Photostability of pyrromethene 567 doped in ORMOSILs with various additives

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Received 2 March 2004; received in revised form 20 May 2004; accepted 26 May 2004

Abstract

In this work, laser dye pyrromethene 567 (p567) was doped into methyltriethoxysilane (MTES)-derived organically modified silicate (ORMOSIL) monolith with various photo-stable additives including 1,4-diazobicyclo[2,2,2]octane (DABCO), 2,2,6,6-tetramethylpiperdin (TMP) and coumarin 440 (C440). The photostability of p567 was determined under continuous ultraviolet irradiation and its dependence on the concentration of each additive was studied. The results illustrated that the photostability of p567 in ORMOSIL with the optimized concentration of DABCO or TMP was improved by at least 100%. The highest photostability of p567 was obtained with the presence of C440, where at least four times of improvement has been observed. The photo-stable mechanisms of additives have also been discussed. © 2004 Elsevier B.V. All rights reserved.

PACS: 42.55.–f; 42.70.–a; 42.70.Jk; 42.70.Hj
Keywords: ORMOSILs; Pyrromethene 567; Photostability; Photo-stable additive

1. Introduction

For its great advantages such as compactness and low maintenance cost compared with the liquid counterpart, solid-state dye laser had a wide range of applications including spectroscopy, non-linear optics, communication, medical treatment, industry and so on. In recent years, intensive work had been devoted to this research field under the goal of making the solid-state dye laser commercially available [1–17]. Among the dyes studied by various researchers, the newly synthesized pyrromethene family, especially pyrromethene 567 (p567), was the most promising species for its high conversion efficiency and long laser lifetime [3,6,9–11]. The p567 dye had been doped into various
host media such as polymer [1,9–15], sol–gel derived ORMOSIL [2–6], composite glass or others hybrid materials [7,16,17]. The photostability of p567 doped into various media had been studied and its mechanism of photo-degradation had been investigated [7,9,11,18–21]. From these researches, the photo-degradation mechanism of p567 was determined and could be catalogued as self-sensitized photo-oxidation and radical-sensitized photo-oxidation, i.e. singlet-state oxygen molecules sensitized by other species such as triplet-state p567 dye molecules or free radicals should be responsible for the permanent degradation of p567 dye in most cases. To obtain higher photostability of p567, anti-oxidant additives acting as singlet-state quencher or free-radical scavenger had been doped into host matrix together with p567 laser dye. Great progress has been made on the photostability of p567 laser dyes and it was observed that DABCO and TMP had better effect to prolong the laser lifetime of p567 dye [11,14,20]. However, in these researches, the host media adopted by various researchers were mainly polymers and the concentration of additives should also have been optimized. In this work, two promising additives, DABCO and TMP, were doped into MTES-derived ORMOSIL with p567 dye, respectively. The influence of the kind of additives and its initial concentration on the fluorescence, laser efficiency and photostability of p567 doped in MTES-derived ORMOSILs are studied. Moreover, the influence of laser dye C440 on the photostability of p567 in ORMOSIL was also investigated.

2. Experimental details

2.1. Preparation of the dye doped ORMOSILs

The p567 laser dye doped MTES-derived samples were prepared by hydrolysis–condensation of the MTES precursors under acid-catalyzed hydrolysis and basic-catalyzed condensation. In all the samples prepared the initial concentrations of p567 were kept constant at $1.0 \times 10^{-4}$ mol/l whereas the additives were doped into ORMOSIL at various initial concentrations, respectively. The molecular structures of DABCO and TMP are shown in Fig. 1. In the case of DABCO, the initial concentrations were given the values $1.0 \times 10^{-4}$, $5.0 \times 10^{-4}$, $1.0 \times 10^{-3}$, $1.5 \times 10^{-3}$ and $2.0 \times 10^{-3}$ mol/l, i.e. the molar ratios between DABCO and p567 were 1:1, 5:1, 10:1, 15:1 and 20:1, respectively. These samples were labeled as DABCO 1, DABCO 5, DABCO 10, DABCO 15 and DABCO 20, respectively. In the case of TMP, the initial concentrations were given the values $1.0 \times 10^{-4}$, $2.0 \times 10^{-4}$, $3.0 \times 10^{-4}$, $4.0 \times 10^{-4}$ and $5.0 \times 10^{-4}$ mol/l, corresponding to the molar ratios between TMP and p567 of 1:1, 2:1, 3:1, 4:1 and 5:1, respectively. Also, these samples were designated as TMP 1, TMP 2, TMP 3, TMP 4 and TMP 5, respectively. When C440 dye was co-doped with p567, at a molar ratio of 5:1, namely an initial concentration of $5.0 \times 10^{-4}$ mol/l of C440 was adopted. Hydrolysis was performed under acid catalysis with HCl as acid catalyst and ethanol as solvent. The pH value of the mixed solution was adjusted to approximately 2. The initial molar ratio of MTES:ethanol:water was 1:3:3. After several hours of hydrolysis, a small amount of amine-modified silane $N$-(3-(triethoxysilyl)-propyl)-ethylenediamine was added to neutralize the acidity of the sol thereby to increase the condensation reaction rate, and then the photo-stable additives were added. After several more hours of stirring, the obtained sol were sealed in cuvettes and removed into 40 °C oven for drying and aging. The ORMOSIL could be machine or hand polished.

2.2. Measurements

The excitation and photoluminescence (PL) spectra were taken by a Hitachi 850 fluorescence
spectrometer. The scan speed was 60 nm/min and the slit width was 1.0 nm. A 30 W ultraviolet lamp emitting at 254 nm was used as the irradiation source of photostability measurement.

The laser performances such as slope efficiency and laser threshold of the p567 doped ORMOSIL were also obtained in this work. The laser cavity parameters were reported elsewhere [21]. The pump source used was a 532 nm, Q-switched Nd:YAG laser with pulse width of 3–5 ns (FWHM) and beam diameter of 5 mm. A longitudinal configuration was adopted consisting a dichroic mirror with high transmission at 532 nm and high reflectance between 570 and 650 nm, and an output coupler with 60–70% transmission at the laser wavelength. The cavity length was 5.0 cm.

3. Results and discussion

Because of the basic nature of the photo-stable additives, a problem arouse with the doping of the DABCO and TMP into MTES-derived ORMOSIL. In the sol–gel preparation process of MTES-derived ORMOSIL, the pH value was the key parameter for any change in pH value might lead to alteration of the relative rates of hydrolysis, poly-condensation reaction and solvent evaporation during the synthesis of the monoliths thereby result in further modification of microstructure of the ORMOSIL. Also, in liquid environment, the acidity/basicity may also change the luminescence and lasing parameters such as the fluorescence quantum yield, peak wavelength of fluorescence, and laser efficiency of p567 [22]. In previous studies, excellent fluorescence and laser performance had been observed in p567 doped into MTES-derived ORMOSIL [23]. However, the introduction of basic additives may lead to changes in the fluorescence and laser performance of p567 dye, possibly deteriorates the above performances. In this work, to eliminate the negative effects of the introduction of basic additives on the sol–gel process, the basic photo-antioxidants were added in the last sequence before the cuvettes being sealed and removed into oven for gelling and aging. To evaluate the effect of doping the photo-antioxidants into MTES-derived ORMOSIL on the luminescence property of p567 dye, the fluorescence spectra of p567 laser dye in the absence and presence of various concentration of TMP were obtained, as shown in Fig. 2. Only slight differences in fluorescence intensity could be observed among the fluorescence spectra of p567 dye with the presence of various additive concentrations. The shifts in peak fluorescence wavelength were in the order of approximately 0.2 nm. The laser slope efficiencies of p567 doped in MTES-derived ORMOSIL with the presence of various content of TMP agents, shown in Fig. 3, also indicated that the

![Fig. 2. Fluorescence spectra of p567 doped in MTES-derived ORMOSIL with various content of TMP additive (excited at 480 nm).](image)

![Fig. 3. Laser output energy of p567 dye doped in MTES-derived ORMOSIL with various content of TMP additive as a function of input laser energy (inset: laser slope efficiency of each sample above).](image)
introduction of a certain amount of TMP, smaller than $4 \times 10^{-4}$ mol/l, might even lead to a slight increase in the slope efficiency of p567. The decrease of laser efficiency of p567 dye with the increase of TMP amount might be attributed to the possible absorption of the additive, which increased the loss in laser action. These results clearly indicated that the addition of photo-oxidants in this work had little negative effects on the fluorescence performance of p567 dye.

Conventionally, the longevity of laser dyes doped into various solid host matrices was determined under the irradiation of laser pulses, and thus the photostability could be calculated [24]. In previous studies, the laser lifetime (defined as the laser pulses emitted before the output decreased to 50% of its initial laser output) of 60,000 pulses had been obtained with the p567 doped in MTES-derived ORMOSIL with the net sample thickness of 4 mm, corresponding to a normalized photostability of 50 GJ/mol [23]. In this work, the sample thickness was increased to 8 mm and it was believed that the laser lifetime of the samples prepared in this work may largely exceed 60,000 pulses even without consideration of possible improvement in laser lifetime resulted from the photo-stable additives. In order to reduce the cost and time, a continuous ultraviolet lamp with peak wavelength at 254 nm was adopted as excitation source to investigate the photostability of p567 in this work. The fluorescence spectra of p567 dye co-doped with various concentrations of additives were obtained after various exposure times and thus the photostability of p567 dye in each case could be compared and determined. Recently, a similar method was also adopted to investigate the photostability of synthesized pyromethene dyes with UV irradiation source where the laser dyes were dissolved in and covalently bonded to polymer and improved photostability was observed in the latter case due to dissipation of absorbed energy, confirming the validity of such a method [25].

To evaluate the photo-stable effect of TMP on p567 dye, the fluorescence intensity of p567 dye versus the corresponding UV exposure time, i.e. the exposure time dependence of fluorescence intensity of p567 doped in MTES-derived ORMOSIL with various content of TMP additive was obtained, as shown in Fig. 4. Obviously, the introduction of TMP additive and its content in MTES-derived ORMOSIL did have great influence on the photo-decay process of p567 laser dye. The fluorescence intensity of p567 dye with no or a small TMP content (p567 and TMP 1) decreased at the beginning of exposure, however, those with more TMP content were kept at their original level for 200 h, and then began to decrease with different decay rate. The best result obtained was the sample labeled as TMP 4, corresponding to an optimized initial concentration of $4 \times 10^{-4}$ mol/l of TMP in ORMOSIL, which decreased to 80% of its initial fluorescence intensity after 370 h of irradiation whereas the fluorescence intensity of p567 without additive decreased to 50% of its initial value after 200 h. It could be suggested that the photostability of p567 had been improved by 100%.

The fluorescence spectra of p567 doped in MTES-derived ORMOSIL after various time of UV lamp irradiation were shown in Fig. 5. With the increase of exposure time, the fluorescence intensity of p567 dye decreased, and blue shifts of the peak fluorescence wavelength could be observed. These clearly indicated the reduction in the actual dye concentration in ORMOSIL and the photo-degradation of p567 laser dye.
The exposure time dependence of fluorescence intensity of p567 doped in MTES-derived ORMOSIL with various content of DABCO additive was also obtained, as shown in Fig. 6. Similar photo-stable effect on p567 with the presence of DABCO was also observed and the optimized initial concentration of DABCO was $1.5 \times 10^{-3}$ mol/l, corresponding to the additive/dye ratio of 15:1. At the optimized additive concentration, the fluorescence intensity of p567 dye decreased to 60% of its initial value after 370 h of UV irradiation. Compared with that without additives, the photostability of p567 laser dye was believed to be improved by 100%.

It could be observed that the fluorescence intensity of p567 laser dye kept at the initial level in the first period of exposure time in the photo-decay curves of p567 laser dye with the presence of considerable content of photo-stable additives and the durations of these periods varied with the variation of the kind of additive and its content. This phenomenon could be attributed to the photo-stable mechanism of each additive. For instance, it had been reported that the quenching process of singlet-state oxygen by DABCO had both physical and chemical reaction [26]. So, it was obvious that the quenching process in chemical nature might result in the decrease of the additive concentration in the host medium and it kept decrease with the increase of exposure time. For a certain photo-stable additive, the quenching rate constant to the photo-degradation reaction and the proportion of the quenching process in chemical nature determined the intrinsic capability of the additive to prevent the dye molecules from photo bleaching. Also, a certain amount of photo-stable additives in the ORMOSIL could effectively offset the reduction of the additive concentration with the increase of exposure time. However, large amount of photo-stable additive led to not only the decrease in laser efficiency, as shown in Fig. 3, but also the decrease in fluorescence intensity after a certain period of UV exposure compared with that of smaller amount of additive. In other words, increasing the additive concentration up to a particular value will not in any way enhance the photostability of the dye.

Recently, improved photostability of p567 incorporated into the MPMMA polymer with C540A laser dye was achieved [10]. In our lab, enhanced laser efficiency and photostability have also been obtained with the pyromethene and perylene dyes co-doped with coumarin dyes, respectively, in ORMOSIL. The exposure time dependence of fluorescence intensity of p567 doped in MTES-derived ORMOSIL with the presence of C440 dye, as shown in Fig. 7, indicated an enhancement of at least four times in the photostability of p567. The photo-stable mechanism of C440 was believed to be the quenching of triplet-state p567 by ground-state C440 dye molecules. This phenomenon will be reported elsewhere.
4. Conclusion

In short, p567 doped MTES-derived ORMO-SILs monolith with various photo-stable additives including DABCO, TMP and C440 were prepared. The photostability of laser dye was determined under continuous UV irradiation and its dependence on the concentration of each additive was studied. The results illustrated that the addition of DABCO and TMP can greatly improve the photostability of laser dye and the optimized concentration of each additive are $1.5 \times 10^{-3}$ and $4 \times 10^{-4}$ mol/l, respectively. At appropriate additive concentration, the photostability of p567 was improved by at least 100%. When co-doped with C440 in ORMO-SIL, at least four times of improvement of the photostability of p567 has been observed.

Acknowledgement

The authors gratefully acknowledge the financial support for this work from the National Natural Science Foundation of China (No. 90101007), the Foundation for the Author of National Excellent Doctoral Dissertation of P.R. China (No. 200134), Trans-Century Training Program Foundation for the Talents by the Ministry of Education of P.R. China and Education Foundation of FOK Ying Tung.

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