

# Poly(lactic acid) promotes healing of photodegraded disperse orange 11 molecules

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## ABSTRACT

We report on the recovery of a photodegraded organic molecule mediated by a biopolymer. Amplified spontaneous emission (ASE) from disperse orange 11 (DO11) dye-doped poly(lactic acid) (PLA) was used to monitor photodegradation while the material was being damaged by a strong pump laser. The ASE signal fully recovers over two hours time when the pump beam is blocked. The fluorescence spectra was also observed to recover after partial photobleaching the dye-doped polymer. PLA is the first biopolymer known to mediate the recovery of a photodegraded organic dye molecule.

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## 1. Introduction

Many organic molecules have delocalized electrons from conjugated bonds allowing the molecule to interact strongly with ultra violet and visible light. Organic molecules are used in many optics and photonics applications as colorant materials [1], photovoltaic materials [2,3], nonlinear optical materials [4,5], and fluorescent markers [6,7]. The fluorescent molecules with significant Stokes shifts and a high quantum yields are also used as laser gain media [8–10], where laser markers have recently been considered for biomedical imaging [11]. Although organic molecules can perform exceptionally well as optical materials, the intensity dependent photodegradation [12–14] of these molecules is a major drawback of their use in solid-state devices.

Much research has uncovered aspects of photodegradation of

organic dyes [15–18]. Placing organic dye molecules in various solid matrices changes the rate of photodegradation [19–21]. Applications such as dye lasers use a large dye-doped liquid reservoir that can be cycled through the laser cell, where the degraded molecules are diluted in the larger bath of optically active molecules to extend the operational lifetime. A phenomenon known as self-healing could potentially be used to create long-lifetime devices made from dye-doped polymer materials [22].

The first reported case of self-healing of an organic dye in a polymer matrix was by Peng et al. for rhodamine B-, fluorescein-, and pyromethene-doped poly(methyl-methacrylate) (PMMA) polymer optical fibers [23]. The anthraquinone dye, disperse orange 11 (DO11), was later placed in a host matrix of PMMA to create a self-healing material that fully recovers after severe photodegradation has occurred [24]. It was shown that dye diffusion was not a contributing factor to the self-healing phenomenon in DO11-doped PMMA [25]. Orientational hole burning was also shown not to be a mechanism of the degradation and recovery process in DO11-doped PMMA [26]. DO11 was shown to degrade with a slow recovery rate in polystyrene (PS), and the degree of recovery

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increases for DO11-doped PMMA/PS copolymers when the concentration of PMMA increases [27], where over an order-of-magnitude reduction in the recovery rate of photodegraded DO11 in pure PS was reported relative to the recovery rate in pure PMMA [28]. No recovery from a photodegraded state is observed when DO11 is dispersed in a methyl methacrylate (MMA) monomer solution [29]. Thus, interactions between DO11 molecules in a solid matrix alone appear to self-heal while some polymer structures can also mediate an expedited recovery.

Studies of DO11-doped PMMA, since its discovery as a self-healing material, seek to elucidate the effects of external electric fields [30], temperature [31], concentration [26], pump wavelength [32], and sample geometry [33] on the rate of healing. PMMA was the only polymer matrix known to mediate the healing of only a few organic dyes until 2015, when Anderson et al. showed that a degraded random laser with a rhodamine 6 g dye-doped polyurethane (PU) gain medium also underwent self-healing as revealed via the restoration of the laser's output power [34]. A self-healing random laser was also created by distributing ZrO<sub>2</sub> nanoparticles into a DO11-doped PMMA matrix [35]. Many anthraquinone dyes have recently been reported to either partially or fully recover their optical properties after being photodegraded by a pump beam [36]. Recently, the phenomenon of self-healing from photodegradation has been observed from photocurrent measurements in perovskite solar cells [37].

In this paper, we report on the degradation and recovery of the amplified spontaneous emission (ASE) of DO11-doped polylactic acid (PLA). After the ASE signal drops by more than 50% during photodegradation, we observe that it fully recovers within a few hours in the dark. As in Ref. [24] the ASE signal was actually found to recover beyond its initial brightness. Greater than unity recovery of ASE emission is a well-known phenomena. This increase in output intensity relative to the initial output has also been observed in a self-healing random laser [38]. Irreversible changes (such as some types of thermally induced changes) to the polymer matrix when irradiated by the pump beam may contribute to the greater than 100% recovery [39].

## 2. Experiment

Films of 2 wt. % DO11-doped PLA were made by dissolving 10 wt. % solids in tetrahydrofuran, and drop casting onto clean glass slides. A glass cover was placed over the films to slow the drying process immediately after the solution was dropped onto the slides. After 30 min, the films were placed in an oven at 130 °C and annealed for one hour.

The DO11-doped PLA films were pumped with a Continuum Minilite II laser operating at a wavelength of 532 nm with a pulse duration of 5 ns. The pump beam energy was approximately 250 μJ, where the pump beams stability was monitored using an Ophir pyroelectric detector as shown in Fig. 1(a). The chemical structures for DO11 and PLA are shown in Fig. 1(b).

The pump beam was expanded through two collimating lenses, which was focused to a thin line using a cylindrical lens as shown in Fig. 1(a). The pump beam profile was taken by placing a 550 nm long wavelength pass filter over a CMOS camera and collecting the fluorescence profile next to marks identifying the length scale on the film. The highly eccentric pump beam profile shown in Fig. 1(c) had a semi-major axis of 2.5 mm and a semi-minor axis of 100 μm for the Gaussian widths ( $1/e^2$ ) of the elliptical beam spot. The electric field polarization of the pump beam was aligned with the semi-minor axis of the beam profile.

The ASE was focused onto the end of a fiber that feeds into an Ocean Optics USB650 spectrometer. We used an integration time of 0.9 s while collecting the data from the spectrometer's CCD array,

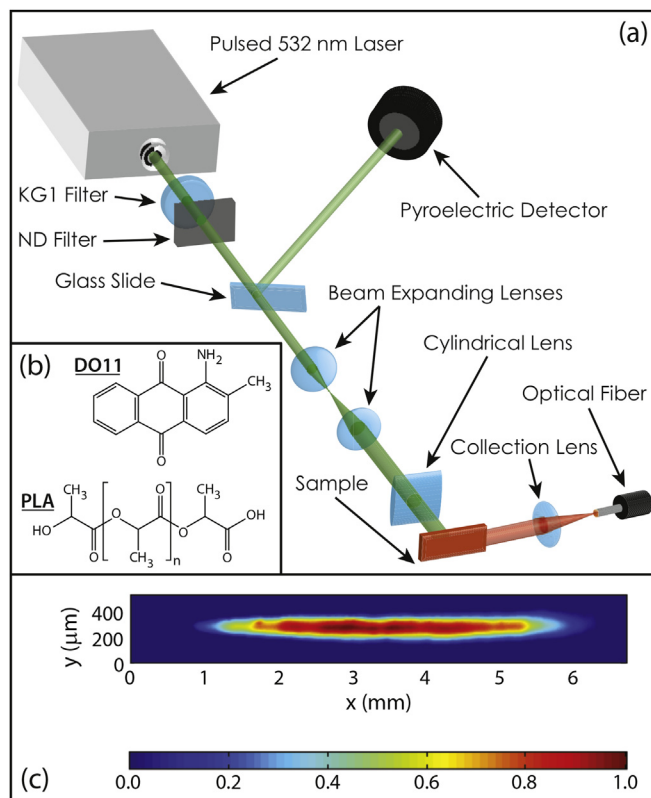


Fig. 1. (a) Diagram of photodegradation experiment. (b) Chemical structures for DO11 and PLA. (c) The pump beam profile captured from fluorescent imaging on the DO11-doped PLA sample.

which corresponds to averaging the normalized signal over 9 pulses from the pump operating at 10 Hz.

The recovery data was collected by the spectrometer in sparsely separated pump intervals. Spectra were recorded for 30 s pump intervals (with single measurements integrated over 0.9 s) followed by an average of all integrated ASE spectra over the 30 s interval. The time between successive measurements for the recovery data was also increased as the sample began to recovery so as to further reduce degradation.

## 3. Discussion

The reasonably high quantum efficiency and large Stokes shift of DO11 makes the molecule a good candidate for dye lasers, where its properties as a laser gain medium have been previously reported [40]. As typical with organic molecules, pumping a population of DO11 into an excited state leads to dye photodegradation, by which we mean the muting of optical phenomena associated with the original optical resonance. ASE is a nonlinear function of both the dye concentration and the pump fluence, thus these measurements are ideally suited to studying the effects of population degradation and recovery on the gain for laser applications. Concentration dependent recovery times have been observed for self-healing optical materials [26].

For a circular beam spot, we observed a broad fluorescent signal at low pump intensity. An ASE peak began to protrude from the fluorescence profile as the pump intensity was increased. The ASE amplitude quickly dominated the fluorescence spectrum at high power. The beam spot was changed to a highly eccentric shape using a cylindrical lens for the degradation and recovery experiment to produce a strong ASE signal using a relatively low fluence.

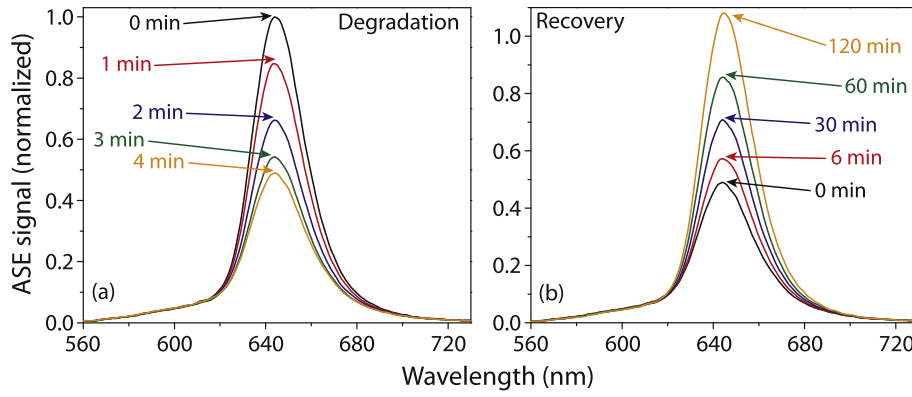


Fig. 2. The ASE spectra over time for the (a) degradation and (b) recovery of a 2 wt % DO11-doped PLA sample.

The strong ASE signal from the 2 wt % dye-doped polymer film quickly photodegraded under illumination as shown from the spectral data given in Fig. 2(a). Doubling the concentration above 2 wt % under the same experimental conditions will result in an ASE signal that is greater than twice the magnitude under the same experimental conditions. The ASE signal is significantly reduced when decreasing the concentration below 2 wt %. Therefore, the rapid decrease in ASE signal is caused by only a small reduction in the concentration.

The ASE spectra collected from periodic probing during the recovery time are shown in Fig. 2(b). The sample recovered to full ASE signal in less than two hours, where the final ASE signal is greater than the initial signal prior to optical degradation by the sustained pump beam. The peak amplitude of ASE as a function of recovery time is graphed in Fig. 3. Note that antecedent to this data, both the 2 wt % and 4 wt % samples were separately photodegraded until the ASE amplitude was just below half of each samples' initial peak value.

The recovery time for the 4 wt % sample is shown in Fig. 3 to be much longer than that for the 2 wt % sample. The longer recovery time is, at least in part, attributed to the greater total illumination required of the 4 wt % sample as compared to the 2 wt % sample to degrade the ASE signal to half its initial value. The healing rate also depends on the population of damaged and undamaged species, as

in Ref. [22] in which highly damaged samples displayed very long recovery times. Therefore, the greater degree of photodegradation occurring in the experiment using the 4 wt % sample results in a longer recovery time.

Although no ASE signal was observed for the 1 wt.% sample, we did record the recovery of photodegraded fluorescence at low fluence with a circular beam spot. The fluorescence spectrum of DO11-doped PLA pumped at 532 nm is shown in the inset of Fig. 4. Assuming negligible aggregation of DO11 at a concentration of 1 wt.%, the full spectrum integration of the fluorescence intensity  $I$  from the first excited state to ground state transition with respect to the angular frequency  $\omega$  is proportional to the dye concentration at a given time,  $c(t)$ . A 550 nm wavelength high pass filter was used in the degradation and recovery experiments to remove the 532 nm pump beam. If the high pass filter cuts off only a small portion of the spectrum,

$$\frac{c(t)}{c_0} = \frac{\int_0^{\omega_{\text{cut-off}}} I(\omega, t) d\omega}{\int_0^{\omega_{\text{cut-off}}} I_0(\omega) d\omega} \approx \frac{\int_0^{\omega_{\text{cut-off}}} I(\omega, t) d\omega}{\int_0^{\omega_{\text{cut-off}}} I_0(\omega) d\omega}, \quad (1)$$

where  $c_0$  is the initial concentration,  $I_0$  is the initial intensity of the fluorescence, and  $\omega_{\text{cut-off}}$  is the upper bound of the angular frequency due to the filter. The integrated fluorescence spectrum divided by the area underneath the initial fluorescence spectrum for the degradation and recovery experiments is shown in the main plot of Fig. 4.

The fluorescence recovery is difficult to measure because of the long recovery times and small changes in amplitude for relatively low levels of signal degradation. The small changes in the fluorescence, however, correlated to a much greater fraction of molecular degradation than the large changes in the ASE signal observed in the 2 wt.% and 4 wt.%. Therefore, by measuring the ASE spectra, we sacrifice a linear relationship for a greater degree of precision.

There are other contributing factors that may affect the rate of photodegradation and recovery in these samples. Since the ASE intensity is a non-linear function of the concentration of molecules in the excited state, small changes in the pump beam's alignment would result in pronounced changes in the ASE signal. Our experimental protocol mitigated alignment changes. Process variations between samples, such as in film thickness from dropcasting, can potentially change the measured degradation and recovery times as

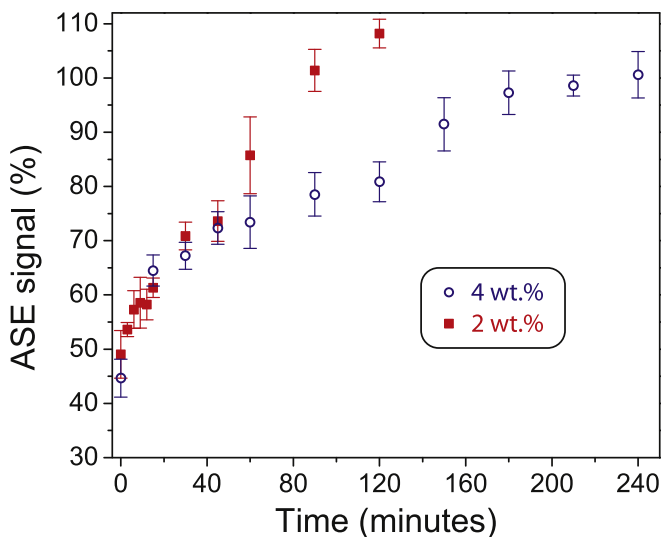
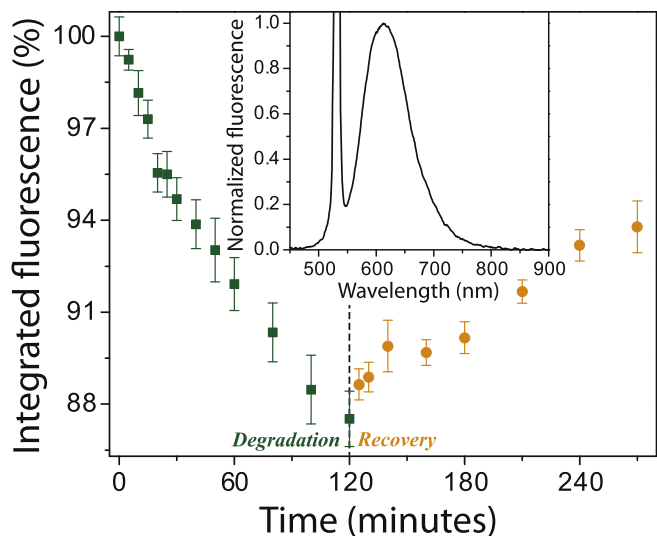


Fig. 3. The peak ASE signal as a function of time from probing of the degraded samples at short intervals during recovery.



**Fig. 4.** The integrated intensity as a function of time for the degradation (green squares) and recovery (orange circles) experiments for a 1 wt.% film of DO11-doped PLA. The inset shows the normalized fluorescence as a function of wavelength for DO11-doped PLA pumped at a wavelength of 532 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

well. In their discovery of self healing in DO11-doped PMMA, Howell and Kuzyk used a thick sample where optical hole burning and gradient degradation through the focal region can occur. Thin film (this study) recovery times are much shorter and appear to be less convolved with competing effects.

#### 4. Conclusion

This paper details the degradation and self-healing of the ASE signal in DO11-doped PLA, where PLA is the third polymer host known to the authors that mediates healing of some classes of photodegraded laser dyes. Note that we disregard PS as a polymer that mediates self healing as there appear to be conflicting reports for this matrix [27,28], and the single study reporting recovery [28] indicates a very slow recovery rate apparently incompatible with the rate equations for polymer-matrix-mediated recovery as seen in PMMA and PU systems. Self-healing materials can significantly improve device lifetime, which can be used in next generation technologies. Furthermore, PLA is a biodegradable polymer used in medical applications [42]. Thus, DO11-doped PLA not only has the advantages of being used in self-healing optical materials, but also is a step towards self-healing laser materials used as markers in medical imaging.

The ability for DO11 to recover from a photodegraded state when doped in PMMA has been well studied. The recent discover of PU as another host matrix that mediates the recovery of some photodegraded dyes provided a basis for identifying a class of polymers that can be used in self-healing optical materials. The structural similarities between PMMA and PU give insights for other potential candidate polymers for creating materials that recover from photodegradation. It appears that the presence of the acrylate functional group in the side chain of PMMA and the ester backbone of PU is key to mediation of the recovery process. Note that the ester group in the backbone of PLA has a methyl methine group as opposed the methylene groups bonded to the oxygen in PMMA and PU. The positive results from ASE degradation and recovery measurements in DO11-doped PLA provides evidence for this structural rule-of-thumb for polymers used in self-healing

optical materials as opposed to other polymers that do not appreciably mediate the recovery of dyes from a photodegraded state. On this basis we expect that, taking careful note of the dye and polymer structure, many more organics and classes of biomaterials displaying self-healing will be identified. We also anticipate polymers with dense distributions of ester groups bonded to short hydrocarbons such as polyester polyol to mediate fast recovery of some photodegraded dyes. Due to the high electron affinity of sulfur, thiol and thione substituted thioester polymers could potentially promote even faster recovery times.

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