt 1995;34:8260.
[8] Popov S. J Appl Opt 1998;37:6449.
[9] Al Dwayyan AS, Khan MN, Al Ghamdi AA, Al-Deyab SS. J Pure Appl Sci 2008;2:221.
[10] Khan MN, Al Dwayyan AS. J Lumin 2008;128:1767.
[11] Costa TMH, Stefani V, Balzaretti NM, Gallas MR, Da jornada JAH. J Mater Chem 2001;11:3377.
[12] Costa TMH, Stefani V, Balzaretti NM, Francisco LTST, Gallas MR, Dajornada JAH. J Non-Cryst Sol 1997;221:157.
[13] Rahn MD, King TA. J Appl Opt 1995;34:8260.
[14] Popov S. J Appl Opt 1998;37:6449.
[15] Deshpande VA, Jathar VL, Jayraj RR. J Fluoresc 2009;19:607.
[16] Ribot F, Sanchez C. J Crit Discuss Curr Literatur 2006;4:20.
[17] Hench LL, Nogues JL. J Sol–Gel Opt 1994;295:59.
[18] Wang R, Narang U, Paras NP, Bright FV. J Anal Chem 1993;65:2671.
[19] Paterson MJ, Ben-Nissan B. J Surf Coat Technol 1996;6:153.
[20] Lev O, Tsionsky M, Rabinovich L, Glezer V, Sampath S, Pankratov I, Gun J. J Anal Chem 1995;67:A22.
[21] Narange U, Rahman MN, Wangsui JH, Prasad PN, Bright FV. J Anal Chem 1995;67:1935.
[22] Ebeid EM, Sabry MMF, El-Daly SA. J Laser Chem 1985;5:223.
[23] Ebeid EM, Habib AM, Morsi SE. J Photochem Photobiol 1983;2:1355.
[24] Suzuki Y, Tamaki T, Hasegawa M. J Bull Chem Soc Jpn 1974;47:210.
[25] Ebeid EM, Abdel-Kader NH, Morsi SE. J Chem Soc Faraday Trans 1982;1:3213.
[26] Azim SA, Ghazy R, Shaheen M, El-Mekawey F. J Photochem Photobiol 2000;133:185.
[27] El-Daly SA. Monatshefte fur Chem 1998;129:835.
[28] He KX, Curley M, Williams A, Wang JC. J Opt Commun 1997;139:39.
[29] Lakowicz JR, Gryczynski I. J Biophys Chem 1993;47:1.
[30] Thipperudrappa J, Biradar DS, Hanagodimath SM. J Lumin 2007;124:45.
[31] Costela A, Moreno IG, Figuera jM, Guerri FA, Saster R. J Laser Chem 1998;18:63.
[32] Suratwala T, Gardlund Z, Davidson K, Uhlmann DR. J Sol–Gel SciTechnol 1997;8:973;
Dunn BS, Mackenzie JD, Zink JI, Stafsudd OM. Proc SPIE Sol–Gel Opt 1990;1328:174;
Dunn B, Zink JI. J Chem Mater 1997;9:2280;
Knobbe ET, Dunn B, Fuqua PD, Nishida F. J Appl Opt 1990;29:2729;
Kobayashi Y, Kurokawa Y, Imai Y, Muto SA. J Non- Cryst Solids 1988;105:198.
[33] Deshpande VA, Jayraj RR, Laxman VJ. J Fluoresc 2009;19:1083.
[34] Choudhary MS, Varma IK. J Eur Polym 1979;15:957.
[35] Gregonis DE, Russell GA, Andrade JD, De Visser AC. J Polym 1978;19:1279.
[36] Seymour RB, and Stahl GA, editors. Pergamon Press: New York; 1982.
[37] Hattori SI. [Ph.D. thesis]. University of Utah: Salt Lake City; 1980.
[38] Johnsen A, Klesper E, Wirthlin T. J Macromol Chem 1976;177:2397.
[39] Macret M, Hild G. J Polym 1982;23:748.
[40] Ilavski M, Dusek K, Vacik J, Kopecek J. J Appl Polym Sci 1979;23:2073.
[41] El- Daly SA, El-Azim SA, Elmekawy FM, Elbaradei BY, Shama SA, Asiri AM. Intern J Photoenergy 2012;17:2012.
[42] Calzaferri C, Rytz R. J Phys Chem 1995;99:12141.
[43] Long G, Bo-xiang Y, Ya-yun D, Li Z, Liang-jian W, Yu-guang. X, Zhi-gang W, Xiao C, Xi-lei S, Jian F, Zhen X, Ai-wu Z, Qi-wen L, Li-jun S, Yong-shuai G, Ying-biao L, Shun-li N, Tao H, Jun C, Jun-guang L. Chin Phys C 2009;33:1.

[44] Elisei F, Gattib F, GorettiC A, Hagnerd T, Masetti F, Mazzucato U, Ranucci G, Schoenertd S, Testerab G, Ullucci P, Vitaleb S. Nucl Instrum Meth Phys Res A 1997;400:53.
[45] Briks JB. Photophysics of Aromatic Molecules. London, UK: Wiley; 1970.
[46] Kumar GA, Unnikrishnan NV. Solid State Commun 1997;1049:29.
[47] Kumar GA, Unnikrishnan NV. J. Photochem Photobiol A Chem 2001;144:107.
[48] El-Daly SA. J. Photochem Photobiol A: Chem 1999;124:127.
[49] El- Daly SA. J Spectrochim Acta (A) 1999;55:143.
[50] Govindanunny T, Sivaram BM. J Opt Commun 1980;32:425.
[51] Deshpande AV, Namdas EB. J Chem Phys Lett 1996;263:449.
[52] Kumar S, Rao VC, Rastogi RC. J Spectrochim Acta Part A 2001;57:41.
[53] Turki H, Abid S, Fery-Forgues S. J C R Chim 2006;9:1252.
[54] Snavely BB, Schäfer FP, editors. Dye Lasers. New York: Springer; 1990.
[55] Pavlopoulos TG. J Prog Quantum Electron 2002;26:193.
[56] Bojinov V, Grabchev I. J Poly Degrad Stab 2004;85:789.
[57] Heldt J, Heldt JR, Szezepanski J, Diehl HA. J Appl Phys Chem B 1988;46:339.
[58] Yang Y, Wang M, Qian G, Wang Z, Fan J. Opt Mater 2004;24:621.
[59] Aguilar GV. J Opt Mater 2006;28:1209.
[60] Rahn MD, King TA. J Appl Opt 1995;34:8260.
[61] Hermes RE, Allik TH, Chandra S, Hutchinson JA. J Appl Phys Lett 1993;63:877.
[62] Mackey MS, Sisk WN. J Dyes and Pigment 2001;51:79.
[63] Rao AP, Rao AV. J. Sci Technol Adv Mater 2003;4:121.
[64] Ebeid EM, Alhazmy SM. Photophysical and Laser-Based Techniques Chemistry, Biology and Medicine. Charleston, SC USA: BookSurge Publisher; 2006.
[65] Abdel Gawad EA. [Ph.D. thesis]. Tanta University: Egypt; 2009.
[66] Fan RW, Jiang YG, Xia YQ, Chen DY. Laser Phys 2011;21:1001;
Chen DY, Jiang YG, Fan RW, Jia EB, Xia YQ, Yao Y. Laser Phys 2009;19:1877;
Jiang Y, Fan R, Xia Y, Chen D. Opt Commun 2011;284:1959.