

Polymer-Filled Nanoporous Silica Aerogels as Hosts for Highly Stable Solid-State Dye Lasers

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New hybrid solid-state dye laser materials based on highly porous silica aerogels have been synthesized. The open porous network of the aerogel was saturated with laser dyes dissolved in appropriate organic monomers, and polymerization took place inside the silica structure. The resulting polymer-filled nanoporous aerogel (PFNPA) was cast in a cylindrical shape, forming monoliths that were used as gain media in solid-state dye lasers. When the PFNPA incorporated pyrromethene dyes, highly photostable laser emission with good lasing efficiency was obtained. Under the demanding conditions of tightly focused transversal pumping with 532 nm, 5 mJ pulses at 10 Hz repetition rate, the commercial dye Pyrromethene 567 exhibited laser action with only a 10% drop in the laser output after 10^6 pump pulses in the same position of the sample.

I. Introduction

The development of tunable solid-state dye lasers, in which an organic dye is incorporated into a suitable solid matrix, is a subject of great interest and activity,¹ because such lasers combine the convenience of solid-state lasers with the broad tuning range and high efficiency of organic laser dyes. Solid-state dye lasers (SSDL) exhibit well-recognized advantages over conventional liquid dye lasers as they avoid the problems of toxicity and flammability posed by the use of organic solvents, present a low-cost gain medium, and are compact and easy to operate and maintain.

The basic requirements imposed on a solid matrix to be used as host for lasing dye molecules are transparency to both pump and lasing wavelengths, high optical quality with low level of scattering, high damage threshold to laser radiation, and good thermal and photochemical stability. A simple technology for doping the matrix material with different classes of organic dyes is also desirable. Although matrixes based on both inorganic glasses and transparent polymers have been tried over the years, no material has been found yet that fully satisfies all the above requirements.

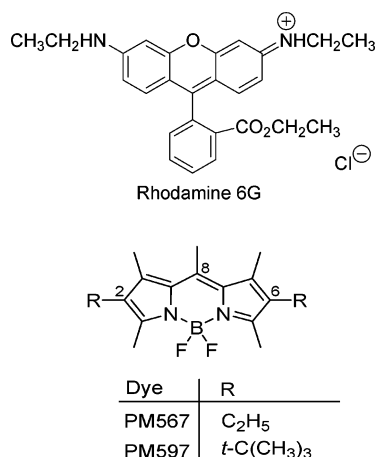
Inorganic glasses exhibit generally better thermal properties (higher thermal conductivity and lower thermal expansion)^{2,3} and a higher damage threshold than polymers.^{4,5} The low-temperature sol–gel process allows the incorporation of organic dyes into silica gel inorganic glasses, resulting in relatively photostable materials with acceptable laser efficiencies.^{1,5,6} Polymers, on the other hand, have better compatibility with organic dyes and superior optical homogeneity,^{5,7} and their structure and chemical composition can be easily modified, which allows their properties to be controlled and optimized

for specific applications.^{1,8} On the side of the disadvantages, it should be said that thermal degradation under laser irradiation ultimately limits the photostability of the dye-doped polymeric materials. In addition, thermal lensing effects, which depend on the thermal coefficient of refractive index $\partial n/\partial T$, can be quite severe in polymers due to the relatively high values of $\partial n/\partial T$ in these media, on the order of -10^{-4} K^{-1} .^{9,10} Thus, concave, or negative, thermal lenses with focal lengths in the few centimeters range have been observed in polymeric SSDL in the pulsed regime, at pump power densities of $\sim 0.5 \text{ J/cm}^2$.¹¹

One way to improve the thermal resistance of the laser material without losing the benefits provided by polymers could be the use of inorganic–organic copolymers, composed of inorganic oxidic structures substituted or cross-linked by organic groups. From the literature of crystalline solid-state laser gain media,³ values for $\partial n/\partial T$ on the order of -10^{-5} K^{-1} can be inferred. Thus, in addition to improved photostability, organic–inorganic copolymers incorporating laser dyes are expected to exhibit lower $\partial n/\partial T$ values than organic polymers, with the corresponding decrease in thermal lensing effects in the material. As the beam divergence $\Delta\theta$ in the laser emission from SSDL oscillators has been found to be a function of the inverse of the focal length of the concave thermal lens,¹¹ a decrease in $\Delta\theta$ is to be expected because of the longer focal lengths, or weaker thermal focusing effects.

Over the past few years we have tried the above approach, and we have studied the laser performance of Rhodamine 6G (Rh6G) and Pyrromethene 567 (PM567) dyes incorporated into different inorganic–organic hybrid materials, prepared from alkoxide precursors by sol–gel processing in combination with simultaneous polymerization of organic monomers. In accordance with our initial hypothesis, we obtained results

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SCHEME 1: Molecular Structures of Dyes Rhodamine 6G and Pyrromethene 567 and 597

indicating an increase in thermal dissipation giving rise to a reduction of dye thermal degradation in the hybrid matrixes.^{12–14}

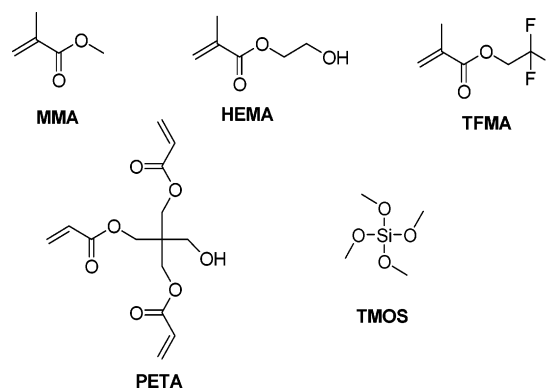
Trying to further improve the photostability of the laser dyes when incorporated into solid hosts, we have synthesized new hybrid matrixes with improved thermo-optical and mechanical properties based on silica aerogels. Silica aerogels are spongelike glasses characterized by an extremely high porosity (80–99%) with well accessible mesopores (20–100 nm) filled with air.¹⁵ By careful selection and control of the experimental conditions during the synthesis process, materials with good optical transparency and adequate mechanical properties can be obtained.^{16,17} The open pore structure of these materials forms an amorphous inorganic three-dimensional network of low density which, under appropriate conditions, can be filled with adequate polymeric formulations incorporating a laser dye.

Here, we describe in some detail the preparation and properties of some solid-state dye laser materials based on polymer-filled nanoporous aerogels (PFNPA–SSDL) and characterize their laser performance under transversal pumping. Pyrromethene 567 (PM567), Pyrromethene 597 (PM597), and Rhodamine 6G (Rh6G) were chosen as reference dyes (Scheme 1) because there were previous studies on the lasing properties of these dyes in polymer, inorganic, and hybrid hosts that would facilitate the evaluation of our results by comparison with those reported in the literature. The organic part of the new hybrid materials consisted of copolymers of methyl methacrylate (MMA) with different linear and cross-linking monomers, chosen in the light of information obtained in our previous studies on the lasing properties of different dyes incorporated into polymeric materials.^{18–20}

II. Experimental Section and Methods

PM567, PM597 (both laser grade from Exciton), and Rh6G (chloride salt, laser grade, Lambda Physik) dyes were used as received. MMA was copolymerized with monofunctional monomers 2-hydroxyethyl methacrylate (HEMA) and 2,2,2-trifluoroethyl methacrylate (TFMA) and with cross-linking monomer pentaerythritol methacrylate (PETA) (Scheme 2). All monomers were purchased from Aldrich. MMA and HEMA were distilled under reduced pressure before use, and TFMA and PETA were used as received. Tetramethoxysilane (TMOS, Scheme 2) (Aldrich, 98% pure) was utilized in the synthesis of aerogels and used as received.

The detailed synthesis of silica aerogels has been published elsewhere.^{16,17} Briefly, silica gels were produced in a one-step-

SCHEME 2: Molecular Structures of Organic Monomers (MMA, HEMA, TFMA, and PETA) and Inorganic Alkoxide (TMOS)**TABLE 1: Structural, Mechanical, and Optical Properties of Typical M and A Silica Aerogel Samples**

	M016	A025
density (g/cm ³)	0.16	0.25
porosity (%)	93	86
pore volume (cm ³ /g)	7.2	3.2
mean-pore diameter (nm)	60	20
surface area (m ² /g)	590	415
hardness (MPa)	1.4	5.7
Young's modulus (MPa)	29	340
transmittance at 900 nm (%)	70	40

synthesis procedure involving hydrolysis and polycondensation of TMOS. Evacuation of the solvent filling the gel pores is performed in supercritical media to prevent volume shrinkage and to preserve the monolithicity and large porosity of the initial framework. There is a direct connection between the sol–gel chemistry and the microstructure of the resulting aerogel, so that, depending on the chosen conditions of reaction (gelification time, type of catalyzer, and solvent) and the nature of the precursors, it is possible to control the density and porosity of the resulting material. Two different routes were followed in the synthesis of the aerogels. In one case, a solution was prepared by addition of methanol (CH₃OH) to TMOS; afterward, water was added containing ammonium hydroxide (NH₄OH). Alternatively, the reactants were acetone (CH₃COCH₃), TMOS, and water. The solution was poured into cylindrical molds, tightly closed, and kept at room temperature until jellification took place; then the gels were covered with the solvents and left to age. Supercritical extraction of the solvent took place in a high-temperature, high-pressure facility. The pressure was initially raised to 80 bar using CO₂ and was monitored and kept stable to great accuracy. Once the final pressure was reached, the temperature was slowly raised to 280 °C. Then the solvent was removed by slow depressurization. In this way, aerogel cylindrical monoliths of up to 12 cm length and 1 cm diameter were obtained. We will denote aerogels M those obtained by the route that uses methanol, and aerogels A those obtained by the route using acetone. In Table 1 are collected some characteristic properties of a typical aerogel M and a typical aerogel A. Aerogels were prepared with densities ranging from 0.09 to 0.28 g/cm³. The estimated error in the density measurements was 10%. As an example of the recipe used to prepare the materials, the molar ratio of the reactants used to prepare aerogels M016 and A025 was the following: TMOS/CH₃OH/H₂O/NH₄OH = 1/12.25/4/0.065 and TMOS/CH₃COCH₃/H₂O = 1/2.92/4, respectively.

The adequate amount of organic laser dyes was dissolved in the selected mixture of polymerizable organic monomers, and

the resulting solutions were placed in an ultrasonic bath until complete dissolution of the dye. 2,2'-Azobis(isobutyronitrile) (Aldrich, purified by recrystallization in ethanol before use) was used as thermal initiator for radical polymerization and added in appropriate concentration (0.007 g/L). The resulting solutions were poured into polypropylene cylindrical molds containing the aerogel cylindrical monoliths. In this way, the open porous network of the aerogel was saturated with the organic solution and, after careful evacuation of air trapped into the aerogel, polymerization took place inside the silica structure under soft thermal conditions, following the procedure described elsewhere.²¹ This procedure led to a material with higher structural and chemical stability than those hybrid matrixes obtained by in situ hydrolysis–condensation of an alkoxide during the simultaneous radical polymerization of a monomer solution incorporating the laser dye.¹² The novelty of our approach is that, to a first approximation, it uncouples the synthesis of the inorganic extremely porous matrix from the organic polymer–dye component. By doing so, it is possible to tailor with greater accuracy the desired properties of each component without deleterious mutual interference.

Materials prepared were the following: aerogel containing PM567 dissolved in copolymers COP(MMA–HEMA 1:1 v/v), COP(MMA–TFMA 7:3 v/v), and COP(MMA–PETA 9:1 v/v), and aerogel containing PM597 or Rh6G dissolved in copolymer COP(MMA–HEMA 1:1 v/v). Dye concentrations were 1.5×10^{-3} , 0.7×10^{-3} , and 1×10^{-3} M for PM567, PM597, and Rh6G, respectively. The index of refraction of the final material was found to depend on the type of polymer and not on the density of aerogel. Measured refractive indices were 1.4925 (MMA–HEMA 1:1), 1.4845 (MMA–PETA 9:1), and 1.4620 (MMA–TFMA 7:3).

Regarding nomenclature, we will identify the aerogels with the letter “M” or “A” followed by a number indicating their density. Thus, aerogel M014 refers to aerogel prepared by the route that uses methanol rendering a material with density 0.14 g/cm³. Material M014[PM567/COP(MMA–HEMA 1:1)] refers to aerogel M014 containing the dye PM567 dissolved in a copolymer of MMA and HEMA with the monomer proportion 1:1 v/v, and so on.

The PFNPA–SSDL samples were cast in cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A lateral cut parallel to the axis of the cylinder defined a lateral flat surface of $\sim 4 \times 10$ mm². All flat surfaces were prepared for lasing experiments by conventional grinding and polishing by hand until a reasonable flatness was obtained. The PFNPA–SSDL rods were transversely pumped at 532 nm with 5 mJ, 6-ns pulses from a frequency-doubled *Q*-switched Nd:YAG laser (Spectron SL282G) at a repetition rate of 10 Hz. The exciting pulses were line-focused onto the lateral flat surface of the solid samples, and typical pump fluences on the active medium were 180 mJ/cm². The oscillation cavity consisted of a 90% reflectivity aluminum mirror and the end face of the sample as the output coupler, with a cavity length of 2 cm. Details of the experimental setup can be found elsewhere.²¹

III. Results and Discussion

We first studied the lasing performance of dye PM567 incorporated into PFNPA samples based on aerogels M and A with different densities, that is, with different microstructures. The organic component of the hybrid material was a copolymer of MMA and HEMA in 1:1 proportion. HEMA was selected as an organic comonomer because its OH side groups increase the compatibility with the inorganic species.

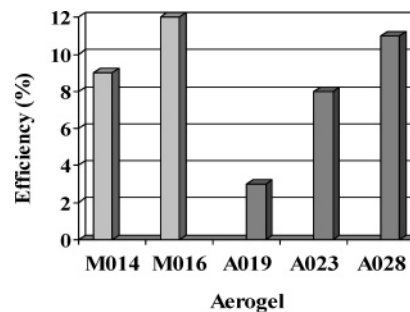


Figure 1. Lasing efficiencies of dye PM567 incorporated into hybrid matrixes of silica aerogels filled with MMA–HEMA 1:1 copolymer. Dye concentration: 1.5×10^{-3} M.

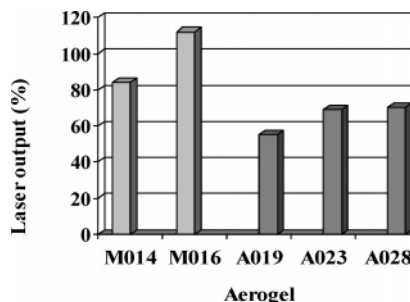


Figure 2. Percent intensity, referred to initial intensity, of laser output after 100 000 pump pulses in the same position of the sample from dye PM567 incorporated into hybrid matrixes of silica aerogels filled with MMA–HEMA 1:1 copolymer. Dye concentration: 1.5×10^{-3} M. Pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively.

The lasing efficiencies of PM567 in the different PFNPA materials under study, defined as the ratio between the energy of the dye laser output and the energy of the pump laser incident on the sample surface, are reported in Figure 1. In all cases the laser emission peaked around 560 nm and the line width (full width at half-maximum) was 4–5 nm.

It is seen in Figure 1 that in both M and A aerogels the lasing efficiency increases with the aerogel density, although as we will see later on this is not always the case. The highest lasing efficiencies, obtained with materials M016[PM567/COP(MMA–HEMA 1:1)] and A028[PM567/COP(MMA–HEMA 1:1)], are slightly above the 10% efficiency obtained with PM567 dissolved in the pure organic copolymer COP(MMA–HEMA 1:1),¹⁹ but they are only half those obtained with PM567 incorporated into organic–inorganic hybrid materials consisting of 1:1 copolymers of MMA and HEMA with different weight proportions of tetraethoxysilane (TEOS), pumped under otherwise identical experimental conditions.¹²

In Figure 2 are represented the intensities of the laser output relative to the initial intensities of the laser emission after 100 000 pump pulses in the same position of the sample at 10 Hz repetition rate. In Figure 3 two examples, corresponding to aerogels M and A, are presented of the actual evolution of the laser output with the number of pump pulses.

In the M samples, the photostability appears to be sensitive to the actual density of the aerogel (Figure 2), whereas in the A samples its dependence with density was moderate. In all cases the stability was much better than in the organic matrixes PM567/COP(MMA–HEMA 1:1), where the laser emission dropped to 25% of the initial output after only 10 000 pump pulses at 1 Hz repetition rate,¹⁹ and improved clearly the stability of the organic–inorganic hybrid materials PM567/COP(MMA–HEMA 1:1 + TEOS), where the best result was a drop of the

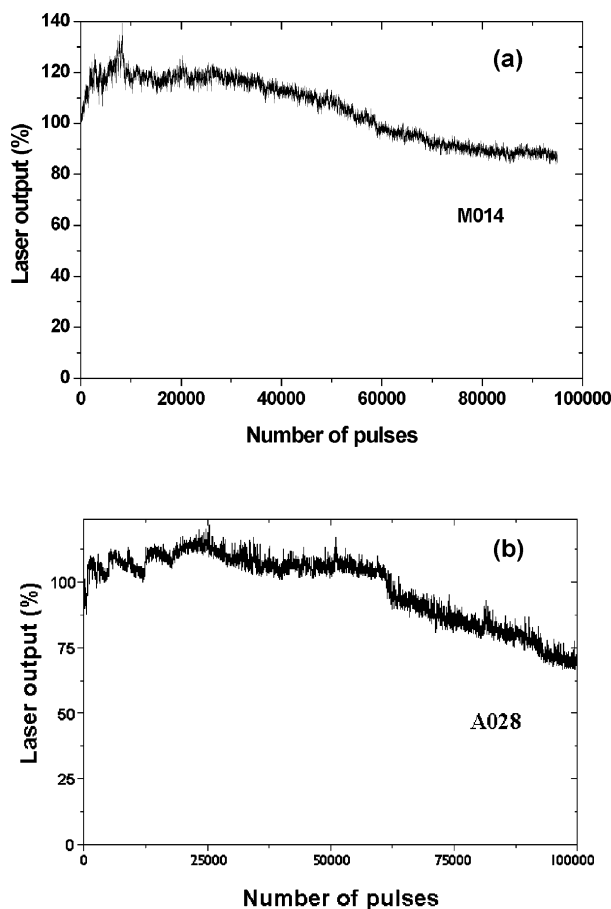


Figure 3. Evolution of laser output with number of pump pulses in the same position of the sample for materials (a) M014[PM567/COP-(MMA–HEMA 1:1)] and (b) A028[PM567/COP(MMA–HEMA 1:1)]. Dye concentration: 1.5×10^{-3} M. Pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively.

laser emission to 70% of the initial laser output after 60 000 pump pulses at 10 Hz repetition rate.¹²

A result in Figure 2 which attracts attention is that obtained with material M016[PM567/COP(MMA–HEMA 1:1)], because in this case the intensity of the laser emission after 100 000 pump pulses in the same position of the sample is actually higher than the initial lasing intensity. Thus, to assess the long-term stability of this material, it was subjected to a longer run of pumping. In Figure 4 is shown the evolution of the laser output of this material over a run of 10^6 pump pulses in the same position of the sample at 10 Hz repetition rate. The laser emission exhibited a rather irregular behavior with some strong fluctuations. It kept on increasing for about 300 000 pulses to decrease later, finally stabilizing at 80/90% of the initial value. Similar irregular behavior has been previously observed with other pyromethene dyes incorporated into silica gel matrixes.²² At the present time we cannot offer any nonspeculative explanation of this result, and further studies would be necessary to clarify this point, although no single cause is expected to fully explain the behavior of these rather complicated systems.

To facilitate comparison between results obtained by different authors under different experimental conditions, Rahn and King²³ introduced a normalized photostability defined as the accumulated pump energy absorbed by the system per mole of dye molecules before the output energy falls to half its initial value. Its units are gigajoules per mole (GJ/mol). In these units, the best previous result, obtained by Ahmad et al.²⁴ with a mixture of PM567 and Coumarin 540 in polymer samples, was

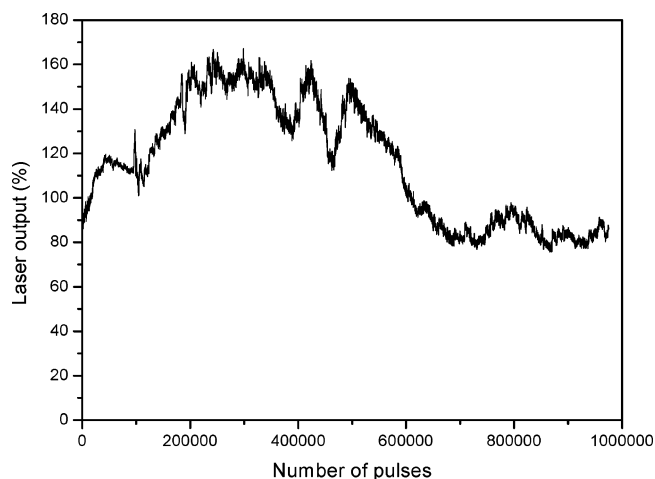


Figure 4. Evolution of laser output with number of pump pulses in the same position of the sample for material M016[PM567/COP-(MMA–HEMA 1:1)]. Dye concentration: 1.5×10^{-3} M. Pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively.

TABLE 2: Dyes Incorporated into Hybrid Matrixes of Silica Aerogel A025 Filled with Different Copolymer Formulations, and Their Laser Emissions When Pumped at 532 nm^a

dye	copolymer composition	$C/10^{-3}$ (M)	λ_{\max} (nm)
PM597	MMA–HEMA 1:1	0.7	576
PM567	MMA–HEMA 1:1	1.5	559
	MMA–TFMA 7:3	1.5	564
	MMA–PETA 9:1	1.5	562
Rh6G	MMA–HEMA 1:1	1	575

^a C, dye concentration; λ_{\max} , peak wavelength of the laser emission.

a normalized photostability of 350 GJ/mol. In our case, we can estimate an accumulated absorbed pump energy of 1700 GJ/mol for material M016[PM567/COP(MMA–HEMA 1:1)] after 10^6 pulses at 10 Hz repetition rate, where the laser emission still remained at about 90% of its initial value. An operational lifetime (defined as the number of pulses emitted before the output energy drops to 50% of its initial value) of over 10^6 pulses was reported by Nhung et al.²² for an oxygen-free and protected PM567-doped hybrid xerogel sample pumped longitudinally at 532 nm with 1 mJ pulses at 10 Hz repetition rate. Thus, the photostability exhibited in our system by dye PM567 when incorporated into aerogel M016 filled with MMA–HEMA 1:1 copolymer is, to the best of our knowledge, the highest achieved to date for solid-state dye lasers in organic, inorganic, or hybrid matrixes doped with any laser dye without rotating or translating the medium to distribute the thermal load over a large volume.

Our next step was trying to improve the lasing efficiencies of the PFNPA materials by optimizing the composition of the organic component. Thus, we prepared matrixes based on aerogels of class A with density 0.25 g/cm³ filled with those copolymer formulations that had resulted in the highest lasing efficiencies in our previous studies with dye PM567 incorporated into organic matrixes.²¹ Samples with dyes PM597 and Rh6G were also prepared for comparison.

The materials obtained and their laser emissions are listed in Table 2. Their lasing efficiencies are shown in Figure 5, and the intensities of the laser output after 100 000 pump pulses in the same position of the sample at 10 Hz repetition rate relative to the initial intensities are collected in Figure 6. The actual evolution of the laser output with the number of pump pulses of some characteristic examples is illustrated in Figure 7.

It is seen in Figure 5 that, as expected, there is a copolymer formulation which optimizes the lasing efficiency of dye PM567,

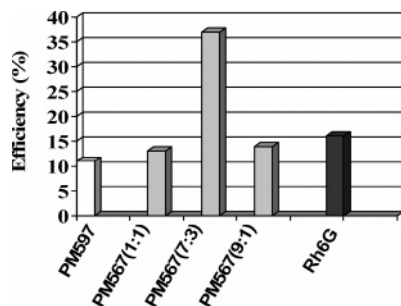


Figure 5. Lasing efficiencies of dyes incorporated into hybrid matrixes of silica aerogels A025 filled with the copolymer formulations listed in Table 2.

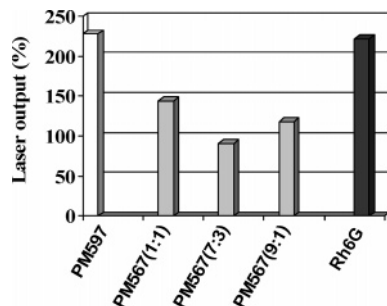


Figure 6. Percent intensity, referred to initial intensity, of laser output after 100 000 pump pulses in the same position of the sample from dyes incorporated into hybrid matrixes of silica aerogels A025 filled with the copolymer formulations listed in Table 2. Pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively.

and efficiencies of 37% were obtained with material A025-[PM567/COP(MMA-TFMA 7:3)]. Lasing efficiency is not initially improved by using dye PM597, but in this case the energy of the laser output keeps increasing, and after 100 000 pump pulses the efficiency has increased to 25% (Figure 6). A similar behavior was followed by Rh6G, with the lasing efficiency increasing with the number of pump pulses (Figures 6 and 7a) to reach the value of 35%, much higher than any obtained with organic-inorganic or polymeric matrixes in our experimental system.^{14,18}

The behavior of dyes PM597 and Rh6G could be understood if the concentration of dye we have used to prepare those samples were too high. As is well-known, for each dye in a given medium there is an optimum concentration which results in the highest lasing efficiency. Concentrations higher than the optimum cause a decrease in lasing efficiency. Because the degradation of dye molecules caused by repeated pumping in the same region of the sample produces a decrease in the effective dye concentration in that region, if in our case the initial dye concentration were too high the result of repeated pumping would be the dye concentration becoming nearer the optimum concentration, and thus the lasing efficiency increasing. In fact, if the sample is translated and a new region is pumped, the lasing efficiency returns to its initial value.

To better assess the effect of the inorganic environment on the laser operation, PM567 was incorporated into a purely organic COP(MMA-TFMA 7:3) matrix and their laser properties were evaluated in the same experimental setup used with the PFNPA materials. The lasing efficiency was 39%, nearly the same as that obtained when the polymer with the dye was incorporated into aerogel A025, but the dye photostability was much worse. As can be seen in Figure 7c,d, whereas in material A025[PM567/COP(MMA-TFMA 7:3)] the laser output, albeit exhibiting some irregularities, remains at about the initial level after 100 000 pump pulses, the emission from the purely

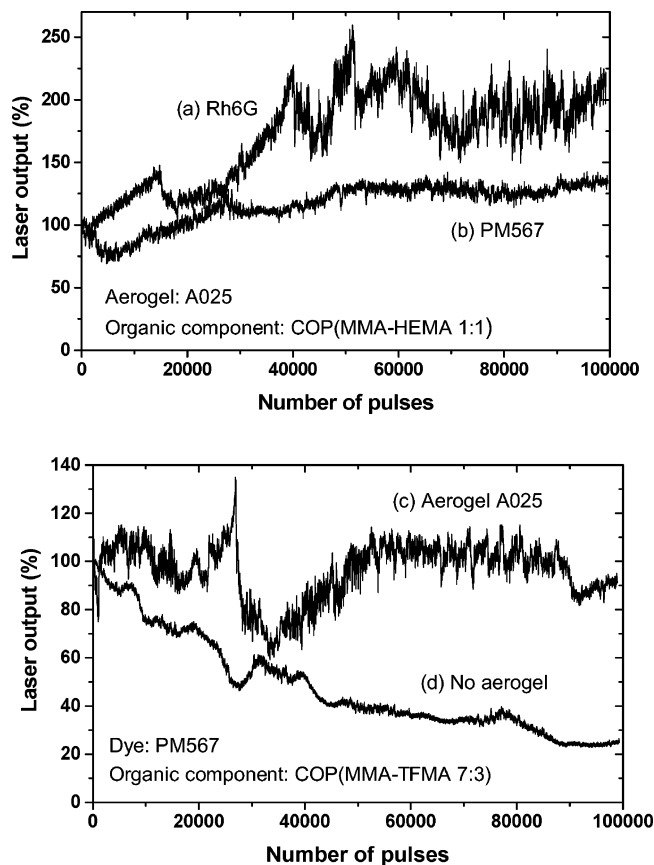


Figure 7. Evolution of laser output with the number of pump pulses in the same position of the sample for materials (a) A025[Rh6G/COP(MMA-HEMA 1:1)], (b) A025[PM567/COP(MMA-HEMA 1:1)], (c) A025[PM567/COP(MMA-TFMA 7:3)], and (d) PM567/COP(MMA-TFMA 7:3) (purely polymeric matrix). Pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively.

TABLE 3: Laser Parameters^a for PM567 Incorporated into Hybrid Matrixes of Silica Aerogels M Filled with MMA-TFMA 7:3 Copolymer^b

aerogel ^c	λ_{\max} (nm)	eff (%)	I_{10000}^d (%)
M009	562	13	109
M014	561	11	105
M019	561	9	31
M022	564	11	53

^a λ_{\max} , peak of the laser emission; eff, energy conversion efficiency.

^b Dye concentration: 1.5×10^{-3} M. Nd:YAG (second harmonic) pump energy and repetition rate: 5 mJ/pulse and 10 Hz, respectively. ^c The number after the letter in the different names refers to density in g/cm³ (i.e., 014 means 0.14 g/cm³). ^d Intensity of the dye laser output after $n = 100\,000$ pump pulses referred to initial intensity I_0 ; $I_n(\%) = (I_n/I_0) \times 100$.

polymeric matrix PM567/COP(MMA-TFMA 7:3) drops to 26% of the initial value in the same pumping interval. This result clearly illustrates the stabilizing effect of the inorganic environment on the laser emission from organic dyes.

Finally, samples were prepared based on aerogels M with different densities containing dye PM567 incorporated into the copolymer composition COP(MMA-TFMA 7:3) which in aerogels A had resulted in the highest efficiency. The results obtained are collected in Table 3. It is seen that the lasing efficiencies are much lower than that obtained with aerogel A025 with the same organic component (Figure 5). These efficiencies are similar to those obtained with the MMA-HEMA 1:1 composition as the organic part (Figure 1), and do not change significantly with density. On the other hand, the

density of the aerogel did have an important influence on stability, which drops significantly for densities around 0.20 g/cm³. These differences in photostability for the dye dissolved in a given polymeric formulation could be related to the pore size of the inorganic host and their distribution. The microenvironment in which the dye molecules are housed will be influenced by the pore size. For an appropriate pore size, the dye molecules are trapped inside, their mobility is restricted, and the possibility of photochemical reactions degrading the dye decreases sharply. When the density of the inorganic aerogel increases, its porosity and pore size are reduced, the dye molecules are no longer trapped in the smaller size cages and, as a result, are less protected, and photobleaching is enhanced. Work is in progress with the aim to better understand and quantify the degradation mechanisms at work in the silica aerogel/organic polymer environment.

The above results indicate that, by using the adequate silica environment in solid-state dye lasers based on polymer-filled nanoporous aerogels, it is possible to stabilize the laser operation of a given dye while maintaining the good lasing efficiency achieved in purely organic matrixes. The presence of the continuous nanoporous glass structure containing the organic polymer seems to favor a more efficient dissipation of the absorbed pump energy that is not converted into emission, avoiding early thermal photodegradation of the dye. Thus, the PFNPA materials avoid some of the shortcomings of the organic hosts for solid-state dye lasers and could be excellent candidates for the implementation of solid matrixes competitive with their liquid counterparts.

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