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Molecular structure and reversible photodegradation in anthraquinone dyes

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ABSTRACT

Reversible photodegradation is a process that has been observed in several dye molecules, but the underlying mechanisms are not still well understood. In this contribution, we characterize a series of anthraquinone dyes to determine how self-healing depends on molecular structure. Past studies have used probing techniques that rely on linear absorption, two-photon fluorescence, and amplified spontaneous emission. Each of these probes provide an indirect measure of the populations of the damaged and undamaged species, requiring calibrations or assumptions to be made that might affect the accuracy of the results. The present studies use fluorescence as a probe, which is shown to directly measure the undamaged population. It is found that certain anthraquinone classes share common structural features that are associated with self healing. Furthermore, the time and temperature dependence of photodegradation and self-healing is found to be consistent with the domain model of self healing.

1. Introduction

Dye molecules under high-intensity illumination degrade [1,2], a process called photodegradation. Photodegradation is typically characterized by the irreversible breaking of bonds, which is accompanied by a change in the linear absorption spectrum when the molecule transitions from its pristine state to a damaged one. Dye lasers are a well known example of a liquid solution [3–6], solid solution [7–9] or in a sol–gel [10,11] in which the active dye solute degrades under such photochemical reactions upon prolonged exposure.

Self-healing of the optical properties of a dye-doped polymer fiber was first observed by Peng and coworkers with fluorescence probing [12], but was not further studied. Howell independently observed self-healing in the anthraquinone dye Disperse Orange 11 (DO11) doped into poly (methyl methacrylate) (PMMA) polymer using Amplified Spontaneous Emission (ASE) as a probe [13], and was the first to apply kinetic models to determine rate constants and predict the intensity-dependence. These studies suggested that the decay rate decreases when cycling the material through several periods of decay/recovery and such cycling could also increase the ASE efficiency. These observations led to the proposal that cycling dye doped polymers through intervals of damage and recovery might be a method for making more robust materials.

It is important to stress that these self-healing materials are not specially designed to heal after photodegradation. The materials studied here and the processes responsible are not related to the large body of literature on self-repair of polymers after microcracking, where the material incorporates a microencapsulated healing agent that is released upon crack intrusion [14]. In the present studies, the dopant dye chromophores and the surrounding polymer undergo light-induced chemical processes in which bonds may be broken or rearranged, which are reversed upon healing – probably at the molecular level.

Howell also showed that dyes that irreversibly photodegrade in liquid solution [15] self-heal when the same experimental protocol is used with dyes that are instead embedded in a polymer host. In the dye laser literature, self healing is associated with the replenishment of fresh dye into regions where dye was damaged through mass transport and mixing. Our definition of self healing is the literal recovery of the pristine molecule from its damaged state rather than a damaged molecule being merely replaced by a fresh one. Howell meticulously made a sample chamber that was uniformly illuminate to eliminate reservoirs of undamaged dyes.

Embaye et al. used photochromism experiments during decay to show that reorientational diffusion (sometimes called orientational

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hole burning) is absent, so is not a likely mechanism [16]. Ramini and Dawson applied an analysis of samples that were imaged during decay and recovery to show that mass transport of molecules away from the burn area during damage and toward it in the dark during recovery was absent based on the evolution of the optically-imaged burn profile [17]. These set of experiments eliminated all of the standard explanations and suggested that a new type of mechanism was at play.

Embaye's observations that the recovery rate accelerates for samples with high dye concentrations [16] suggested that aggregates of dyes might be responsible for recovery, where larger aggregates both protect the molecules within them and foster their recovery. The fact that increasing the temperature decreases the recovery rate led to the hypothesis that domains form in analogy to condensates, where the average size of an aggregate decreases as the temperature increases.

Ramini and coworkers developed a statistical mechanical condensation model based on only one adjustable parameter that quantifies the sticking energy of a molecule to a domain [18]. This model was applied to Disperse Red 1 azo-dye-doped PMMA polymer data to determine the sticking energy (about 0.26 ± 0.1 eV), from which the distribution of sizes was determined. The measured temperature-dependence agreed with the model over a wide range of measurements.

Later, Anderson developed an imaging technique that has the ability to determine the population of damaged molecules as a function of intensity over a broad range of doses, [19] which was used to fine tune the domain model [20]. The resulting model was found to apply to even a broader range of experimental parameters, strengthening the case for its veracity.

The domain model assumes that each molecule sticks to two others, so domains are inherently quasi-one-dimensional. Domain models with higher-order dimensionality make predictions that disagree with the data. To further investigate this property, the effect of an applied electric field on the kinetics of photodegradation and self-healing were experimentally studied [21]. The quasi-one-dimensional model was generalized to take into account the effect of an applied field, which induces a dipole moment in each molecule, thus affecting the interactions between them. These self-consistent dipole field models correctly predict the measurements, reinforcing the confidence in the model.

There is no doubt that self healing is a real phenomenon. Indeed, the effect is being used to make lasers that heal [22,23]. However, many questions remain, such as the mechanisms of domain formation and how domains mediate healing. Dirk proposed that a TICT configuration might be responsible [24]. To test such hypotheses requires independent measurement techniques. Each suffers from unique challenges.

Amplified spontaneous emission in ASE-active materials such as the anthraquinones studied in the present work is a highly sensitive probe because it differentiates strongly between the pristine molecule and the damaged species. Extensive measurements of the dye disperse orange 11 (DO11) suggest that ASE emissions are registered only for the undamaged molecule and since the ASE intensity is a nonlinear function of the population density, its sensitivity is greater than for a linear measurements such as absorption spectroscopy.

The downside is that ASE is also a highly sensitive function of pump intensity, thus being more susceptible to laser drift. As such, photodegradation and self-healing are easily observed; but, the measured time constants are prone to inconsistencies. Indeed, drift over the long time periods required to fully characterize recovery (on the order of 24 h) can distort what is a simple single exponential curve to what appears to be multi-exponential. Furthermore, calibrating the ASE intensity as a function of concentration requires carefully controlled measurements that take into account absorption gradients that develop during photodegradation. These factors can lead to difficulties in obtaining quantitative data.

Linear absorbance, on the other hand, is a linear process, so the amount of light absorbed is directly proportional to the number of molecules in the beam's path. However, since the absorption spectrum of the pristine and damaged species overlap, both contribute. To unentangle one from the other requires the determination of the wavelength dependence of the absorption cross section of the pristine dye (which is simple since pristine samples are available); but a purely decayed sample cannot be made because self healing continually converts the damaged product back to the original one. Separating the two is especially difficult if the two spectra have substantial overlap. The issue is complicated even more by the fact that an irreversible species is also present, so that when enough of the self-healing species is present to be measurable, the data is contaminated with the irreversible species.

In the present work, we use fluorescence spectroscopy as a probe [25]. It is a linear process so does not have to be well calibrated, and as we will later show, the damaged species do not appear to contribute a measurable amount of signal in the spectral range of the measurement. As such, fluorescence probing appears to have all of the advantages without any of the drawbacks. We describe when the technique is applicable and use it to characterize self healing in a large number of anthraquinone molecules to both characterize the kinetics and to determine which structural features are associated with healing.

2. Experiment

Fig. 1 shows a schematic diagram of the fluorescence spectroscopy experiment that is used to probe optical damage. A pump laser from a Coherent Innova model 70C series ion laser at a wavelength of 488 nm and 3.46×10^5 W/m^2 average passes a pair of polarizers, which are used to control the power. A glass plate splits a small portion of the beam to a Thorlabs model S20MM power meter that monitors the stability of the beam, which is focused onto a thin-film dye-doped polymer sample in an oven chamber. The temperature is controlled with a resistive heater driven by a Micromega CN 77322-C2 unit, and the temperature is monitored with an Omega model CN-2010 Thermocouple. A shutter is used to turn the pump on and off as needed. The fluorescence produced by the sample is collected with a lens that directs the light to a fiber which guides the light into an Ocean Optics model SD2000 spectrometer.

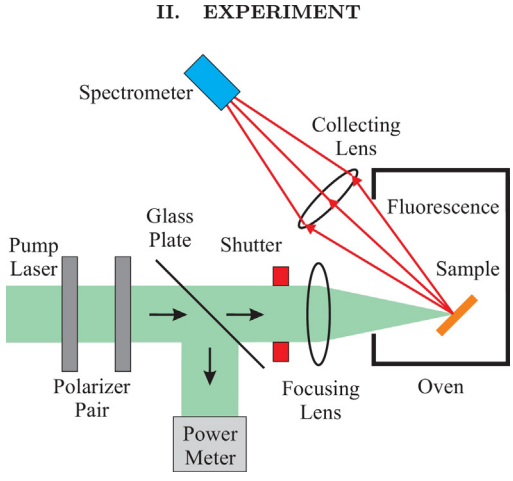

Fig. 1. Temperature-dependent fluorescence experiment. The pump beam both damages the sample and produces fluorescence that is used to monitor the population of undamaged molecules.