Tunable Laser Applications

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Solid-State Organic Dye Lasers

Publication details
F.J. Duarte
Published online on: 09 Feb 2016

How to cite: F.J. Duarte. 09 Feb 2016, Solid-State Organic Dye Lasers from: Tunable Laser Applications CRC Press
Accessed on: 14 Oct 2020
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3.1 INTRODUCTION

From the mid-1960s, dye lasers have been attractive sources of coherent tunable visible radiation because of their unique operational flexibility [1,2]. Dye lasers can emit both pulsed and continuous-wave forms, can be pumped with a wide variety of excitation sources, and exhibit an inherent ability to yield high pulse energies and high average powers. Hundreds of dyes have been demonstrated to lase measurably, covering the range from the ultraviolet to the near infrared. The introduction of wavelength-selective elements in the laser cavity allows narrow-linewidth operation and tunability, and the large gain bandwidth of these molecules makes possible the generation of ultrashort pulses. The versatile nature of these lasers has resulted in their applicability to a wide range of different fields, from basic science, such as physics, chemistry, and spectroscopy, to medicine and industry.

Organic dyes are fluorescent molecules with high molecular weights, characterized by containing extended systems of conjugated double bonds. In a dye laser, these molecules are dissolved in an organic solvent or incorporated into a solid matrix. A simplified diagram of the rather complex energy level structure of an organic dye is shown in Figure 3.1. When pumped with visible or ultraviolet light, higher vibrational levels of the first excited electronic singlet state \( S_1 \) of the dye molecules are populated. After fast radiationless relaxation, the excited dye molecules accumulate in the lowest vibrational level of \( S_1 \), which constitutes the upper level of the laser transition. Laser emission depopulates this level into higher-lying vibrational–rotational levels of the ground electronic state \( S_0 \). Finally, nonradiative processes remove molecules from the lower level of the laser transition. Competing with the radiative depopulation of \( S_1 \), there are radiationless transitions into the lower triplet state \( T_1 \). This
intersystem crossing process populates the lower metastable triplet state and could cause considerable losses if the triplet–triplet absorption bands overlap the lasing band, inhibiting or even halting the lasing process. The triplet losses can be reduced by adding small quantities of appropriate triplet quenchers. These losses are not very important under pulsed excitation with nanosecond pulses because the usual intersystem crossing rates are not fast enough to build up an appreciable triplet population in the nanosecond time domain.

The levels shown schematically in Figure 3.1 are spaced closely enough to form a continuum due to line-broadening mechanisms. Thus, the different fluorescent lines overlap, and absorption and fluorescence spectra consist of a broad continuum, as illustrated in Figure 3.2. Although dyes have been demonstrated to lase in the solid, liquid, or gas phase, it is in the liquid and solid phases that dyes have made a significant impact as laser media. From the early days of the development of dye lasers, attempts were made to incorporate the dye molecules into solid hosts, and the first solid-state dye lasers (SSDLs) were demonstrated by Soffer and McFarland in 1967 [3] and by Peterson and Snavely in 1968 [4] with pulsed laser and flashlamp pumping, respectively. Over the next decade, a variety of materials and pumping arrangements were tried for the operation of dyes in the solid state, but the lasing efficiencies were low, and the dye molecules experienced fast photodegradation, with the result that the laser emission faded rather quickly [5]. Thus, liquid solutions of dyes in organic solvents, in which the active medium can be obtained with high optical quality and cooled by simply using a flow system, became the standard media for dye lasers. Nevertheless, this approach was never fully satisfactory because of the serious inconveniences evidenced by the liquid dye lasers, mainly related to the need to handle large volumes of messy and sometimes toxic liquids. In addition, continuous

FIGURE 3.1 Schematic energy-level diagram for a typical dye molecule.
circulation of the solution requires pumps and the design of complex and bulky cells, which, together with the large dye/solvent reservoirs, increases the size and cost of these dye laser systems and has restricted their use outside the laboratory.

The problems posed by liquid dye lasers stimulated further consideration of the SSDL approach, and in the early 1990s the development of improved host materials with higher laser-damage resistance [5,6] and the synthesis of new high-performance laser dyes [7–9] spurred a renaissance in the field of SSDLs. The 1990s witnessed a great deal of activity in the field, and, as a result, significant advances were made toward the development of practical, tunable SSDLs [2,10]. In recent years, approaches involving the use of new polymeric formulations, organic–inorganic hybrid materials, polymeric media with dispersed silica nanoparticles, or silicon-modified organic matrices as host materials for laser dyes are resulting in SSDLs that are fully competitive with their liquid counterparts. These promising results have been obtained with dyes emitting in the green to red spectral region. Much less work has been done with dyes emitting in the blue region, and the results obtained in solid state are still far from the performance of the same dyes in liquid solution.

In this chapter, we present an overview of the main recent developments of SSDLs and outline the state of the art in the field. The focus will be on those developments that could lead to the practical implementation of SSDL in the short term. Thus, we shall concentrate mainly on the results obtained using dyes with emission in the spectral region from the green to the red. SSDL narrow-linewidth oscillators are discussed in Chapter 4, and medical applications of dye lasers are described in Chapter 8.

**FIGURE 3.2** UV/VIS absorption and fluorescence spectra of the laser dye pyrromethene 567 in methanol solution.
3.2 MATERIALS

The basic requirements imposed on a solid matrix to be used as host for lasing dye molecules are high optical quality with a low level of scattering, transparency at both pump and lasing wavelengths, 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. Thus, in the development of materials for tunable solid-state lasers, the problems to be addressed are the design and optimization of solid matrices with the required properties, the selection or design of dyes with the desirable characteristics, and the development of the appropriate fabrication technology.

Over the years, a variety of materials have been tried as solid hosts for lasing dyes: from mixtures of solvents at low temperature, gelatin, or organic molecular crystals, to inorganic glasses, transparent polymers, and organic–inorganic hybrid materials [5,10]. From work done over the last decade, it is becoming apparent that properly modified polymeric formulations and advanced hybrid materials are well-positioned candidates for developing efficient and stable SSDLs.

3.2.1 ORGANIC POLYMERS

Polymers have been tried as solid hosts for lasing dyes from the early days of SSDLs. These materials exhibit some features that make them very attractive in this application: good chemical compatibility with organic dyes; excellent optical homogeneity, important to avoid interference in the gain medium due to microscopic variation of the refractive index; adaptability to inexpensive fabrication techniques; and ease in modifying in a controlled way relevant characteristics, such as free volume, chemical composition, molecular weight, microstructure, or viscoelasticity. The main limitations of polymers as materials for SSDL are related to photodegradation processes, due to the low power-damage threshold of the matrix, as well as to thermal lensing effects due to the relatively high values of $\partial n/\partial T$ in these media [11].

A great part of the damage caused by laser radiation in the polymeric materials used in the early studies on SSDL, three decades ago, was due to the presence of absorbing centers in the material, such as molecular impurities and foreign absorbing inclusions. The first significant improvements in the laser-damage threshold of organic polymers came from the generalized use of processes such as distillation, sonication, and microfiltration in the preparation of the materials. Optical uniformity of the polymer matrix, avoiding or minimizing the intrinsic anisotropy developed during polymerization, requires strict control of the polymerization rate and the thermal conditions during the polymerization step.

There was soon enough evidence to establish that the resistance to laser damage depended on the viscoelastic properties of the matrix. This opened a new way to enhance the laser resistance of the material and led to two different approaches in the search for improved materials, which can be called external and internal plasticization. External plasticization of the polymer is achieved by adding different low-molecular-weight additives. It reduces the induced elastic limit of the polymer to below the brittle-fracture point, improving the laser resistance by several orders of magnitude.
magnitude [12]. The low-molecular-weight additives have some mobility in the polymer matrix and can migrate and leach out over time, with unpredictable effects. This problem can be overcome by using internal plasticization: copolymerization of the matrix basic compound with aliphatic acrylic comonomers [13].

By using the former approach, Maslyukov et al. [14] demonstrated, in 1995, lasing efficiencies in the range 40%–60% with matrices of modified poly(methyl methacrylate) (MPMMA) doped with rhodamine dyes and pumped longitudinally at 532 nm. The useful lifetime or normalized photostability of the samples (defined as the number of pump pulses that produce a 50% drop in the laser output) was 15,000 pulses at a pump repetition rate of 3.33 Hz. The internal plasticization approach was followed by Costela et al., who, also in 1995, demonstrated laser action with efficiency of 21% using the dye rhodamine 6G (Rh6G) dissolved in a copolymer of 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) under transversal pumping at 337 nm [13]. In this case, the useful lifetime of the samples was 4500 pulses (20 GJ/mol, in terms of total input energy per mole of dye molecule when the output energy is down to 50% of its initial value). Comparative studies on the laser performance of Rh6G incorporated either in copolymers of HEMA and MMA or in MPMMA were carried out by Giffin et al. in 1999 [15]. When longitudinally pumped, under identical experimental conditions, the MPMMA materials demonstrated higher efficiency, but the copolymer formulation exhibited superior normalized photostability (up to 240 GJ/mol).

When organic polymers are used as hosts for lasing dyes, the interesting possibility arises of covalently binding the chromophore to the main chain of the polymer. One important mechanism of dye degradation when incorporated into polymeric matrices seems to be the thermal destruction of the dye due to poor thermal dissipation in the polymer host. When the dye is a part of the polymer chain, additional channels are open for the dissipation, along the polymer backbone, of the absorbed pump energy that is not converted into emission, with a corresponding increase in the laser photostability [16]. This effect is more important when a spacing group is introduced between the chromophore and the polymerizable double bonds incorporated into the dye molecule, so that the pendant group of the chromophore is distant from the polymeric main chain, resulting in no direct interaction between the excited dye group and the macromolecule chains. Using this approach, Costela et al. demonstrated, in 1996, an increase of the useful lifetime to 12,000 pulses when the Rh6G chromophore was linked covalently to the polymeric chains [16].

At the beginning of the 1990s, the rhodamine dyes, with emission in the yellow-red region of the spectrum, were known to give excellent laser results in liquid solution. Thus, they were an obvious first choice in any attempt to develop a dye laser in the solid state. The promising results obtained in solid state with rhodamine dyes notwithstanding, a line of research aiming to obtain more efficient and stable laser dyes was vigorously pursued. As a result, a new class of laser dyes with reduced triplet–triplet absorption over the lasing spectral region was synthesized and characterized by Boyer and coworkers during the late 1980s and early 1990s ([17] and references therein). These dyes are dipyrromethene.BF₂ (PM.BF₂) complexes (Figure 3.3), with emission covering the spectral region from the green-yellow to the red, depending on the substituents on the chromophore. They are ionic and highly
polar laser dyes, have high fluorescence quantum yields and low triplet extinction coefficients over the laser action spectral region, and exhibit good solubility in many solvents, including alcohols and MMA. These dyes have been demonstrated to lase with good performance both in liquid solution and when incorporated into solid hosts, and some of them outperform the most widely employed laser dye, Rh6G, considered in those days the benchmark for efficiency and photostability [10].

One disadvantage of the dipyrromethene dyes is the presence of amine aromatic groups in their structure (Figure 3.3), which renders them vulnerable to photochemical reactions with oxygen and makes these dyes relatively unstable in air-saturated solutions [17]. In 1999, Ahmad and colleagues showed that this problem could be dealt with by incorporating quenchers of singlet oxygen in the liquid and solid solutions of the pyrromethene (PM) dyes [18]: when the singlet oxygen quencher 1,4-diazabicyclo (2,2,2) octane (DABCO) was present, the photostability of dye PM567 doubled, while the lasing efficiency remained about the same. In this way, laser conversion efficiencies in the range 60%–70% were obtained for longitudinal pumping at 532 nm of PM567 dissolved in PMMA with DABCO as the additive. The useful lifetime was 550,000 pulses, corresponding to a normalized photostability of 270 GJ/mol, at a 2 Hz repetition rate. A substantial increase in the photostability of PM567, of up to 350 GJ/mol, was also achieved by the addition of coumarin C540A laser dye, as coumarin reduces the effectiveness of in situ oxygen degradation of PM567 [19].

As pointed out, by the mid-1990s, studies with rhodamine dyes had demonstrated that, when the dyes were incorporated into polymer hosts, lasing efficiencies and photostability depended on the viscoelastic properties of the medium. In particular, studies carried out by our group showed that for each dye there is an optimum copolymer formulation that results in the best matrix/dye combination [10]. A next logical step was to extend our research to the new, high-performance dipyrromethene dyes and probe their lasing properties when incorporated into appropriate polymers. We began by using commercial PM dyes and, after characterizing their photophysical and lasing properties in a variety of solvents, proceeded to incorporate them into carefully chosen polymeric formulations, to gather information on the polymer parameters and structure composition that optimized the laser operation. Next, we proceeded to synthesize new PM.BF₂ complexes and demonstrated that with

![FIGURE 3.3 Molecular structures of some commercial dipyrromethene.BF₂ complexes. Et: C₂H₅; Bu: CH₃(CH₂)₃.](image-url)
appropriate chemical modifications in the pyromethene chromophore, new dyes could be obtained that outperformed the commercially available laser dyes.

In our studies, the solid samples were typically rods, 10 mm in diameter and 10 mm in length, with a cut along the axis of the cylinder defining a lateral flat surface. Pumping geometry was transversal, with the pump radiation (typically nanosecond pulses from a frequency-doubled Nd:YAG laser, 532 nm) being focused onto the lateral flat surface of the samples [19]. The dyes were incorporated into PMMA or into a variety of copolymers of MMA with different acrylic and methacrylic monomers (Figure 3.4). MMA was chosen as the pivotal component in the formulations developed, because the excellent optical transparency and relatively high laser resistance of PMMA make this material an obligatory reference in any strategy directed toward improving laser performance in polymeric SSDLs.

In a first study, commercial dye PM567 was dissolved in homopolymer PMMA and copolymers of MMA with a number of linear and cross-linking acrylic and methacrylic monomers in different vol./vol. proportions [20]. In this way, the polarity and rigidity of the final material were carefully controlled. It was found that an important parameter governing the lasing performance of the dye in polymeric materials is the polymer-free volume, which is controlled by the degree of cross-linking. As the degree of cross-linking in the material increases, the polymer-free volume decreases, which induces a significant reduction of rotational and vibrational molecular freedom. As a result, nonradiative decay of excited dye molecules is prevented, leading to a significant increase of the emission quantum yield of the dye. For a certain concentration of the cross-linking monomer, the free volume available within the polymeric matrix will be completely occupied by the dye. Increasing the degree of cross-linking beyond this point will result in the dye molecules being

![Molecular structures of some monomers used in solid-state dye lasers: methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2,2,2-trifluoroethyl methacrylate (TFMA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol triacrylate (PETA), and pentaerythritol tetraacrylate (PETRA).](image)

**FIGURE 3.4** Molecular structures of some monomers used in solid-state dye lasers: methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2,2,2-trifluoroethyl methacrylate (TFMA), trimethylolpropane trimethacrylate (TMPTMA), pentaerythritol triacrylate (PETA), and pentaerythritol tetraacrylate (PETRA).
partially excluded from the shrinking free volume, and dimers and higher aggregates, with their deleterious effect on laser operation, will be formed. Thus, for any given dye, there will be an optimum degree of cross-linking that optimizes the dye-lasing performance. This effect is illustrated in Table 3.1, which lists relevant laser parameters for solid solutions of dye PM567 in homopolymer PMMA and copolymers of MMA with cross-linking monomers having three (TMPTMA, PETA) and four (PETRA) polymerizable double bonds in lateral chains attached to the same carbon atom (Figure 3.4).

The complexity of the mechanisms involved in the laser action of dyes in a solid matrix can be appreciated from the results obtained in matrices containing the monomers TMPTMA and PETA. Both monomers are triple functionalized, so that when copolymerized with MMA in the same vol./vol. ratio, they determine the same degree of cross-linking. On the other hand, PETA is acrylic, which results in increased plasticity of the resulting polymer (i.e., an increased mobility of the local segments between the cross-linking points of the resulting macromolecular net), and incorporates in its structure a hydroxyl group, which should result in a more polar polymer. As a result, the photostability of PM567 in the matrix containing PETA is lower than in the matrix containing TMPTMA.

Figure 3.5 illustrates the effect on the lasing photostability of the dye of modifying the relative proportions of monomers in a given copolymer. In terms of the accumulated absorbed pump energy per mole of dye molecule, laser emission from dye PM567 dissolved in COP(MMA-PETRA 95:5) matrix remained at 70% of its initial value after absorption of 90 GJ/mol. It should be noticed that the evolution of the laser output with the number of pump pulses shown in Figure 3.5 was obtained at a repetition rate of 5 Hz, whereas the results in Table 3.1, which show faster degradation, were obtained at 10 Hz repetition rate. Thus, when the pump repetition rate increases, so does the degradation rate. It seems that at high repetition rate, the dissipation channels for the energy released to the medium as heat are not fast enough, and as a result the thermal degradation of the dye is enhanced. This interpretation

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\Delta \lambda$ (nm)</th>
<th>Eff (%)</th>
<th>$I_{30\text{,000}}$ (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>562</td>
<td>7</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td>COP(MMA-TMPTMA 95:5)</td>
<td>564</td>
<td>5</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>COP(MMA-PETA 95:5)</td>
<td>568</td>
<td>5</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>COP(MMA-PETRA 95:5)</td>
<td>564</td>
<td>6</td>
<td>18</td>
<td>80</td>
</tr>
</tbody>
</table>

$\lambda_{\text{max}}$: peak of the laser emission; $\Delta \lambda$: FWHM of the laser emission; Eff: energy-conversion efficiency. Dye concentration $1.5 \times 10^{-3}$ M. Pump energy and repetition rate: 5.5 mJ and 10 Hz, respectively. FWHM, full width at half maximum.

$^b$ Intensity of the laser output after $n$ pump pulses in the same position of the sample referred to initial intensity $I_0$, $I_n$ (%) = ($I_n/I_0$) × 100.
was confirmed in studies on the effect of heat load on the stability of polymeric dye lasers, in which the capability of each material to dissipate the heat generated in the sample as a consequence of the pump energy excitation was characterized by photothermal deflection spectroscopy [21,22]. These studies demonstrated that the accumulation of heat into the material increases significantly for pumping repetition rates higher than 1 Hz.

Recently, Jiang and coworkers have demonstrated slope efficiency of 51.63% and normalized photostability of 180.7 GJ/mol for PM567 doped into modified copolymers of MMA and PETRA with organic modifying additive methanol under 5 Hz pumping [23]. With dye PM580 incorporated into MPMMA with methanol, both broadband and narrowband laser emission was demonstrated, with slope efficiencies of 66.0% and 42.7%, respectively [24]. The lifetime performance depended on the laser operating wavelength and pump intensity. At the central emission wavelength of 562.5 nm, the emission remained almost constant over 20,000 shots when pumped by 0.48 J/cm² at 1 Hz. Increasing the pump fluence to 1.43 J/cm² resulted in the output energy decreasing to 47.5% of its initial output value after 20,000 shots at 1 Hz. Thus, when operating at low pump laser intensity, a solid-state dye sample based on MPMMA doped with PM580 could be used to obtain a stable narrowband dye seed laser.

Earlier studies to improve the lasing performance of the PM dyes had demonstrated that their photophysical and lasing properties depend on their molecular structure, and that adequate substituents in the molecular core can enhance the laser action [25,26]. Pursuing this approach, we studied the effect of introducing a number of substitutions at the 8 position of the PM567 molecule while maintaining the four...
methyl groups in the 1, 3, 5, and 7 positions and the ethyl groups in positions 2 and 6. In particular, we synthesized analogues of PM567 (Figure 3.6) in which the methyl group at position 8 was replaced by a methacryloyloxypolymethylene or an acetoxy-polymethylene chain with \(n\) methylenes, resulting in monomeric dyes \(P_nMA\) and their model compounds \(P_nAc\), and analogues in which the substituents at position 8 were \(p\)-(methacryloyloxypolymethylene)phenyl or \(p\)-(acetoxy polymethylene)phenyl groups with one or three methylene groups (dyes \(PArnMA\) and \(PArnAc\), respectively). The model dyes (\(P_nAc\) and \(PArnAc\)) were dissolved in different polymeric matrices, whereas the monomer dyes (\(P_nMA\) and \(PArnMA\)) were bonded covalently to the polymeric chains.

With dyes \(P_nAc\) and \(P_nMA\), lasing efficiencies of up to 40% were obtained, whereas the maximum efficiency obtained with dye PM567 in the same materials and under the same experimental conditions was 30% [27]. Some of the most relevant results obtained with these dyes incorporated into different polymeric formulations are shown in Table 3.2. The highest photostabilities were reached in cross-linked materials with the chromophores linked covalently to the polymer chains. In some of them, the laser output remained stable or dropped by less than 15% after 100,000 pump pulses in the same position of the sample at a 10 Hz repetition rate. Figure 3.7 shows those materials for which the laser output remained stable or decreased by less than 10% after 60,000 pump pulses. Figure 3.8 compares the evolution of the laser output with the number of pump pulses of a monomer dye linked covalently to the polymer matrix, the corresponding model dye dissolved in the same material, and PM567 incorporated into homopolymer PMMA. The figure clearly shows an improvement in photostability in the covalently bonded material. We estimate for material TERP[5MA-(MMA-PETRA 95:5)] in Figure 3.8 an accumulated absorbed pump energy per mole of dye molecule of 180 GJ/mol after 95,000 pump pulses at 10 Hz repetition rate, with the laser emission still remaining at 88% of its initial value.

With dyes \(PArnAc\) and \(PArnMA\), the lasing efficiencies were lower, of the order of 20%, but the laser emission remained at about the initial level after 100,000 pump pulses at 10 Hz repetition rate with the chromophores linked covalently to the polymeric chains (Table 3.2) [28].

<table>
<thead>
<tr>
<th></th>
<th>(R)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM567</td>
<td>-Me</td>
<td>-</td>
</tr>
<tr>
<td>(P_nAc)</td>
<td>-(CH(_2)(_n))OCOMe</td>
<td>1,3,5,10,15</td>
</tr>
<tr>
<td>(P_nMA)</td>
<td>-(CH(_2)(_n))OCOCMe=CH(_2)</td>
<td>1,3,5,10,15</td>
</tr>
<tr>
<td>(PArnAc)</td>
<td>(CH(_2)(_n))OCOMe</td>
<td>1,3</td>
</tr>
<tr>
<td>(PArnMA)</td>
<td>(CH(_2)(_n))OCOCMe=CH(_2)</td>
<td>1,3</td>
</tr>
</tbody>
</table>

**FIGURE 3.6** Molecular structures of modified dipyrromethene.BF\(_2\) complexes. Me: CH\(_3\).
### TABLE 3.2
Laser Parameters$^a$ for Model (PnAc, PARnAc) and Monomeric (PnMA, PARnMA) Dyes in Copolymers (COP) and Terpolymers (TERP)

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\Delta \lambda$ (nm)</th>
<th>Eff$^a$ (%)</th>
<th>Laser Output$^b$ I$_{60,000}$ (%)</th>
<th>I$_{100,000}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1Ac/COP(MMA-PETRA 95:5)</td>
<td>591</td>
<td>12</td>
<td>27</td>
<td>107</td>
<td>—</td>
</tr>
<tr>
<td>COP(P3 MA-MMA)</td>
<td>569</td>
<td>6</td>
<td>34</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>TERP[P3 MA-(MMA-HEMA 7:3)]</td>
<td>569</td>
<td>4</td>
<td>37</td>
<td>87</td>
<td>—</td>
</tr>
<tr>
<td>TERP[P3 MA-(MMA-TMPTMA 95:5)]</td>
<td>565</td>
<td>5</td>
<td>28</td>
<td>112</td>
<td>133</td>
</tr>
<tr>
<td>COP(P3MA-MMA)</td>
<td>568</td>
<td>5</td>
<td>36</td>
<td>75</td>
<td>—</td>
</tr>
<tr>
<td>P5Ac/COP(MMA-HEMA 7:3)</td>
<td>565</td>
<td>6</td>
<td>39</td>
<td>83</td>
<td>—</td>
</tr>
<tr>
<td>TERP[P5MA-(MMA-TFMA 7:3)]</td>
<td>565</td>
<td>9</td>
<td>38</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>TERP[P5MA-(MMA-PETA 95:5)]</td>
<td>562</td>
<td>5</td>
<td>23</td>
<td>87</td>
<td>—</td>
</tr>
<tr>
<td>P10Ac/COP(MMA-TFMA 7:3)</td>
<td>561</td>
<td>8</td>
<td>40</td>
<td>50</td>
<td>—</td>
</tr>
<tr>
<td>TERP[P10MA-(MMA-HEMA 7:3)]</td>
<td>566</td>
<td>5</td>
<td>27</td>
<td>80</td>
<td>—</td>
</tr>
<tr>
<td>P10Ac/COP(MMA-PETRA 95:5)</td>
<td>563</td>
<td>10</td>
<td>34</td>
<td>87</td>
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<td>TERP[P10MA-(MMA-PETA 95:5)]</td>
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<td>COP(Par1MA/MMA)</td>
<td>558</td>
<td>9</td>
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<tr>
<td>COP(Par3MA/MMA)</td>
<td>555</td>
<td>9</td>
<td>16</td>
<td>96</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ $\lambda_{\text{max}}$: peak of the laser emission; $\Delta \lambda$: FWHM of the laser emission; Eff: energy conversion efficiency. Dye concentration: $1.5 \times 10^{-3}$ M. FWHM, full width at half maximum.

$^b$ Intensity of the dye laser output after $n$ pump pulses in the same position of the sample referred to initial intensity $I_0$, $I_n(\%) = (I_n/I_0) \times 100$. Pump energy and repetition rate: 5.5 mJ and 10 Hz, respectively.

---

**FIGURE 3.7** Percent intensity (referred to initial intensity) of the laser output from a number of newly synthesized dipyrromethene.BF$_2$ dyes incorporated into linear and cross-linked copolymers of MMA, after 60,000 pump pulses at the same position of the sample. PnAc/MMA-monomer: model dyes dissolved in copolymer; PnMA-MMA-monomer: monomer dyes linked covalently to polymeric chains, producing terpolymers with the indicated MMA-monomer proportion. Pump energy and repetition rate: 5.5 mJ/pulse and 10 Hz, respectively.

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Further improvements in photostability were obtained by double cross-linking of the chromophore to the polymeric chains (Figure 3.9). In this case, instead of incorporating one methacryloyloxypropylene group at position 8 in dye PM567, two polymerizable methacryloyloxypropylene groups were attached to positions 2 and 6 of PM567 dye (Figure 3.3, with R: Et-CH₂OCOC(Me)=CH₂). The copolymer of this new dye with MMA exhibited lasing efficiency of 37% with the laser emission remaining at 67% of the initial output after 400,000 pump pulses at 30 Hz repetition rate, corresponding to an accumulated absorbed pump energy of 950 GJ/mol [29].

Bichromatic laser emission was obtained from some of the aforementioned analogues, both monomeric and model compounds, of dye PM567 incorporated into solid polymeric matrices [30]. Depending on dye concentration, matrix structure, dye–matrix interaction, and pump fluence, two peaks separated by 10–14 nm appear in the laser emission spectral band. This unusual feature could be explained in terms of reabsorption/reemission effects and spectral broadening of the S₀–S₁ transition. The short-wavelength emission corresponds to the usual homogeneous
$S_0 - S_1$ transition and dominates at low dye concentration. The long-wavelength emission appears when reabsorption/reemission and inhomogeneous broadening dominate, so that gain at the vibrational shoulder competes advantageously with that of the short-wavelength mode.

Over recent years, a number of modifications of the molecular structure of the PM chromophore system with adequate substituents have been tried, giving rise to new dyes of this family with a good balance between efficiency and photostability [31–35]. In particular, efficiencies of over 50% with stable laser emission for more than 100,000 pulses under repeated transversal pumping at 10 Hz were demonstrated for derivatives of PM567 and PM597 in which fluorene atoms were replaced by carboxylate or cyano groups, respectively, incorporated into PMMA matrices [34,35]. Emission displaced toward longer wavelengths was obtained from diiodinated [36] and chlorinated [37] PM dyes, or by using energy transfer processes in multichromophoric systems incorporating two donor and one acceptor PM dyes [38]. The matrix material was PMMA. Energy transfer processes in cassettes based on PM and rhodamine pairs resulted in efficient and photostable laser emission in poly(2-hydroxyethyl methacrylate) (PHEMA) matrices [39].

Improvements in the lasing properties of gain media based on dyes PM567 and PM597 have been demonstrated by using polymers with fluoride atoms incorporated into their structure [40]. The presence of fluoride atoms in the polymer matrix results in high thermal stability and enhanced chemical resistance compared with nonfluorinated analogues, as a result of the bond energy of C–F (116 kcal/mol) being higher than that of C–H (99 kcal/mol), as well as the low polarity and relatively small size of the fluoride atom [41]. Fluorine-modified organic matrices were prepared, in which the total fluoride content was varied, adding to MMA different volumetric proportions of monomers with three (TFMA, Figure 3.4), five (PFMA, as in Figure 3.4 but with end group CF$_2$–CF$_3$), and seven (HFMA, as in Figure 3.4 with end group CF$_2$–CF$_2$–CF$_3$) fluoride atoms. Lasing efficiencies of up to 35% (PM567) and 42% (PM597) were obtained under transversal pumping. The highest photostability was recorded for PM597 dissolved in an MMA–HFMA 7:3 copolymer, with the laser output remaining at the initial level after 500,000 pump pulses in the same position of the sample at 30 Hz repetition rate, corresponding to an accumulated pump energy of 12,300 GJ/mol (Figure 3.10).

Some efforts have been made recently to extend the tuning range of SSDLs to the red-edge spectral region (600–750 nm), within what is often termed the optical window. The potential advantages of emission in this spectral region are the nearness to the second low-loss window of typical polymer optical fibers (a window that lies at 650 nm [42]), and significant reduction of the background signal in biological applications because of the lower autoabsorption and autofluorescence of biomolecules, low light scattering, and deep penetration of the light at these wavelengths in biological systems [43]. Fan et al. [44] demonstrated laser emission at 650 nm from dye LDS698 incorporated into MPMMA. Under longitudinal pumping, normalized photostability of 102 GJ/mol with slope efficiency of 13.5% was obtained. At about the same time, photosensitive materials based on a variety of commercial dyes with emission in this red-edge region (sulfurhodamine B, perylene red, rhodamine 640, LDS698, LDS722, LDS730) incorporated into different linear, cross-linked,
Some results are summarized in Table 3.3, which shows data on lasing efficiency, peak of the laser emission, and laser photostability (with respect to initial intensity) after 100,000 pump pulses in the same position of the sample. Lasing efficiencies ranged from 20% for the styryl dyes to 46% for the xanthene chromophores, under transversal pumping at 532 nm. For the sake of clarity, in Figure 3.11, the actual evolution of the laser output with the number of pump pulses at 10 Hz repetition rate is shown graphically for some of the materials. For comparison with the results reported in [44], the normalized photostability of dye LDS698 in Table 3.3 was 3920 GJ/mol. When these materials were placed in a grazing-incidence grating tunable resonator, tunable laser emission was obtained with linewidths of the order of 0.15 cm⁻¹ and a tuning range of up to 70 nm, continuously covering the region from 575 to 750 nm (Table 3.3 and Figure 3.12).

Some potential important applications of SSDLs, such as photodynamic therapy or treatment of port-wine stains and other vascular anomalies, would require the laser energy to be applied in high-repetition rate pulses. Thus, we prepared solid laser samples in the form of coin-sized disks, 2 mm thick, consisting of dyes Rh6G or PM567 incorporated into polymeric matrices, and pumped them longitudinally with the green line of a copper-vapor laser at an average power of up to 800 mW and repetition rate of up to 1 kHz [49]. With PM567 dissolved in COP(MMA-PETA 95:5), 290 mW average power (37% lasing efficiency) at peak wavelength of 550 nm was obtained. The laser output decreased to 150 mW (52% of the initial power) after 30 min irradiation time at 1 kHz (1.8 × 10⁶ shots) and to 32 mW (11% of the initial...
### TABLE 3.3

<table>
<thead>
<tr>
<th>Dye</th>
<th>c×10^4 (M)</th>
<th>Material</th>
<th>λ_{max}^a (nm)</th>
<th>Eff^b (%)</th>
<th>I_{100,000} (%)^b</th>
<th>Tuning range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SulRhB</td>
<td>6</td>
<td>COP[(HEMA-MMA 7:3)-PETRA 9:1]</td>
<td>608</td>
<td>46</td>
<td>99</td>
<td>575–645</td>
</tr>
<tr>
<td>PerRed</td>
<td>5</td>
<td>COP(MMA-TFMA 7:3)</td>
<td>618</td>
<td>21</td>
<td>95</td>
<td>605–655</td>
</tr>
<tr>
<td>Rh640</td>
<td>6</td>
<td>COP (HEMA-PETA 9:1)</td>
<td>640</td>
<td>36</td>
<td>79</td>
<td>620–660</td>
</tr>
<tr>
<td>LDS698</td>
<td>4</td>
<td>PHEMA</td>
<td>660</td>
<td>21</td>
<td>55</td>
<td>635–695</td>
</tr>
<tr>
<td>LDS722</td>
<td>4</td>
<td>COP(HEMA-TMSPMA 8:2)</td>
<td>674</td>
<td>23</td>
<td>55</td>
<td>650–720</td>
</tr>
<tr>
<td>LDS730</td>
<td>8</td>
<td>COP(HEMA-TMSPMA 7:3)</td>
<td>730</td>
<td>20</td>
<td>100</td>
<td>690–750</td>
</tr>
</tbody>
</table>

**Note:** Structure of TMSPMA, see Figure 3.19.

*a c: dye concentration; λ_{max}: peak of the laser emission; Eff: energy-conversion efficiency.

*b Intensity of the laser output after n pump pulses in the same position of the sample referred to initial intensity I_0, I_n (%)= (I_n/I_0) × 100. Pump energy and repetition rate: 5.5 mJ and 10 Hz, respectively.

---

**FIGURE 3.11** Evolution of the normalized laser output of (a) perylene red in COP(MMA-TFMA 7:3), (b) rhodamine 640 in COP(MEMA-PETRA 9:1), and (c) LDS722 in COP(HEMA-TMSPMA 8:2). Pump wavelength, pulse duration, energy, and repetition rate are 532 nm, 12 ns, 5.5 mJ/pulse, and 10 Hz, respectively. Structure of TMSPMA, see Figure 3.19. (García-Moreno, I. et al., Materials for reliable solid state dye laser at the red spectral edge. *Adv. Funct. Mat.* 2009. 19. 2547–2552. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
power) after 70 min operation \((4.2 \times 10^6\) shots) (Figure 3.13). Output power of up to 1 W at 6.2 kHz was obtained for short periods of time. When the pump repetition rate was increased to 10 kHz, by using as pump source a diode-pumped, \(Q\)-switched, frequency-doubled Nd:YLF laser (emission at 527 nm), the output power of Rh6G/COP(MMA-HEMA 1:1) decreased to half the initial value after about 6.6 min (or about 4.0 million shots). In the case of PM567/COP(MMA-PETRA 95:5), the output power decreased to half the initial value after about 7.8 min (Figure 3.14) [50].

A high-repetition rate (16 kHz) laser emission, tunable in the wavelength range 605–635 nm, based on rhodamine B dye incorporated into a copolymer of MMA and MAA (methacrylic acid) was demonstrated by Kytina et al. [51].
A disk-shaped polymer gain medium (94 mm diameter, thickness 20 mm) was rotated at a frequency of 42 Hz and pumped transversely with radiation from a copper-vapor laser. Lasing efficiency of 15% (output power 1.5 W) was obtained. The laser output remained stable for 4 h, within 3% accuracy, in a cyclic operation mode with duty cycle 1/6 (1 min operation, 10 s pause). In permanently pumping mode (no pause in pumping with the copper-vapor laser), the maximum operation time (decrease of the output power of the dye laser to 70% of its initial value) was about 2 h for optimized transmission of the laser cavity output mirror.

The use of PMMA solid host incorporating pyrromethene dyes as laser amplifier has been reported. A 25 mm diameter, 7 mm thickness sample of dye pyrromethene 650 (PM650) in PMMA rendered a single-pass gain of 500 at 616 nm [52]. Up to 62% amplifier efficiency was observed in disks (25 mm diameter, 3 mm thickness) of PM567 dispersed in a modified PMMA matrix incorporating small amounts of PETRA and DABCO [53]. The photodegradation rate was found to be reduced substantially by an increase in the rate of stimulated emission, indicating an important role played by excited-state reactions in photodegradation.

In 2006, a continuous-wave (CW) SSDL tunable from 565 to 615 nm was reported [54]. The laser medium consisted of a thin film (thickness between 50 and 100 µm) of Rh6G dissolved in a photopolymer sandwiched between two digital versatile disc (DVD) substrates. The resonator design was a folded cavity, derived from conventional liquid solvent dye laser geometry. The dye laser disk was rotated (50–100 Hz) and
translated perpendicularly to the rotation axis (100–300 μm/s) by a combined motor-translation stage unit. Lasing threshold was 550 mW and slope efficiency 2%. Using one disk, 30 min lasing operation was achieved before irreversible photodegradation. An improved and more sophisticated device showing both excellent long- and short-time power stability was presented recently [55]. In the improved design, the thickness of the disk was significantly larger (3 mm), the dye was perylene orange, and the polymer host material was PMMA. An output power of 800 mW around 575 nm with a spectral width of less than 3 GHz, tunability over 30 nm, and a nearly circular mode profile with an M² better than 1.4 was obtained. The excellent power stability provides CW laser output over hours without noticeable power loss. The device, including pump laser, could be integrated in a compact housing with dimensions 60×40×20 cm³.

3.2.2 Organic–Inorganic Hybrid Materials

Silicate-based inorganic–organic hybrid polymers are a priori good candidates for laser matrices, since, due to their inorganic Si–O–Si backbone, they present improved thermal and mechanical properties compared with common organic polymers. These hybrid materials are prepared from organosilane precursors by sol–gel processing in combination with organic cross-linking of polymerizable monomers [56].

In one approach, the porous structure of a sol–gel inorganic matrix is filled with organic molecules by immersing the bulk in a solution containing laser dye, polymerizable monomer, and catalyst or photoinitiator. In a subsequent step, organic polymerization is started by ultraviolet irradiation or heating, and an interpenetrating polymer incorporating the laser dye is formed.

Hybrids can also be obtained from organically modified silicon alkoxides. In this method, both organic and inorganic networks are obtained in a two-step reaction. An initial inorganic network is formed by polycondensation of the silicon alkoxide. In a second step, organic polymerization is initiated, thermally or photochemically, via free radicals. The possibility of selecting different organic:inorganic ratios as well as the choice of the reaction conditions allows materials with a wide range of properties to be obtained. Materials obtained in this way are usually called organically modified ceramics (ORMOCERs) or organically modified silanes (ORMOSILs).

The first studies on laser emission from dyes incorporated into inorganic and inorganic–organic matrices prepared using sol–gel techniques were carried out in the late 1980s, and showed this to be a promising approach. In 1995, Rahn and King [57] carried out a direct comparison study of laser performance of dyes Rh6G, PM567, perylene red, and perylene orange in organic, inorganic, and hybrid hosts. They found that the nonpolar perylene dyes had better performance in partially organic hosts, whereas the ionic rhodamine and pyrromethene dyes performed best in the inorganic sol–gel glass host. The most promising combinations of dye and host for efficiency and photostability were found to be perylene orange in polycom glass and Rh6G in sol–gel glass. Nevertheless, lasing efficiencies and photostabilities were modest in all cases.

In 2002, Ahmad and colleagues demonstrated high efficiency and photostability for xanthene dyes in wet and dried sol–gel phases, but not for pyrromethene laser dyes [58]. In the next couple of years, lasing slope efficiencies of 79% and 60%
were reported for dyes PM567 and PM597, respectively, incorporated via the sol–gel technique into ORMOSIL host matrices (PM567) [59] and hybrid xerogel matrices (PM597) [60]. These efficiencies were obtained under longitudinal pumping at 532 nm in optimized laser cavities. The useful lifetime for PM567 was 60,000 pulses, 50 GJ/mol in normalized photostability, at a pump repetition rate of 2 Hz and pump fluence of 0.1 J/cm², in samples of 4 mm thickness [59]. For PM597, the laser emission dropped to 50% of the initial value after 210,000 pump pulses, when pumped with 1.8 mJ pulses at 10 Hz repetition rate [60]. Under the same irradiation conditions, PM567 in xerogel matrix exhibited a slope efficiency of 80% and a useful lifetime of 180,000 pulses.

With dye perylene red incorporated into ORMOSIL matrices, slope efficiencies of up to 53% with normalized photostabilities of 24 GJ/mol were obtained with samples of 4 mm thickness at a pump fluence of 0.1 J/cm² and 2 Hz repetition rate [59]. By codoping perylene red with an optimized coumarin dye concentration, the slope efficiency of perylene red in ORMOSIL matrix increased by a factor of 2, whereas the slope efficiency of PM567 was only marginally increased [61].

Under transversal pumping, slope efficiencies of 32% [62], 43%, and 20% [56] have been obtained for dyes PM567, PM597, and Rh6G, respectively, incorporated into ORMOSIL glass samples and placed in an optimized laser cavity consisting of a full reflector and a 50% broadband reflector as output coupler. Pumped by 1 mJ (20 mJ/cm²) pulses, the useful lifetime of PM597 in ORMOSIL was 12,000 pulses, which increased to 22,000 pulses when the dye was incorporated into composite glass [62].

Beginning in 2002, our group carried out a detailed investigation on the laser performance of rhodamine and pyrromethene dyes incorporated into organic–inorganic hybrid materials. For inorganic components, we used tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) (Figure 3.15) in different weight proportions. The organic part was composed of MMA or MMA–HEMA. The synthesis route of the

![Molecular structure of inorganic alkoxides TEOS, TMOS, TRIEOS, and DEOS.](image-url)
hybrid materials was based on the *in situ* and simultaneous hydrolysis–condensation of the inorganic component during the free radical copolymerization of the organic monomers. The geometry of the samples was as previously described (10×10 mm rods with a lateral cut defining a flat surface), and the pumping arrangement was transversal.

The lasing stability of TMOS-based hybrid matrices was significantly worse than in the materials based on TEOS, evidencing the influence of the size of the lateral substituent group of the alkoxide on the laser properties of the resulting material. When Rh6G is used as gain medium, both the lasing efficiency and the photostability first increase with the proportion of the inorganic component, peaking at compositions with 10%–15% (wt%) proportions of TEOS. With pumping at 532 nm, laser efficiencies of up to 26% and laser emission with no sign of degradation, albeit with some oscillations, were obtained after 100,000 pump pulses in the same position of the sample at 10 Hz repetition rate [63]. Higher proportions of the alkoxide in the sample result in a drastic decrease in both efficiency and useful lifetime or stability of the laser emission. It is clear that the presence of the inorganic component in the matrix plays an important role in the photochemical degradation of the dye. The pump radiation leads to a fraction of the dye molecules being converted into active species (radicals, triplets) which, in turn, react with nearby dye molecules, impurities, oxygen, radicals, and groups from the polymer chains or any other active species present in the material. An increase in the proportion of the inorganic alkoxide in the material leads to an increase in the remanent acidity of the medium, which could boost these reactive processes. In addition, because the photochemical mechanism is at least bimolecular, the process can be highly dependent on the microstructure and flexibility of the polymeric chains in these materials. Thus, to optimize the photostability of the dye/hybrid system, a compromise must be reached between the enhancement of thermal dissipation in the material and the increase in the photochemical destruction of the dye by carefully controlling the inorganic–organic matrix composition.

When the pyrromethene dye PM567 was used as gain medium, the laser operation was optimized in matrices with 5% content of TEOS [64]. The lasing efficiency was 26%, and, after an initial decrease, the laser output stabilized and remained at 70% of its initial value after 60,000 pump pulses in the same position of the sample (Figure 3.16).

The presence of the inorganic component in the hybrid matrices increases the rigidity and fragility of the resulting materials. A possible way to decrease the rigidity of the materials while maintaining, or even increasing, the proportion of the inorganic component is by decreasing the functionality of the inorganic compounds, selecting double- and triple-functionalized alkoxides instead of the usual tetrafunctionalized ones, TEOS and TMOS. Pursuing this idea, we prepared hybrid matrices in which the inorganic compounds were trifunctional methyltriethoxysilane (TRIEOS) and difunctional dimethyldiethoxysilane (DEOS) (Figure 3.15), and we performed a systematic study of the influence on the laser action of the composition and structure of these new hybrid matrices [65–67]. DEOS, with only two reactive positions, leads to rapidly growing linear chains, inducing broad inorganic domains less miscible with the organic components, which is detrimental to the
optical transparency of the samples. TRIEOS, on the other hand, results in a material with better structural and morphological uniformity, without phase separation at the nanometric scale. Laser operation with no decrease in the laser output after 100,000 pump pulses in the same position of the sample at 10 Hz repetition rate was obtained with Rh6G (in matrices with 20% content of TRIEOS), and PM597 (in matrices with 15% TRIEOS, Figure 3.17).

Trying to further improve the photostability of the laser dyes when incorporated into solid hosts, we next synthesized new hybrid materials with improved thermo-optical and mechanical properties based on silica aerogels. These are sponge-like glasses characterized by an extremely high porosity (80%–99%) with easily accessible mesopores (20–100 nm) filled with air. 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.

When using silica aerogels filled with fluorinated modified polymers, lasing efficiencies of up to 37% were obtained with dye PM567 [68,69]. Laser emission with a drop of only 10% after $10^6$ pulses in the same position of the sample at 10 Hz repetition rate was demonstrated in nonfluorinated polymers, although this emission exhibited a rather irregular behavior with some strong fluctuations. In fluorinated samples, laser emission stable over 100,000 pump pulses was obtained by pumping at 10 Hz with pulses of 5.5 mJ (Figure 3.18; compare with Figure 3.16). By pumping with 3.5 mJ/pulse, the laser emission remained stable over 100,000 pulses at 30 Hz repetition rate.

Over recent years, some more attempts have been made to improve the laser performance of dyes in sol–gel glass and organic–inorganic hybrid materials. Thus,
FIGURE 3.17 Normalized laser output as a function of the number of pump pulses for PM597 (6 × 10^{-4} M) in hybrid matrices of P(HEMA-MMA 1:1) with different wt% proportions of TRIEOS: (a) 15% and 10 Hz, (b) 15% and 30 Hz, and (c) 5% and 30 Hz. Pump energy: 5.5 mJ/pulse. Initial lasing efficiency: 23%. (Reprinted with permission from García-Moreno, I. et al., J. Phys. Chem. B, 109, 21618–21626, 2005. Copyright 2005, American Chemical Society.)

FIGURE 3.18 Normalized laser output as a function of the number of pump pulses for PM567 (1.5 × 10^{-3} M) incorporated into (a) silica aerogel filled with the copolymer COP(MMA:TFMA 7:3) and (b) organic matrix without silica aerogel. Pump energy and repetition rate: 5.5 mJ/pulse and 10 Hz, respectively. (Reprinted from Chem. Phys. Lett., 427, García, O. et al., Efficient optical materials based on fluorinated-polymeric silica aerogels, 375–378, Copyright (2006), with permission from Elsevier.)
rhodamine B was incorporated into polymer, sol–gel glass, and organic–inorganic hybrid hosts, and its laser behavior in the different materials was evaluated [70]. The polymer used was glycidyl methacrylate (GMA), and the inorganic component was TEOS. Relatively high efficiencies (of up to 48% in the hybrid material) were obtained under transversal pumping at 532 nm. The lasing efficiency was consistently higher in hybrid matrix than in sol–gel glass (37.6%) and polymer (33.2%) hosts. Nevertheless, the photostabilities were not as good, and the higher photostability (decrease of the emission to 30% of its initial value after 30,000 pump pulses at 10 Hz and 15 mJ/pulse pumping) was reached in the polymer host, attributed to covalent bonding of the dye to GMA.

Two different approaches to obtaining new mesoporous sol–gel materials specifically designed to incorporate Rh6G were developed by de Queiroz et al. [71]. The first is based on SiO2 and phenyl-modified silica xerogel, and the second uses mesoporous sodium aluminosilicate glasses. The dye dispersion in the silica xerogels results in high quantum yields (up to 87%), with no substantial decrease in efficiency when dye concentration is increased. On the other hand, sodium aluminosilicate samples exhibit a drastic decrease in quantum yield at concentrations higher than $10^{-4}$ M. As a result, only the sodium aluminosilicate samples containing $2.1 \times 10^{-5}$ moles of Rh6G per host formula unit exhibited laser action, while the silicate xerogels worked well with Rh6G concentrations of up to $10^{-3}$ M. Although emission photostabilities were not high, with a half-life of 6560 pulses under transverse pumping with pulses of 2 m at 10 Hz repetition rate, the emission linewidths remained rather stable during operation, and the ability of the silicate xerogels to host high concentrations of dye makes these materials interesting candidates for biological applications.

3.2.3 Silicon-Modified Organic Matrices

Despite the good results obtained with the hybrid materials, these compounds present their own problems, such as a complex and lengthy synthesis process, fragility that makes mechanization and polishing of the final material difficult, and sometimes optical inhomogeneity caused by refractive index mismatch between organic and inorganic parts. A possible way to avoid these problems while maintaining the combined advantages of polymer and inorganic materials would be to use organic compounds with silicon atoms directly incorporated into their structure. Thus, the matrix would remain organic, which means plasticity and a relatively more simple synthesis procedure, but with improved thermal properties due to the presence of the silicon atoms. Following this approach, we incorporated dyes PM567 and PM597 into copolymers of MMA or HEMA with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA, Figure 3.19) and into terpolymers of MMA, HEMA, and TMSPMA,

![Molecular structure of monomer 3-TMSPMA](image)

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Tunable Laser Applications

and proceeded to study the photophysical, structural, and laser properties of these novel materials [72,73].

A highly photostable laser operation was obtained with the silicon-modified organic matrices, with lasing efficiencies of up to 34% with PM567 and up to 42% with PM597 under transversal pumping at 532 nm in nonoptimized laser cavities. At 10 Hz repetition rate, formulations were found with no sign of degradation in the laser output after 100,000 pump pulses in the same position of the sample for both PM567 and PM567 dyes. This corresponds to an accumulated pump energy absorbed by the system per mole of dye molecules of 518 and 1295 GJ/mol for PM567 and PM597, respectively. When the pump repetition rate increased to 30 Hz, the dye PM567 exhibited a steady decrease in the laser output, which was rather drastic in the samples with the highest content of silicon (Figure 3.20). Dye PM597 was much more stable, and in all but one of the formulations the laser emission remained stable after 100,000 pump pulses at 30 Hz repetition rate (Figure 3.20; compare with Figure 3.17b and c), corresponding to an accumulated pump energy of 2472 GJ/mol.

In two selected matrices, COP(MMA:TMSPMA 1:1) and COP(HEMA:TMSPMA 1:1), the laser emission of the dye PM597 remained stable after 700,000 pump pulses in the same position of the sample at 30 Hz repetition rate (Figure 3.21), corresponding to an accumulated pump energy absorbed per mole of dye molecules of 17,300 GJ/mol. By incorporating an acetoxymethyl substituent at position 8 in the PM597 chromophore, the laser emission of the resulting dye, in COP(HEMA:TMSPMA 7:3) matrix, was displaced from 577 to 607 nm, tunable over the range 585–625 nm [74]. The lasing efficiency was 42%, and the output remained at 90% of the initial value after 100,000 pump pulses at 30 Hz (accumulated pump energy: 3137 GJ/mol).

![FIGURE 3.20](image-url) Normalized laser output as a function of the number of pump pulses for dye PM567 in (a) COP(MMA:TMSPMA 3:7) and (b) COP(HEMA:TMSPMA 7:3), and for dye PM597 in (c) COP(HEMA:TMSPMA 7:3) and (d) TERP(MMA:HEMA:TMSPMA 5:5:10). Dye concentration: 1.5×10⁻⁴ M (PM567) and 6×10⁻⁴ M (PM597). Pump energy and repetition rate: 3.5 mJ/pulse and 30 Hz, respectively. (Reprinted from Costela, A. et al., *J. Appl. Phys.*, 101, 073110, 2007. Copyright 2007, AIP Publishing LLC. With permission.)
3.2.4 Polymers with Nano- and Micro-Particles

Recently, Duarte and James [75,76] demonstrated a class of dye-doped, organic–inorganic, solid-state gain media that exhibit lower $|\frac{dn}{dT}|$ values and improved optical homogeneity than previous composite gain media. The solid matrix consisted of silica nanoparticles uniformly dispersed in PMMA. Using Rh6G as laser dye and a longitudinal pumping scheme, laser conversion efficiencies of 63% were obtained. The laser beam exhibited near-TEM$_{00}$ profile with a beam divergence of 1.9 mrad ($\sim 1.3$ times the diffraction limit). In Chapter 4, the use of these media in SSDL is discussed in detail.

The effect of incorporating dielectric-oxide microparticles into both solid host materials and liquid solutions has been investigated by Ahmad [77]. In particular, PMMA samples containing $\beta$-alumina microparticles with diameter less than 0.2 $\mu$m, doped with PM567 and Rh6G, were prepared. In these conditions, the photostability of the samples was greatly enhanced: when using samples 8 mm long doped with a PM567 dye concentration of $3.4 \times 10^{-4}$ M and longitudinal pumping at 2 Hz repetition rate and pump fluence of 0.16 J/cm$^2$, the number of pulses for the conversion efficiency to fall to half of its initial value is seen to increase from 200,000 without microparticles to 400,000 for samples containing microparticles. The addition of both DABCO and microparticles results in an increase in the operational lifetime to 600,000 pulses, corresponding to a total absorbed pump energy of 365 GJ/mol. When the dye was Rh6G, the addition of microparticles to a solid PMMA sample resulted in proportionally the same enhancement of the photostability as with PM567.

In Section 2.3, it was shown that the use of polymeric hosts with a certain silicon content to increase the thermal conductivity of the polymer resulted in reduced dye...
degradation. In this way, the dye-lasing photostabilities were significantly enhanced with respect to those of the nonsilylated polymers. Nevertheless, the lasing efficiencies were somewhat lower than those obtained with some hybrid materials, and although the photostabilities increased with the silicon content, the presence of silicon in the polymer backbone was accompanied by a decrease in the glass transition temperature, which eventually renders soft materials inappropriate for polishing. The results of Duarte and James discussed in Section 3.2.4 showed that the design and synthesis of materials with silica incorporated at molecular level might overcome the abovementioned problems. Thus, the approach of implementing polymer matrices incorporating nanoparticles based on polyhedral oligomeric silsesquioxanes (POSS) was explored [78]. These compounds have a compact hybrid structure with a well-defined cage-like inorganic core made up of silicon and oxygen (SiO$_{1.5}$)$_n$ externally surrounded by nonreactive or reactive polymerizable organic ligands, R (Figure 3.22). The type and number of substituents control the interactions between the organic ligand and the medium, defining the compatibility and thus the final properties of the POSS-modified systems. The reduced size of the POSS nanoparticles (1 nm) should avoid, in principle, any optical inhomogeneities. If the functional groups are polymerizable, the POSS cages will be bonded directly to the polymer chains, giving place to an organic–inorganic hybrid network (Figure 3.23) with enhanced thermal, mechanical, and physical properties.

Surprisingly, these enhanced properties led to the best laser performance reported to date for different dye-doped solid matrices, for both rhodamine and pyrromethene dyes [78,79]. With efficiencies as high as 60% for PM567 dye doped into a copolymer COP(MMA:8MMAPOSS 87:13), the laser emission remained unchanged after $8.5\times10^5$ pulses at 30 Hz repetition rate (Figure 3.24, curve A) and 5.5 mJ/pulse transversal pumping, corresponding to an estimated accumulated absorbed pump energy of 4768 GJ/mol. As a comparison, the same dye in PMMA with no POSS provided an efficiency of 39%, and the laser emission dropped to one-third of the initial value after just $1\times10^5$ pulses at the lower repetition rate of 10 Hz (Figure 3.24, curve B). The presence of POSS nanoparticles was found to enhance the laser action of dyes of very different families, both polar (Rh6G, rhodamine 640, sulforhodamine B, LDS772, LDS730) and nonpolar (perylene red, pyrromethene 567, pyrromethene 597) with respect to the effectiveness recorded in pure organic solvents and polymeric solutions pumped under the same experimental conditions (Figure 3.25) [80]. In this way, dye-doped POSS solutions could be defined as a kind of universal gain

![FIGURE 3.22  Structure of octameric POSS. R = H or organic group.](image)
media to optimize the laser action that has overcome the dye/host specificity imposed up to now, which has represented one of the most important limitations of these laser systems from an application point of view.

Detailed experimental and theoretical studies seem to indicate that the remarkable improvement in the laser performance of dye-doped POSS systems was a direct consequence of scattering processes \cite{80,81}. The dispersion of POSS nanoparticles

**FIGURE 3.23** Schematic representation of copolymer network formed by 8MMAPOSS (octa[propyl methacryl] polyhedral oligomeric silsesquioxane) and MMA.

**FIGURE 3.24** Normalized laser output as a function of the number of pump pulses in the same position of the sample for dye PM567 in: (a) COP(MMA:8MMAPOSS 87:13) pumped at 30 Hz and (b) pure PMMA pumped at 10 Hz. Pump energy: 5.5 mJ/pulse. (Reprinted with permission from García, O. et al., *J. Phys. Chem. C*, 112, 14710–14713, 2008. Copyright [2008], American Chemical Society.)
at a molecular level defines highly homogeneous materials that, when doped with laser dyes, allow coherent laser emission, but, in addition and despite their nanometer size, the POSS particles sustain a weak optical scattering that helps lasing by elongating the light path inside the gain media, thus providing an extra feedback, a phenomenon central to the process called incoherent random lasing or lasing with intensity feedback [82]. In this way, the laser action in systems based on dye-doped POSS materials is significantly enhanced in both liquid and solid phases [78–80].

The unique chemical and optical properties exhibited by POSS nanoparticles led us to design new hybrid photonic systems based on POSS labeled with fluorescent dyes as pendant groups on their rigid inorganic cores [83]. In particular, we synthesized new hybrid organic–inorganic dyes based on azide-functionalized POSS as the inorganic part and a derivative of PM567 as the organic component. By using a copolymer of MMA with 13% weight ratio of 8MMAPOSS doped with hybrid dye, lasing performance remained at the same level previously demonstrated with PM657 dye simply dissolved in the POSS-containing matrix; lasing efficiency
was now 56%, and the laser output remained stable, without any sign of degradation, after 400,000 pump pulses of 5.5 mJ/pulse at 30 Hz repetition rate. These new hybrid systems based on dye-linked POSS nanoparticles may be used as new alternative sources of photonic materials for optoelectronic devices, competing with dendrimerized or grafted polymers.

Recently, Valiev et al. [84] demonstrated lasing efficiencies as high as 85% for PM567 in pure PMMA with 8MMAPOSS additives, under transversal pumping with pump power density of 54 mW/cm². Nevertheless, under pumping at 10 Hz repetition rate, the lasing efficiency dropped during the first minutes of irradiation, stabilizing finally at the 50% efficiency level and remaining there after 140,000 pump pulses. Although the initial lasing efficiencies were lower, when the dye was incorporated into PMMA media with careful purification of initial methylmethacrylate and initiator of polymerization, the long-term operation remained at the same level as when the matrix incorporated 8MMAPOSS, demonstrating that proper purification of the initial substances can result in operating lifetime characteristics of media based on purely polymeric materials highly competitive with those of the matrices with 8MMAPOSS additives.

### 3.3 APPLICATIONS

The unique operational flexibility of dye lasers has resulted in applications in many fields in science and technology. Their capability of providing coherent, tunable, narrow-linewidth radiation spanning the visible spectrum has made them an invaluable tool in high-resolution atomic and molecular spectroscopy. Isotope separation, remote sensing, and photochemistry are examples of applied fields in which dye lasers have been successfully utilized. In the life sciences, dye lasers have found applications in biology, studying biomedical reaction kinetics of biological molecules, and in medicine, in cancer photodynamic therapy, dermatology, and the treatment of vascular lesions. The medical applications of dye lasers are considered in detail in Chapter 8.

We have already mentioned the problems posed by liquid dye lasers, which have seriously restricted their use outside the laboratory. SSDLs are much more appropriate for use in industrial and medical environments, but the photodegradation problems exhibited by these systems for many years were an insurmountable handicap for any practical use. As shown in this chapter, the technology of SSDLs has greatly improved over the last decade, and new dyes and hosts with performance comparable to that of liquid dye lasers have been developed. These improved SSDL systems, stable, cheap, and user friendly, offer a promising alternative to liquid dye lasers as practical sources of coherent, tunable laser radiation.

### REFERENCES


