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Sulforhodamine B doped polymeric matrices: A high efficient and stable solid-state laser

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ABSTRACT

We report the first systematic study on the laser action of Sulforhodamine B (SRB). Rhodamine B (RB), with similar molecular skeleton but with different phenyl substituents, was analysed to define the structural keystones in influencing their optical properties. Synthesis and laser characterization of photosensitized homopolymer, linear and crosslinked copolymers, and silicon-modified organic matrices were carried out. High lasing efficiencies, of up to 57%, were obtained with high photostability since the laser output remained stable, with no sign of photodegradation after 100,000 pump pulses at 10 Hz in the same position of the sample. These are, to the best of our knowledge, the topmost results achieved with new red-photosensitized materials to apply in advanced optical devices in this spectral region.

1. Introduction

In the development of solid state dye lasers, most of the work has been done using polymers [1,2] or silica gels [3,4] as host media. Initially, the sol–gel materials seemed to show higher photostability than those based in organic polymers, although refractive index inhomogeneities were a problem [5–7]. The use of synthetic polymers still presents additional advantages from both the technical and economic points of view: high optical homogeneity, better chemical compatibility with organic dyes, chemical versatility to change, in a controlled way, the final properties of the material (i.e., polarity, viscosity, molecular weight), high laser-radiation-damage threshold, inexpensive fabrication techniques which, combined with their light weight, facilitate both miniaturization and the design of integrated optical systems [8]. For these reasons, many efforts have been done to develop new photonic materials based on polymers doped with rare-earth-ions [9,10] as well as commercial [11] and newly synthesized dyes [12]. Up to date, the highest lasing efficiency and photostability from polymeric matrices doped with organic dyes has been recorded in the green-yellow region of the spectra [8]. Advanced optoelectronic and biophotonic applications require extending the wavelength-tuning emission of the dye-doped solid-state laser to the red part of the visible spectra.

Sulforhodamine B (SRB) and Rhodamine B (RB) (Fig. 1) are widely used laser dyes in the yellow-red spectral region, applied to generate femtosecond pulses in passive mode-locked, single-mode lasers amplifiers and hybrid mode-locked femtosecond lasers [13–15]. Proper understanding of the optical and spectroscopic properties of the RB and SRB dyes is complicated by the fact that these compounds exist in solution in a number of neutral and ionic forms [16]. Consequently, the properties of RB and SRB show great sensitivity to the solvent environment [17,18] and their photophysical properties have been extensively studied as a function of dye concentration, viscosity, polarity and polarizability of the solvents as well as the pH of the solution [13–27]: photophysics and photochemistry of RB and SRB depend not only on the solvent polarity [21–26] but also on the solvent viscosity [27,28] by the rotational motion of the *n*-diethyl groups around the xanthene amine bond. The data reported in these earlier works have been interpreted in different ways by different authors, leaving open the answer to the question onto which mechanism dominates the photodegradation process of these dyes [16,29–31]. Besides, no broad-based systematic studies have been carried out to analyse the photophysical influence on the laser behavior of RB and SRB [32–35].

In this paper, we present a careful analysis on the laser action of RB and SRB in relationship to chemical composition and macroscopic properties of the media into which they are incorporated. In addition, the present study is promoted by the similarity between RB and SRB, with the same xanthene skeleton but with different phenyl substituents, with the aim to identify which structural features are important in influencing the lasing properties of these dyes. Since the photophysical properties depend on environment, concentration of fluorophores and excitation conditions, we analyse first, the laser behavior of each dye in liquid phase, to proceed

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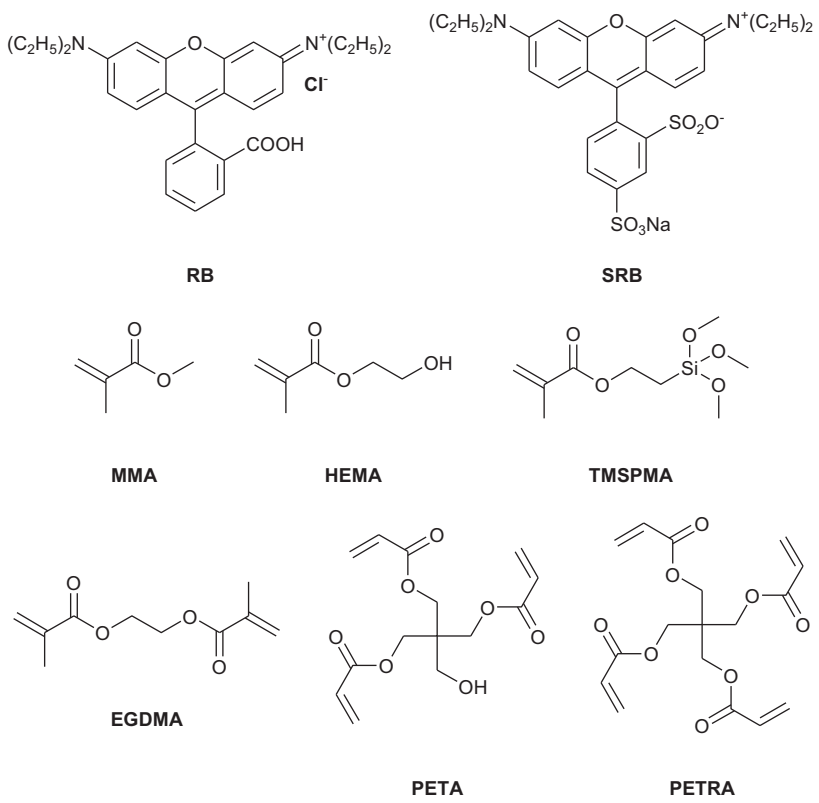

Fig. 1. Molecular structures of Rhodamine B (RB) and Sulforhodamine B (SRB) dyes as well as the monomers selected in this work: methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), ethylene glycol dimethacrylate (EGDMA), pentaerythritol triacrylate (PETA), and pentaerythritol tetraacrylate (PETRA).

then to a thorough study in solid matrices. Taking into account that the laser action of RB and SRB in solid-state materials has been scarcely studied [32–40], the present work represents, to the best of our knowledge, the first systematic study on the solid-state laser action of these dyes doped organic and hybrid matrices. Among the almost unlimited possible compositions and structures of solid materials to be doped with laser dyes, the liquid-phase analysis guides the selection of the best dye/host matrix in order to optimize the laser action attending to both lasing efficiency and photostability. Attention has been paid to the influence of the crosslinking degree of the materials on the laser action, since the well known effect of cage confinement on molecular motions could enhance the photostability of the encapsulated dye molecules in solid state [41–43]. More importantly, the substituents in the phenyl ring of these dyes could provide an excellent opportunity to analyse the effect of hydrogen bonding inside different polymer environments. The SRB-doped materials herein synthesized are found to be the most efficient and photostable solid-state laser dyes recorded up to now with emission at ca. 600 nm.

2. Experimental

2.1. Materials

Rhodamine B (chloride salt) and Sulforhodamine B (laser grade, Exciton) were used as received with a purity >99% (checked by spectroscopic and chromatographic methods). Solvents for laser studies were of spectroscopic grade (Merck, Aldrich or Sigma) and were used without purification. Linear copolymers were obtained by copolymerization of 2-hydroxyethyl methacrylate (HEMA) with different volumetric proportions of methyl methacrylate (MMA) and of the sililated monomer 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). Crosslinked matrices were obtained by copolymerization of HEMA/MMA with monomers with more than one polymerizable double bond per molecule. Di-, tri- and tetra-functionalizated comonomers, such as ethylenglycol dimethacrylate (EGDMA), pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETRA), respectively, were selected. All monomers were purchased from Aldrich. MMA, HEMA and TMSPMA were purified by distillation prior to use while EGDMA, PETA and PETRA were used as received. Fig. 1 shows the molecular structures of these monomers.

2.2. Preparation of solid polymeric samples

Sulforhodamine B was incorporated into the different solid matrices following the procedure previously described [44]. The solid monolith laser samples were cast in a cylindrical shape, forming rods of 10 mm diameter and 10 mm length. A cut was made parallel to the axis of cylinder to obtain a lateral flat surface of $\approx$6 mm $\times$ 10 mm. This surface as well as the ends of the laser rods were prepared for lasing experiments by using a grinding and polishing machine (Phoenix Beta 4000, Buehler) until optical-grade finished. The planar ground stage was carried out with a Texmet 1000 sand paper (Buehler) using a diamond polishing compound of 6 μm as an abrasive in mineral oil as a lubricant. The final polished stage was realized with a G-Tuch Microcloth (Buehler), using a cloth disk Mastertex (Buehler) with diamond of 1 μm in mineral oil as an abrasive type.

2.3. Methods

Lasing efficiencies and photostabilities were evaluated in a simple plane–plane oscillation cavity consisted of a 90% reflectivity