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New organic–inorganic hybrid matrices doped with rhodamine 6G as solid-state dye lasers

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ABSTRACT We report on the laser action of rhodamine 6G (Rh6G) incorporated into new hybrid organic–inorganic monolithic materials. The synthesis of these materials proceeded via the simultaneous sol-gel process of the inorganic part (tetraethoxysilane or tetramethoxysilane) and the free-radical polymerization of an organic monomer part (2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate and a 1 : 1 v/v copolymer of this monomer with methyl methacrylate). The wt. % proportion of the alkoxide was systematically varied in each organic formulation, and the effect of each organic–inorganic composition on the lasing properties of Rh6G was evaluated. The laser samples were transversely pumped and the influence on the laser action of dye concentration, pump wavelength and pump repetition rate was analyzed. Lasing efficiencies of up 26% and good stabilities, with a 90% drop in the initial laser output of up to 12 000 pump pulses at 2.5 Hz, were obtained when the samples were pumped at 355 nm with 5.5 mJ/pulse from the third harmonic of a Q-switched Nd:YAG laser.

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1 Introduction

The development of tunable solid-state dye lasers in which a polymer or glass host medium is doped with an appropriate dye is an area of active research [1]. Solid-state dye lasers exhibit some attractive features as compared with conventional liquid-dye lasers, such as lack of toxicity and flammability, compactness and low-cost gain medium which, in addition to being an essentially maintenance-free system, make them suitable for applications in fields such as medicine, remote sensing and spectroscopy.

Both organic polymers and silica-based inorganic polymers obtained by the sol-gel process have been used as hosts for solid dyes [1]. Inorganic glass hosts generally have better thermal properties (higher thermal conductivity and lower thermal expansion and thermal coefficient of refractive index, $\partial n/\partial T$) [2, 3] and a higher damage threshold than plastics [4, 5]. The low-temperature sol-gel process allows the incorporation of organic dyes into silica gel inorganic glasses, resulting in relatively photostable materials with acceptable laser efficiencies [6, 7]. Nevertheless, new modified polymers have been obtained recently with thresholds of damage by laser radiation as high as those of the inorganic materials, and with higher stabilities than those of the silica gels under the same experimental conditions [8, 9]. To minimize thermal lensing effects in the solid samples, low values of $\partial n/\partial T$ are desirable [10]. Recent measurements of the thermal coefficients of the refractive index of Rhodamine 6G-doped sol-gel silica and poly(methyl methacrylate) slabs found higher values of $\partial n/\partial T$ in the sol-gel silica samples than in the polymeric ones [11]. Polymers exhibit, also, some other important advantages over the silica gels, such as a higher capacity to solve organic dyes, a superior homogeneity [5, 12] and great adaptability to techniques of cheap production. No less important is the relative ease with which the structure and the chemical composition of polymers can be modified, which allows the introduction of controlled changes to optimize their properties when used in a particular application [1, 13].

The above considerations led us to proceed to the synthesis of materials of hybrid character (organic–inorganic) in which the excellent thermal properties of the inorganic glasses could be combined with the excellent optical properties of the polymeric materials. These new hybrid materials are composed of inorganic oxide structures substituted or crosslinked by organic groups. They are prepared from organosilane precursors by sol-gel processing in combination with organic crosslinking of polymerizable monomers. Control of the properties of the final material is achieved by controlling the composition, monomer functionality, chemical nature of the organic and inorganic phases, size and morphology of these domains, from nanometer (nanocomposites) to sub-nanometer (molecular composites) scales, and nature of the interphase interactions.

In this work, the dye rhodamine 6G (Rh6G) was incorporated into hybrid matrices of 2-hydroxyethyl methacrylate (HEMA), 2-hydroxy propyl methacrylate (HPMA) or a 1 : 1 v/v copolymer of methyl(methacrylate) (MMA) and HEMA, with different weight proportions of tetraethoxysilane (TEOS) as the inorganic component, as well as into hybrid matrices of HEMA with different weight proportions of tetramethoxysilane (TMOS) as the inorganic compound. Rh6G was chosen as the reference laser dye because some detailed studies of the lasing properties of this dye in both polymer and inorganic hosts have been carried out in past

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years [1, 14], so that we were able to compare our results with others previously reported in the literature. Likewise, pump wavelengths of 337 and 355 nm were used to facilitate comparison with our previous results on solid-state dye lasers based on Rh6G incorporated into polymeric materials pumped under otherwise similar experimental conditions with pulses from a nitrogen laser [9, 15]. Here, we describe in detail the synthesis route and the preparation of these new materials and characterize their lasing properties under transversal pumping as a function of the organic/inorganic composition of the hybrid matrix. Attention is also paid to the effect on photostability of dye concentration and repetition rate.

2 Experimental

2.1 *Materials*

Rhodamine 6G (chloride Salt, laser grade, Lambda Physik) was used as received with a purity > 99% (checked by spectroscopic and chromatographic methods). Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and 2-hydroxy propyl methacrylate (HPMA) were purchased from Aldrich. All these monomers were distilled under reduced pressure before use. Tetraethoxysilane (TEOS), tetramethoxysilane (TMOS) (ABCR, purity of 99%) and hydrochloric acid (35%) (HCl) from Panreac were used as received, without further purification. Distilled water was used to perform the silicon alkoxide (TEOS or TMOS) hydrolysis. 2, 2′-azo*bis*(isobutyronitrile) (AIBN), purchased from Aldrich, was recrystallized in ethanol before use. The molecular structures of the dye, alkoxides and monomer molecules selected in this work are shown in Fig. 1.

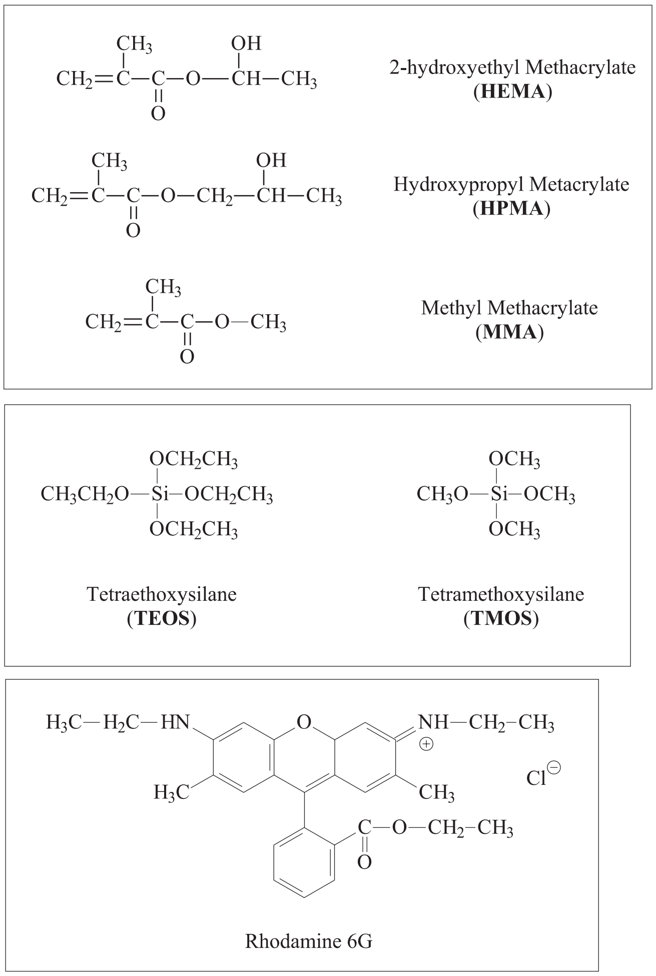

FIGURE 1 Molecular structure of Rh6G dye, organic monomers (HEMA, HPMA and MMA), and inorganic alkoxides (TEOS and TMOS)

2.2 *Synthesis*

The synthesis of new organic–inorganic hybrid materials was carried out through the simultaneous and in situ sol-gel process of the inorganic part (TEOS or TMOS) and the free-radical polymerization of an organic monomer part (HEMA, HPMA) or monomer mixture (MMA : HEMA 1 : 1).

The sol-gel polymerization of the alkoxide ($\mathrm{T}x\mathrm{OS} =$ TEOS or TMOS) was catalyzed by adding, under continuous stirring, a mixture of water and hydrochloric acid (HCl), maintaining in all cases the following molar ratios: $[\mathrm{HCl}]/[\mathrm{T}x\mathrm{OS}] = 1.85 \times 10^{-2}$ and $[\mathrm{H_2O}]/[\mathrm{T}x\mathrm{OS}] = 2$. The total content of the silica precursors was adjusted as a function of the maximum proportion of silicon content that allowed the synthesis of hybrid monoliths under perfect conditions, that is, without suffering breaks and maintaining good optical properties. In the present case, this content was varied from 1 wt. % until a maximum of 30 wt. % TxOS.

The theoretical prediction of the total content of silica present in the hybrid has been calculated assuming that the sol-gel reactions are complete:

$$\mathrm{Si(O{-}C}_n\mathrm{H}_{2n+1})_4 + \mathrm{H_2O} \rightarrow \mathrm{SiO_2} + 4\mathrm{C}_n\mathrm{H}_{2n+1} - \mathrm{OH} \qquad (1)$$

In this case, the following equations have been applied:

$$\frac{m_2}{m_1} = \left(\frac{1}{\alpha} - 1\right)\frac{M_{\mathrm{SiO_2}}}{M_{\mathrm{T}x\mathrm{OS}}} \qquad m_1\frac{M_{\mathrm{SiO_2}}}{M_{\mathrm{T}x\mathrm{OS}}} + m_2 = m_1 \qquad (2)$$

where m_1 and m_2 are the involved masses of the alkoxide (TxOS) and of the acrylic monomer, respectively; α is the silica content of the resulting hybrid; and $M_{\mathrm{SiO_2}}$ (≈ 60 g/mol) and $M_{\mathrm{T}x\mathrm{OS}}$ (≈ 208 g/mol for TEOS and ≈ 152 g/mol for TMOS) the molecular weights of silica and the alkoxide, respectively.

The adequate amount of Rh6G was dissolved in the corresponding monomer or in the mixture MMA : HEMA with a 1 : 1 v/v proportion, and the resulting solutions were placed in an ultrasonic bath in order to assure the complete dissolution of the dye. The simultaneous organic polymerization was carried out by radical bulk polymerization using a thermal initiator, 2, 2′-azo*bis*(isobutyronitrile) (AIBN), at an appropriate concentration (0.5 wt. %), with regard to the total amount of monomer in the polymerization mixture. AIBN was the thermal polymerization initiator of choice, since it leaves UV-transparent end groups on the copolymer. As an example of the preparation procedure, the detailed steps followed in the preparation of HEMA/TEOS-30 wt. % were as described below:

First, HCl aqueous solution was prepared by mixing 10 ml of distilled water with 0.44 ml of the hydrochloric acid solution (35%). Then, if a final volume of 6 ml was required, 0.58 ml of the above solution was added to

0.010 mol of TEOS (3.42 ml) under continuous stirring for at least 30 min. Then, 0.0165 mol of HEMA (2 ml), 0.011 g of AIBN (0.5 wt. %) and the dye (Rh6G, 10^{-3} M) were mixed together. The final organic solutions were then dropped, under stirring, onto the TEOS solution. The resulting mixture was kept under vigorous stirring for another 30 min, and was filtered using a 0.45-µm-pore-size filter, followed by a 0.2-µm-pore-size filter (Whatman lab., polytetrafluoroethylene disposable filters). Then, it was poured into cylindrical molds of polypropylene (≈ 14 mm diameter), with the purpose of obtaining a geometric configuration close to that required by the final solid dye laser piece. The molds were then heated in an oven at 45 °C for approximately 1–2 months, followed by a slow increase of temperature during one week to 80 °C. Finally, the temperature was reduced in steps of 5 °C per day until room temperature was reached, and only then were the samples unmolded. Hybrid cylindrical solid monoliths of approximately 3–4 cm^3 were so obtained, having both optical transparency and good mechanical properties.

2.3 *Methods*

The solid monolithic laser samples were cast in a cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A cut was made parallel to the axis of the cylinder to obtain a lateral flat surface of approximately 6 × 10 mm. This surface, as well as the ends of the laser rods, was prepared for lasing experiments by grinding and polishing until reasonably flat surfaces were obtained.

The hybrid rods were transversely pumped by the third harmonic of a Q-switched Nd:YAG laser (Spectron SL284G), which provided 355-nm pulses of 6 ns duration and 5.5 mJ energy at a repetition rate of up to 10 Hz. The exciting pulses were directed towards the lateral flat surface of the sample with a combination of spherical ($f = 50$ cm) and two cylindrical quartz lenses. The first, with $f = -15$, widened the spherical cross section of the pump beam to illuminate the complete 1-cm length of the dye sample; then, the second lens, with $f = 15$ cm and perpendicularly arranged, focused the pump pulses onto the input surface of the solid sample to form line of 0.3 × 10 mm, so that the pump fluence was 180 $\mathrm{mJ/cm}^2$. Some experiments were carried out with pumping at 337 nm, with 1.7-mJ, 7-ns pulses from a nitrogen laser, at repetition rates of up to 10 Hz. In both cases, the oscillator cavity consisted of an approximately 90%-reflectivity flat aluminum mirror with the end face of the cylindrical sample as the output coupler, with a cavity length of 4 cm. The cavity was not optimized and did not have tuning elements to select the wavelength.

The dye and pump laser pulses were characterized with the following instruments: GenTec ED-100A and ED-200 pyroelectric energy meters, ITL TF1850 fast rise-time photodiode, Tektronix 2430 digital storage oscilloscope, CM110 monochromator (CVI Laser Corporation) and EMI 9783B photomultiplier. The dye and pump laser signals were sampled with boxcars (Stanford Research Model 250). All the integrated signals were digitized and processed using a PC computer via a Computerboard DASH-8 interface [16]. The estimated error of the energy measurements was 10%.

3 Results and discussion

Broadband laser emission was obtained from all the monolithic materials under study. The lasing properties of Rh6G incorporated into these new hybrid organic–inorganic materials were characterized through the evaluation of the energy conversion efficiency, defined as the ratio of the energy of the dye laser output and the energy of the pump laser incident on the sample surface, the laser emission spectrum and the dye laser photostabilty, defined as the evolution of the laser output as a function of the number of pump pulses in the same position of the sample at a selected repetition rate. This parameter is reported as the number of pump pulses that induce a drop in the laser output of the solid sample ranging from 90 to 98%.

Different studies were carried out in order to analyze the dependence of the laser performance on different experimental parameters, such as dye concentration, pumping wavelength and repetition rate, and the composition of the matrix host was changed by varying the nature and proportion of the organic monomers as well as the inorganic components.

3.1 *Influence of the dye concentration*

Studies on the dependence of the lasing properties of Rh6G-doped P(HEMA : TEOS 25%) on dye concentration were performed by varying this parameter over the range 5×10^{-4} M to 10^{-3} M and pumping the samples at 355 nm and a repetition rate of 1.25 Hz.

The lasing efficiency and the useful lifetime were found to be very dependent on the Rh6G concentration in the sample. The highest photostability and efficiency were obtained with the 10^{-3} M dye concentration. Decreasing this parameter was detrimental to the laser action. Increasing the dye concentration above 10^{-3} M resulted in a lower solubility of the rhodamine in the material and implied some additional phenomena, such as re-absorption and re-emission effects and the dimerization of the dye, leading to a loss in the laser emission [17]. The same dye concentration had been previously determined to be that which optimized the laser performance of Rh6G embedded in a polymeric matrix and pumped under otherwise identical experimental conditions [15].

3.2 *Influence of the inorganic composition of the hybrid matrix*

Solid samples of Rh6G with the optimal concentration of 10^{-3} M were prepared, where the dye was dissolved in hybrid matrices of HEMA with two different alkoxides, TMOS and TEOS, added in wt. % proportions up to 10% and 30%, respectively. A preliminary study was carried out in which different samples with TMOS or TEOS as alkoxide were irradiated at different repetition rates with 337-nm pulses of 1.2 mJ. In all cases, repetition rates above 2 Hz resulted in a steady decrease of dye photostability. It seems that at high repetition rate the dissipation channels for the energy released to the medium as heat are not effective enough, and as a result the thermal degradation of the dye is enhanced [18–20].

In order to gain a better insight into the laser performance of these new hybrid materials, their lasing properties were also investigated with pumping at 355 nm (third harmonic of

Nd:YAG) with pulses of 5.5 mJ, well over the pump threshold for this dye [15]. Repetition rate was kept at the moderate value of 2.5 Hz.

Laser-emission maxima and oscillation bandwidths of Rh6G incorporated into these materials are listed in Table 1. The laser-emission spectrum is much narrower than that of the fluorescence, with bandwidths typical of a laser with many modes running simultaneously, due to the lack of wavelength-selection elements in the cavity. Increasing the proportion of TEOS in the matrix results in red shifts of the maxima of both the fluorescence and the laser spectra. These shifts are probably related to changes in the polarity of the media.

The evolution of lasing efficiency and stability with the nature and proportion of the inorganic part of the hybrid materials are also compared in Table 1. In Fig. 2, the dependence of the laser output of Rh6G dye with the number of pump pulses is shown graphically for matrices based on HEMA with 5, 10 and 15 wt. % proportion of TEOS as the inorganic component of the hybrid hosts. Low lasing efficiencies and lifetimes are obtained with samples with TMOS as alkoxide. When the alkoxide in the matrix was TEOS, the laser emission of Rh6G varied significantly with the increased presence of TEOS.

Material	λ_{max} (nm)	$\Delta\lambda$ (nm)	Eff (%)	Lifetime[b]
TMOS 5%	585	6	4	700
TMOS 10%	585	7	4	1500
TEOS 5%	580	7	3	2000
TEOS 10%	582	7	7	5500
TEOS 15%	583	7	16	12 000
TEOS 20%	585	7	6	4600
TEOS 25%	587	8	4	1700
TEOS 30%	588	11	3	350

[a] λ_{max}: peak of the laser emission; $\Delta\lambda$: FHWM of the laser emission; Eff: energy conversion efficiency

[b] Number of pump pulses that induced a 90% drop in the laser output.

TABLE 1 Lasing parameters[a] of Rh6G dissolved in hybrid matrices of HEMA with different alkoxides added in various wt. % proportions, pumped with 5.5 mJ/pulse at 355 nm (3rd harmonic of Nd:YAG) and 2.5 Hz repetition rate. Dye concentration: 10^{-3} M

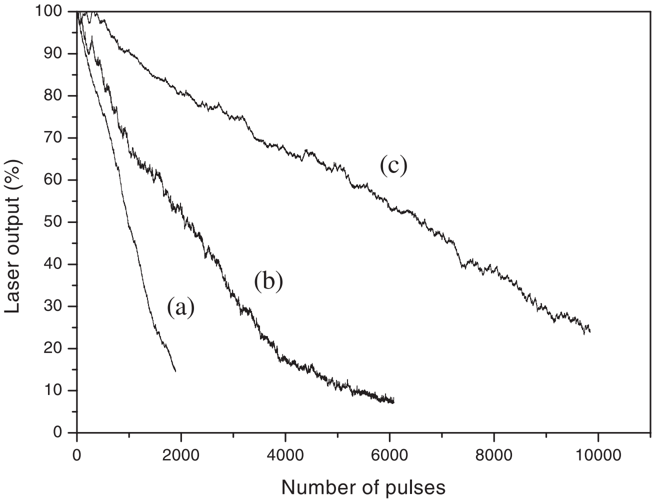

FIGURE 2 Normalized laser output as a function of the number of pump pulses for Rh6G dissolved in HEMA with different wt. % proportions of TEOS: a = 5%, b = 10% and c = 15%. Dye concentration: 10^{-3} M. Pump wavelength, energy, and repetition rate: 355 nm, 5.5 mJ/pulse and 2.5 Hz, respectively

Both laser parameters, energy conversion efficiency and photostability, exhibit the same dependence on the inorganic composition of the hybrid matrix. As seen in Table 1, the lasing efficiency and lifetime first increase with the proportion of TEOS, peaking at the composition with a 15 wt. % proportion of TEOS. A higher proportion of the alkoxide in the matrix is detrimental to the laser action, with a progressive shortening of the lifetime to levels below those obtained with the TMOS alkoxide added to HEMA.

A note of caution is needed when analyzing the values of the lasing efficiency reached with the hybrid materials herein studied. As indicated in the experimental section, the finishing of the surface of the solid samples relevant to laser operation was not laser grade. Thus, improvements in lasing efficiency are to be expected in these samples with enhanced optical quality of their surfaces. In addition, the reflectivity of the output coupler in the oscillator cavity was not optimized for laser operation in any case. Our main concern in this work was not so much to optimize the laser output as to study comparatively the photostability and relative efficiencies of operation in different materials under otherwise identical conditions. These experimental conditions are also equivalent to those used in our previous studies, so that the results here obtained are directly comparable to the previous ones.

It is interesting to remark on the apparent direct relationship between lasing efficiency and photostability observed in the TEOS material: the higher the efficiency, the lower the rate of degradation. This behaviour was observed in our previous work on Rh6G embedded into polymeric matrices and pumped at 337 nm under otherwise identical experimental conditions [15].

Taking into account that the synthesis reaction of these hybrid materials is a highly exothermic process, it is critical to analyze the influence of this inherent increase in the temperature, which can autoaccelerate the reaction rate, on the laser performance of the final sample. With this aim, materials containing Rh6G incorporated into HEMA with 10, 15 and 20 wt. % proportions of TEOS were prepared with the synthesis being carried out in a water-filled bath, which allowed a more strict control of the temperature by continuous cooling of the medium. Neither the efficiency nor the photostability of the Rh6G dye laser were significantly changed by this modified polymerization process, revealing that the exothermicity of the reaction did not play an important role in the laser action. Consequently, the reaction process and the correct thermal treatment of the sample can be carried out in an oven which allows the synthesis of a high number of samples at the same time.

3.3 *Influence of the organic composition of the hybrid matrix*

To study the effect on laser operation of modifying the organic composition of these new materials, the lasing properties of Rh6G dissolved in hybrid matrices of TEOS as the inorganic part, added in wt. % proportions ranging from 5% to 20%, and HEMA, HPMA or a 1 : 1 v/v copolymer of MMA : HEMA as organic component, were investigated. The methacrylic monomers HEMA and HPMA were selected, since, due to their OH side groups, no addition of solvents was necessary because these monomers are good cosolvents of TEOS, allowing the maintenance of a viscosity low enough to achieve a good mixing level. In addition, these hydroxyl groups can participate in the polycondensation process of TEOS silanols, and thus a great compatibility of HEMA or HPMA units with the inorganic species was achieved, allowing a very fine and interpenetrated polymer silica morphology with excellent optical transparency to be obtained. Also, the monomer mixture MMA : HEMA = 1 : 1 was selected since, in previous studies on polymeric solid-state dye lasers based on Rh6G, we demonstrated that both lasing efficiency and photostability were greatly improved by internally increasing the PMMA's plasticity by copolymerization with HEMA, this being the composition that had been shown to be the best host material for Rh6G [7]. The experiments were carried out pumping the samples at 355 nm with 5.5 mJ/pulse and 2.5 Hz as the repetition rate. The results obtained with HEMA have already being presented in Table 1. In Table 2, the effect on laser action of the presence of organic components MMA : HEMA = 1 : 1 and HPMA is reported. For the sake of clarity, the experimental photostability, defined as the number of pump pulses required to induce a 90% efficiency drop, are also represented in Fig. 3 as bar diagrams.

The dependence of the laser action on the proportion of TEOS is independent of the organic component present in the matrix, following the same behaviour described in the above section: the lasing efficiency and photostability first increase with the proportion of TEOS, peaking at the composition with 10% and 15 wt. % proportions of the alkoxide added to HPMA and MMA : HEMA 1 : 1, respectively. A higher proportion of TEOS in the matrix results in a progressive worsening of laser performance.

Taking into account the experimental results reported in Tables 1 and 2, it seems that, for matrices up to 10 wt. % proportion of inorganic component, the best lasing efficiency and stability of Rh6G is reached in the host with HPMA as organic component. Increasing the proportion of the alkoxide, the best laser performance was induced by the presence of homopolymer HEMA and copolymer HEMA : MMA = 1 : 1 when the proportion of TEOS was 15 wt. %.

It has to be pointed out that for each wt. % proportion of TEOS, both the presence of monomer HPMA and the addition of MMA to HEMA results in materials with a laser efficiency higher than that obtained in matrices with HEMA as the sole organic component. In fact, Rh6G dissolved in a hybrid (HPMA-10 wt. % TEOS) host reaches a lasing efficiency of 26%, close to the efficiency (31%) of a 10^{-3} M solution of the dye in ethanol, placed in the same experimental set-up (using the end-face of the 1-cm-optical-path cell as the output coupler).

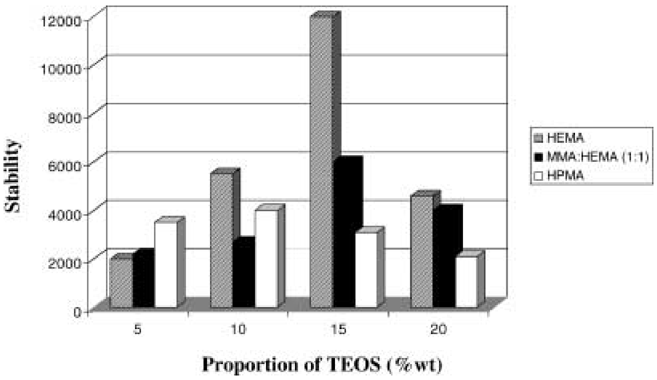

FIGURE 3 Dependence of the laser stability (number of pump pulses required to induce a 90% efficiency drop) with the percentage of TEOS added to different organic compositions, HPMA, HEMA and 1 : 1 v/v copolymer of MMA : HEMA. Dye concentration: 10^{-3} M. Pump wavelength, energy and repetition rate: 355 nm, 5.5 mJ/pulse and 2.5 Hz, respectively

For all the materials synthesized in this work, it was observed that increasing the inorganic part in the matrices increased the fragility of the material, making it difficult for the subsequent mechanization and polishing. Although differences in the optical quality of the samples could influence the lasing efficiency of the dye embedded in the different matrices, it is unlikely that this was the reason for the large changes in these parameters observed in Tables 1 and 2. Rather, it would be differences in microstructure, polarity and free volume that should play a central part in the performance of the various materials, although the detailed mechanism at work is not yet completely understood.

3.4 *Comparison with previous results*

The results here presented compare well with our previous results on solid-state dye lasers based on Rh6G incorporated into polymeric materials and pumped under similar experimental conditions with pulses from a N_2 laser [15]. The lasing efficiency of Rh6G dissolved in some of the new hybrid materials studied in the present work reaches the same level and even exceeds the values reported for this dye embedded in pure polymeric matrices (a maximum efficiency of 21.5% obtained with MMA : HEMA = 1 : 1 composition [15]). The photostability results here reported are of the same order as those obtained with the polymeric matrices, where the highest stability was obtained again with the

TABLE 2 Lasing parameters[a] of Rh6G dissolved in hybrids matrices with different wt. % proportion of TEOS as inorganic part added to two different organic components, MMA : HEMA 1 : 1 and HPMA. Pumping conditions: 5.5 mJ/pulse at 355 nm (3rd harmonic of Nd:YAG) and 2.5 Hz repetition rate. Dye concentration: 10^{-3} M

	MMA : HEMA 1 : 1				HPMA			
Material	λ_{max} (nm)	$\Delta\lambda$ (nm)	Eff (%)	Lifetime[b]	λ_{max} (nm)	$\Delta\lambda$ (nm)	Eff (%)	Lifetime[b]
TEOS 5%	590	8	8	2200	578	6	11	3000
TEOS 10%	594	7	13	2900	583	7	26	4000
TEOS 15%	598	7	19	5800	584	6	16	3600
TEOS 20%	599	8	16	4000	585	7	10	2200

[a] λ_{max}: peak of the laser emission; $\Delta\lambda$: FHWM of the laser emission; Eff: energy conversion efficiency
[b] Number of pump pulses that induced a 90% drop in the laser output.

TABLE 3 Summary of previous results on laser parameters of Rh6G incorporated into inorganic and hybrid hosts obtained by other authors

Material[a]	λ_p (nm) (L/T)[b]	Eff (%)	Useful lifetime[c]	Reference
Aluminosilicate gel	540 (T)	25		21
Aluminosilicate gel	511 (T)		1500	21
ORMOSIL I	539 (T)		2700	22
ORMOSIL G	539 (T)		2700	22
ORMOSIL	532 (T)	30	11000[d]	23
ORMOSIL (impregnated)	532 (L)	35	< 1000	24
ORMOSIL (titania)	532 (L)	13	(12 GJ/mol)[e]	25
Sol-gel glass	532 (L)	24	4500	6
ORMOSIL 1	532 (T)	19.1	4500	14
Zirconia-ORMOSIL 2	532 (T)		6500	14

[a] ORMOSIL: organically modified silicate; ORMOSIL I: epoxy-diol modified silicate; ORMOSIL G: epoxy-diol/MMA/silica copolymer; ORMOSIL (impregnated): material subjected to impregnation treatment; ORMISIL (titania): titania-containing ORMOSIL; Zirconia-ORMOSIL: silica materials containing zirconium *n*-propoxide.

[b] After each pumping wavelength, λ_p, it is indicated in parantheses if the pump configuration was longtitudinal (L) or transversal (T).

[c] Number of pump pulses that produces a 50% drop in the laser output measured at 1 Hz as repetition rate.

[d] Useful lifetime measured at 30 Hz as repetition rate.

[e] Photostability defined as the total input energy per mole of dye molecules when the output energy was down to 50% of its initial value.

P(MMA : HEMA = 1 : 1) matrix, where the laser intensity underwent a 90% reduction after 10 000 pump pulses.

The lasing properties reported in the present work also compare well or, in some cases, are an improvement on the laser parameters reported by other authors for Rh6G incorporated into inorganic and other hybrid hosts. For the sake of clarity, a summary of the most representative results previously obtained with this dye embedded into these solid materials is presented in Table 3.

4 Conclusions

In summary, a systematic and comprehensive study of the lasing properties of Rh6G in several inorganic–organic monolithic hybrid hosts has been carried out. The results obtained indicate that both the efficiency and photostability of the dye in these hybrid materials are very dependent on both the nature of the organic component and the amount of alkoxide added to it. The addition of small amounts of TEOS to methacrylic monomers results in hybrid matrices where the laser action exhibited by Rh6G compares well or, in some cases, is an improvement on that described in polymeric matrices as well as in other inorganic and hybrid hosts analyzed by other authors. In order to obtain the best efficiency and photostability of a dye/hybrid system, a balance must be reached between the advantages of inorganic materials, for instance, high thermal dissipation capability, and those offered by organic polymers, such as higher capacity to solve organic dyes, a superior homogeneity, real adaptability to techniques of cheap production, and the relative ease with which the structure and the chemical composition can be modified, allowing controlled changes to optimize their properties. The best laser performance (efficiency and useful lifetime) were reached when Rh6G was dissolved in the following hybrid matrices: (HPMA – 10 wt. % TEOS); (HEMA – 15 wt. % TEOS) and (MMA : HEMA 1 : 1 – 15 wt. % TEOS). The highest lasing efficiency was 26%, reached in the (HPMA 10 wt. % TEOS) material. The highest photostability, a drop of the initial laser output by 90% after 12 000 pump pulses, was obtained with the (HEMA 15 wt. % TEOS) composition. These results were obtained with transversal pumping at 355 nm with 5.5 mJ/pulse and a repetition rate of 2.5 Hz.

A substantial lifetime increase ought to be expected if the pump wavelength were changed from 355 nm to 532 nm, as the lower energy difference between pump and laser photons at the 532-nm pump wavelength should minimize the photochemical degradation of the dye as well as the energy released to the medium as heat, which should also result in less thermal degradation of the dye. In fact, in previous work [15] we have demonstrated that, at 10 Hz repetition rate, the lifetime of the solid solutions of Rh6G in P(MMA : HEMA = 1 : 1) increases from 8500 to 45 000 pulses when the pump wavelength is changed from 337 to 532 nm.

Taking into account that for good laser performance of a dye in a solid medium a proper adjustment of the host material structure and composition is required in order to obtain appropriate optical, thermal and mechano-dynamic properties of the matrix, which optimize the laser action, work in progress is directed to developing new organic–inorganic hybrid materials with double and triple functionalized alkoxides instead of the quadrupole ones, TEOS and TMOS. In this way, it could be possible to increase the inorganic proportion in the matrix while relaxing in a controlled way the rigidity and fragility of the final material. This information would be of great value in the search for strategies to improve the laser properties of dyes incorporated into hybrid and inorganic hosts.

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