

RESEARCH ARTICLE

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Engineering & Applied Sciences**Photobleaching of cresyl violet in poly(methyl methacrylate)****Michael J. Holmes, 2nd Lt., USMC**

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Abstract

This study investigates the rapidity with which an optical dye in a solid plastic host irreversibly degrades when it is brightly illuminated by visible light. Specifically, the organic dye cresyl violet perchlorate dispersed in plexiglas was optically excited by a continuous-wave dye laser pumped by an argon-ion laser. After resonantly absorbing and emitting many times, an individual dye molecule photochemically bleaches. The decay of the overall fluorescence signal was measured and fit to a theoretical model describing the time-dependence of the bleaching in terms of a quantum efficiency for photooxidation. Under ambient conditions, it takes a few million excitation-relaxation cycles to bleach a dye molecule at incident intensities on the order of 100 W/cm². This permanently destroys the dye, thereby limiting applications of such organic materials under exposure to high optical intensities, in laser sensors or fibers, for example.

Introduction

Laser dyes are organic compounds that relax radiatively after optical excitation, emitting in the visible or infrared range. The first laser dye, phthalocyanine, was discovered in 1966 by Sorokin and Lankard but is seldom employed in lasers today. Only a year later, rhodamine 6G (Rh6G) was discovered and continues to be the most widely used laser dye (Drexhage 1990). Today a large variety of luminescent dyes have been optimized for use in circulating liquid lasers.

These dyes have a range of practical applications when rigidized in a polymer host. One area that may be revolutionized by the use of organic luminophores in plastics is the flat-screen monitor industry. Current thin screens typically use expensive, delicate plasma technology. Organic emitters doped in a polymer layer offer an inexpensive, malleable, and easy-to-produce alternative. Organic dyes are also of interest for sensors, optical amplifiers, and fiber optics.

If organic fluorescent molecules are to be effectively used in such applications, they must be able to withstand repeated excitations and the large amounts of energy that will be cycled through them. Unfortunately, upon repeated absorption, the dye molecules begin to photooxidize, and they consequently lose the ability to fluoresce (Mackey 2001).

Cresyl violet (C₁₆H₁₂N₃O₅Cl), technically known as 5,9-diaminobenzo[a]phenoxazonium perchlorate (or oxazine 9 for short) and commonly referred to in the trade as LC6700 or CV670, is an efficient emitter at far red wavelengths (Castelli 1975). It is stable under ambient conditions, with minimal power saturation even at peak intensities as high as 100 MW/cm² (Moore 1978). It has a molecular weight of 361.74 g/mol, and its absorption spectrum is a good match to the emission from an Rh6G dye laser — the laser dye most widely used today.

Our experiment consisted of irradiating cresyl violet (CV) doped in thin solid slabs of poly(methyl methacrylate) with progressively higher intensities of Rh6G-laser light tuned to an absorption peak of the CV molecule. We expected the molecules would eventually photooxidize during this process of repeated excitation and relaxation of the electronic energy levels responsible for the violet color of the CV dye. This occurs because there is a weak but measurable probability that an excited molecule will make a transition into a chemically altered state as a result of a reaction with oxygen or water (originally dissolved in the dye and polymer solvents), rather than simply relaxing back to the ground state of the unreacted molecule (Schäfer 1992). By measuring the rate at which this occurs for different laser intensities, our goal was to quantify the quantum efficiency or probability for such a chemical transformation to occur. This can be accomplished by continuously monitoring the photoluminescence emitted by the relaxing CV molecules and fitting the decrease in this signal to a theoretical model describing the rate of photooxidation.

Optical Setup

As the block diagram in Figure 1 shows, our measurements were performed using a continuous-wave (cw) 6-W argon-ion laser, a 2-W dye laser, a darkened 90° sample chamber, a 0.32-m monochromator, and a thermoelectrically cooled CCD array detector. The monochromator was IEEE-interfaced to a PC for data collection and analysis. All measurements were made at room temperature in air.

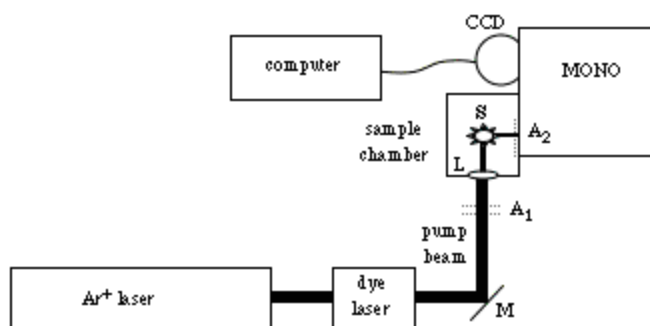


Figure 1 . The optical setup. The computer controls both the CCD detector and the monochromator (MONO). Other symbols used in the drawing: M = mirror, A1 = attenuators before the sample, A2 = attenuators at the entrance slit, L = lens, and S = sample.

The ion laser was used to pump the dye laser. The latter utilized rhodamine 6G perchlorate mixed in ethylene glycol, which gave us the ability to tune the pump wavelength over a range of 560 to 640 nm. Tuning was accomplished using a three-plate intracavity birefringent filter, spectrally calibrated against a standard Hg-Xe penlamp.

Initial alignment of the optics was performed using a multi-color helium-neon laser. This provides a simple method to excite samples for use in student laboratories in which a dye laser is not available or convenient, albeit at low powers and discrete wavelengths.

It is important to take precautions to avoid spurious effects in such a setup. The pump laser must strike the sample near the edge closest to the entrance slit to the monochromator. Otherwise the fluorescence may be reabsorbed or scattered by the parts of the sample between the pumped volume and the slit. The alignment of the sample and optics must not be disturbed during a run. The sample should be monitored for burning of physical holes at high pump intensities due to the thermal load from nonradiative de-excitations. This load can be estimated from the quantum yield (*i.e.*, the number of photons emitted per photon absorbed). As a baseline, the quantum yield for

