

Photostability of Silylated Coumarin Dyes in Polyceram Hosts

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Abstract. Numerous silylated coumarin dyes have been incorporated within silica : polydimethylsiloxane Polyceram hosts using the sol-gel process to form crack-free, polishable monoliths. The use of silylated laser dyes allows for covalently bonding the laser dyes to their hosts. Photostability of the samples was evaluated by measuring the decrease in the dye absorption in the Polyceram upon ultraviolet lamp exposure and by monitoring the fluorescence intensity as function of pump pulses from a N₂ laser at 337 nm. Both methods showed a significant improvement in photo- and thermal-stability of the silylated dye Polyceram compared to that of the unsilylated dye Polyceram at a dye : Si mole ratio of 10⁻⁴ : 1. The improved stability is attributed to the immobilization and higher degree of caging of the silylated dye Polyceram with respect to the unsilylated dye Polyceram.

Keywords: silylated dyes, laser dyes, Polyceram, photostability, solid-state dye laser

1. Introduction

Organic fluorescent dyes possessing high quantum efficiencies and broad fluorescent bandwidths are attractive for use as laser media. Most commercial dye lasers are solvent based and require pumping of the dye solution through a resonator to slow down photodecomposition. Incorporating laser dyes within a solid host can eliminate inherent problems with physical pumping and the use of a solvent system. In addition, a solid-state medium provides ease of use and replacement. Dye/host interactions, in principle, could enhance control of the fluorescence spectra, improve photostability, and even improve the fluorescence efficiency.

Laser dyes in sol-gel hosts are attractive materials for the development of a solid-state dye laser, and considerable research effort has been placed in this area over the past decade [1-6]. We have recently reported the use of silylated or grafted laser dyes [7-9]. These are laser dyes which are chemically attached to an alkoxysilane group. When used with sol-gel techniques, the silylated dye can participate in hydrolysis

and condensation reactions, allowing the dye to be covalently bonded to various host matrices. Numerous coumarin silylated dyes have been synthesized and incorporated within xerogels at high concentrations. The use of a silylated laser dye resulted in (1) improved solubility of the silylated dye with respect to its unsilylated counterpart, allowing for higher concentration of active molecules within a sol-gel matrix [7]; (2) higher fluorescence efficiency, attributed to the greater rigidity and isolation of the silylated dye within its host [7]; (3) improved chemical stability, associated with the lack of leachability of the dye from the host [7]; (4) control of dye/matrix interactions affecting optical spectra [9]; and (5) improved photostability [8].

To make solid-state dye laser, it is desirable to form gain media with different geometries. Unfortunately, xerogels are very difficult to form into rods due to their poor drying behavior and poor mechanical properties. Polycerams, also called Ormosils, are polymer modified ceramic materials in which the inorganic and organic components are combined on a molecular level. Polycerams are synthesized using sol-gel chemistry

techniques and permit the fabrication of a wide variety of compositions as thick coatings or crack-free monoliths.

In the present investigation, silylated coumarin dyes are incorporated within Polyceram monoliths. Photo- and thermal-stabilities of the Polycerams are measured and evaluated.

2. Experimental

Recrystallized 7-hydroxy-4-methylcoumarin (Coumarin 4 or Coum) (Aldrich) and various silylated coumarin dyes, 7-(*N*-triethoxysilyl)-*O*-(4-methylcoumarin) urethane (derCoum), 5,7-di(*N*-triethoxysilyl propyl)-*O*-(4-methylcoumarin) urethane (2derCoum), and 7-(3-(triethoxysilyl) propoxy)-4-methylcoumarin (derPCoum) were used in this study (Fig. 1). Dye synthesis is reported elsewhere [9].

A low molecular weight (400–700) silanol-terminated polydimethylsiloxane (PDMS) (United Chemical Technologies) was the reactive polymer used to make the Polycerams. The hydroxyl end groups of

the PDMS can participate in condensation reactions with the silylated dye, a hydrolyzed metal alkoxide, or another silanol-terminated PDMS. This can result in DYE-PDMS, Metal-PDMS, or PDMS-PDMS linkages, respectively.

Typically, tetraethoxysilane (TEOS), PDMS, tetrahydrofuran (THF), dye, and H₂O (acidified to 0.15*M* with HCl) were mixed in a flask at a dye: THF:H₂O:TEOS molar ratio of 10⁻⁴:20:2:1. The final Polycerams contained 80 volume% polymer. The solutions were refluxed for 1 hour and then concentrated. Monoliths were prepared by pouring the solutions in polypropylene beakers and drying for ≈3 weeks. Thick films were also made by coating the solutions on microscope slides. Polishing of the monoliths was accomplished on an Ecomet 3 (Buehler®) polisher. A typical polishing sequence involved processing the samples with 600 grit SiC paper, 800 grit SiC paper, 6.0 μm diamond suspension, followed by 1.0 and 0.3 μm Al₂O₃ micropolish paste. The resulting Polyceram disks were clear and colorless with dimensions of 2 cm in diameter and 0.4 cm thick.

Photostability was measured by two methods. Samples were exposed to a long wave UV lamp (>300 nm, 8 Watts) located 1.5 inches away. The absorption spectra of the samples was monitored periodically with a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 3B). The maximum absorption of the dye was normalized to the absorption before UV exposure and plotted as a function of UV exposure time. The permanent drop in the absorption represents the degradation of the dye. Photostability was also measured by pumping the samples with a N₂ laser (Molelectron UV400) at 337 nm with a pulse rate of 7.7 Hz, a pulsewidth of 20 ns, and a fluence of 0.07 J/cm² (1.9 mJ/pulse, 0.03 cm² spot area). A solid angle of the fluorescence was focused onto a silicon detector (Laser Precision) after passing through a 385 nm bandpass filter to block the pump light. A schematic of the setup is shown in Fig. 2.

3. Results and Discussion

The absorption spectra of the dyes in Polyceram hosts are shown in Fig. 3. The coumarin dyes in Polycerams have absorption maxima near 320 nm, similar to the same dyes in solvent and xerogel hosts [9]. The only exception was the derCoum Polyceram which had an absorption spectrum that was slightly blue shifted.

Typical fluorescence photostability curves measured by pumping with the N₂ laser are shown in Fig. 4. The fluorescence intensity initially dropped exponential

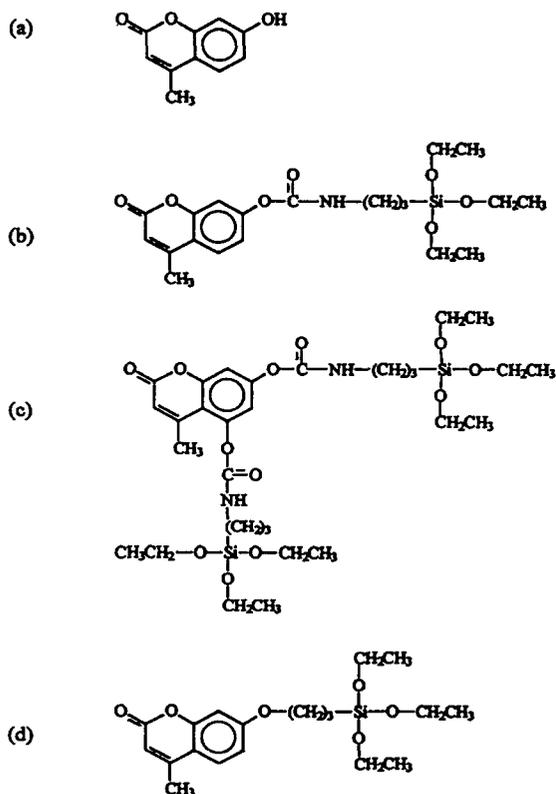


Figure 1. Structure of coumarin dyes: (a) Coum, (b) derCoum, (c) 2derCoum, (d) derPCoum.

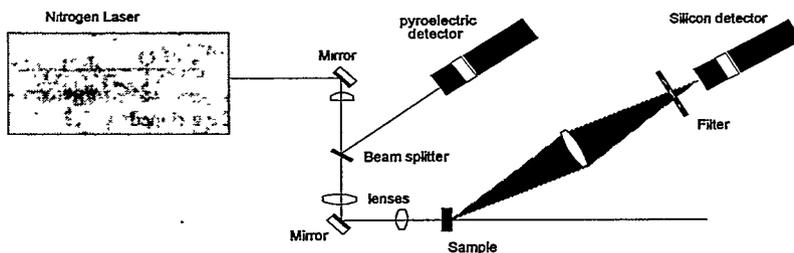


Figure 2. Schematic of the photostability measurement setup using a N₂ laser.

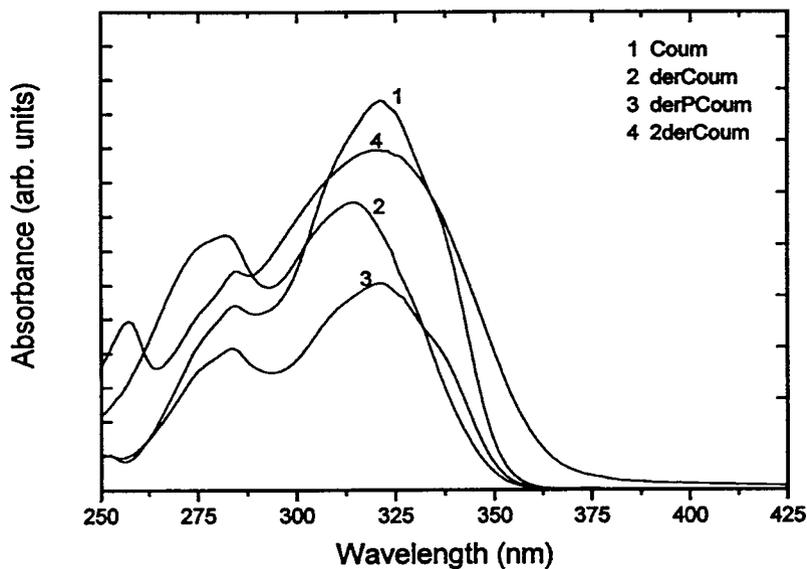


Figure 3. Absorption spectra of coumarin dyes in Polyceram hosts.

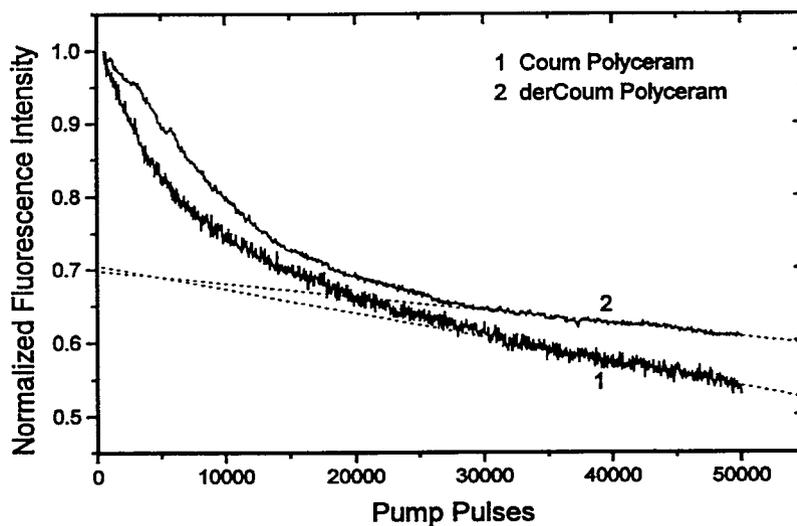


Figure 4. Fluorescence photostability for: (1) Coum and (2) derCoum Polycerams. The dotted lines represent the linear regression curve fits used to calculate the photostability FOM.

and then decayed linearly over long times. The shapes of these curves are very similar to those of the same dyes in xerogel hosts [8]. The initial decay was found to be partially reversible in the Polyceram monoliths and xerogels. Therefore the initial decay in the fluorescence does not solely represent permanent dye degradation. Hence the long term linear decay was used to compare the samples. It is speculated the cause of the initial decay is due to thermal lensing, which is currently being investigated. To compare the samples quantitatively, a figure of merit (FOM) was defined to describe the rate of permanent dye photodegradation. The FOM is defined as:

$$\text{FOM} = \frac{m}{b}$$

where m is slope and b is the y -intercept of the linear regression fit of the permanent fluorescent decay. Dividing the slope by the y -intercept provided normalized rates of fluorescence decay, and this allowed the comparison of samples with different fluorescence output intensities. The FOM values are negative, and a value of 0 would mean there is no decay in the fluorescent output. The linear fit is illustrated for the Coum and derCoum Polycerams by the dotted lines in Fig. 4, and the FOM for all the dyes in Polyceram are summarized in Table 1. The FOM for derCoum ($-2.64 \cdot 10^{-6}$ pulses $^{-1}$) and derPCoum ($-3.25 \cdot 10^{-6}$

Table 1. Photostability FOM for Coumarin dyes in Polycerams at $10^{-4}M$.

Dye-doped Polyceram	Photostability FOM ($\times 10^6$) (pulses $^{-1}$)
Coum	-4.69
derCoum	-2.64
derPCoum	-3.25
2derCoum	-6.90

pulses $^{-1}$) were significantly better than that for the Coum Polyceram ($-4.69 \cdot 10^{-6}$ pulses $^{-1}$).

Photostability measured by UV lamp degradation of the same compositions cast as films (Fig. 5) showed the same trend as the results measured using the N_2 laser. The Coum Polyceram degraded much faster than the derCoum Polyceram, indicating that silylated dyes are more photostable in the host.

The bifunctionalized dye (2derCoum) Polyceram had a much lower FOM. 2derCoum was synthesized from 5,7-dihydroxy-4-methylcoumarin, while the monofunctionalized dyes were synthesized from Coum. It was found that 5,7-dihydroxy-4-methylcoumarin is inherently less photostable than Coum [9]. Hence the lower photostability of 2derCoum can be associated with the inherent lack of such stability of its underivatized precursor.

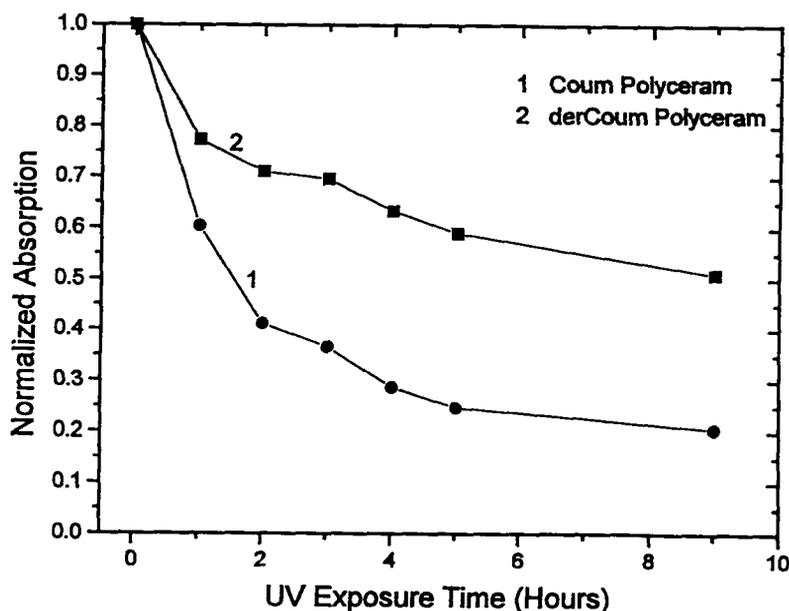


Figure 5. Absorption photostability for: (1) Coum and (2) derCoum Polycerams.

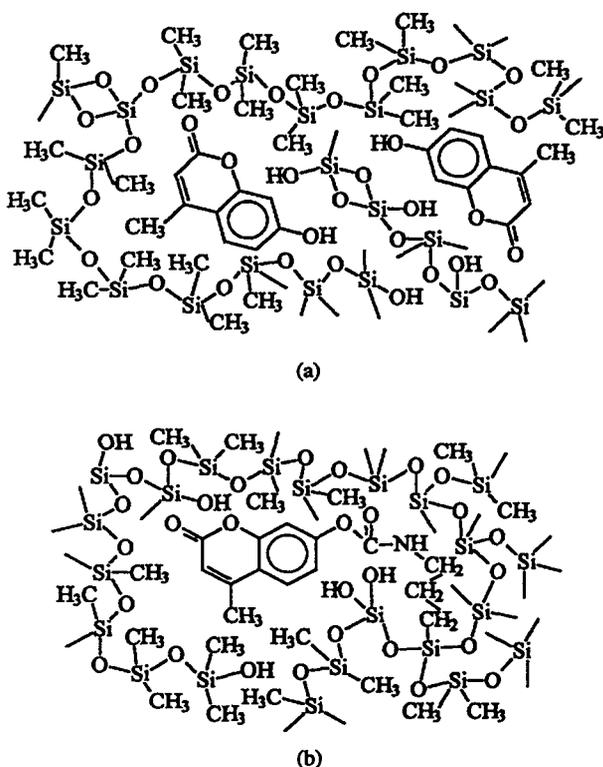


Figure 6. Proposed structures of: (a) Coum and (b) derCoum Polycerams.

Dye degradation depends on the structure of dye molecule, the composition and structure of the host, and the presence of impurities such as O_2 . A photoexcited dye molecule has a number of photophysical and

photochemical pathways which it can follow. Photochemical reactions, such as dimerization and oxidation, result in dye damage and a permanent loss of fluorescence. O_2 has triplet ground state and a very low excited singlet state. The easily excited singlet oxygen is very reactive toward organic molecules by photo-thermal-oxidation [10, 11]. The 4-methyl group in coumarin dyes is particularly prone to photo-oxidation [12, 13]. Significant improvement in photostability has been found with coumarin dyes when measured in deoxygenated atmospheres [8]. The same has been found for other dye/host systems [14, 15].

Improved photostability of the dye within solid hosts has been attributed to caging and immobilizing the dye, thereby preventing excited-state interactions with other species. Proposed structures of Coum and derCoum within a Polyceram matrix are shown in Fig. 6. The silylated dye which is bonded within the matrix has a higher probability of being caged, and cannot move through the matrix to react with other species. With a higher probability of caging, it is more difficult for reactive species to react with the immobile dye. Photodegradation of the silylated dye Polycerams is likely governed by O_2 diffusion, and may reflect incomplete caging of some of the silylated dye within the host matrix.

Coum, on the other hand, is free to move through the network. The mobility of Coum in xerogel films has previously been demonstrated from dye extraction experiments [7]. Coum mobility within the Polycerams was also observed (Fig. 7). Coum and derCoum Polycerams were heated at $75^\circ C$ and the absorption

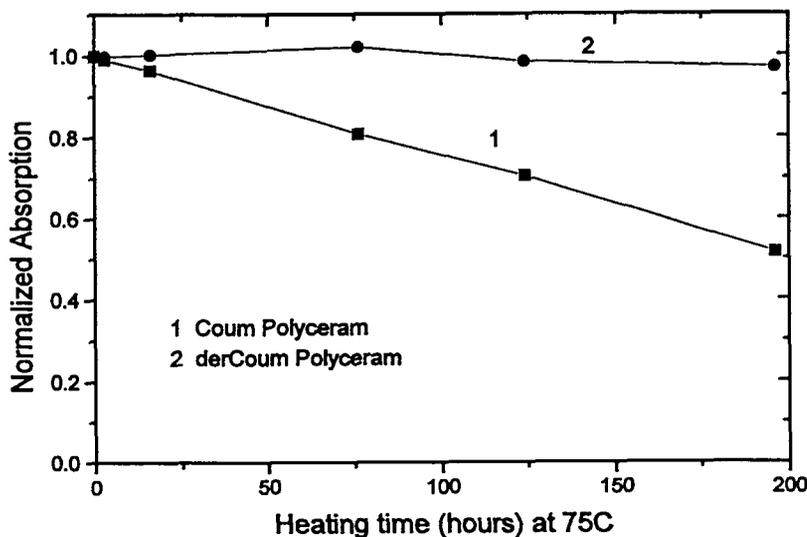


Figure 7. Normalized absorption of: (1) Coum and (2) derCoum Polycerams as function of heating time at $75^\circ C$.

at the absorption maximum of the dye (320 nm) was monitored. The heating temperature was well below the degradation temperature of the coumarin dyes, and any drop in absorption is attributed to dye sublimation from the host matrix. Dramatic dye loss was observed from the Coum Polyceram, while little or no dye loss was observed from the derCoum Polyceram. The high Coum mobility was also confirmed from the observation of crystallization on the surface of the Polyceram monoliths at high dopant levels. With a lower probability of being caged and a higher mobility, Coum can have greater interaction with singlet O₂ and other Coum molecules to undergo oxidation and dimerization, respectively, resulting in lower photostability.

Acknowledgments

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