Polylactic acid promotes healing of photodegraded organic molecule

Najee Stubbs[1], Mauricio Bridgewater[1], Micheala Stubbs[2], Amin Kabir[1], Michael Crescimanno[3], Mark G. Kuzyk[4], and Nathan J. Dawson[1,4,5,*]

[1]*Department of Physics, University of The Bahamas, Nassau, Bahamas*
[2]*Department of Chemistry, University of The Bahamas, Nassau, Bahamas*
[3]*Department of Physics and Astronomy, Youngstown State University, Youngstown, OH, 44555, USA*
[4]*Department of Physics and Astronomy, Washington State University, Pullman, WA, 99164, USA*
[5]*Department of Natural Sciences, Hawaii Pacific University, Kaneohe, HI, 96744, USA*
[*]*dawsphys@hotmail.com*

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 polylactic 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. PLA is the first biopolymer known to passively promote healing of an organic molecule.

OCIS codes: (160.3380) Laser materials; (160.1435) Biomaterials; (160.5470) Polymers; (140.3330) Laser damage.

References and links

1. H. Zollinger, *Color Chemistry: syntheses, properties, and applications of organic dyes and pigments* (VCH, New York, 1987).
2. S. S. Sun and N. S. Sariciftci, *Organic photovoltaics: mechanisms, materials, and devices* (CRC Press, Boca Raton, 2005).
3. Y. Su, S. C. Lan, and K. H. Wei, "Organic photovoltaics," Mater. Today **15**, 554–562 (2012).
4. P. N. Prasad and D. J. Williams, *Introduction to nonlinear optical effects in molecules and polymers* (Wiley, New York, 1991).
5. S. R. Marder, "Organic nonlinear optical materials: where we have been and where we are going," Chem. Commun. pp. 131–134 (2006).
6. M. S. T. Gonçalves, "Fluorescent labeling of biomolecules with organic probes," Chem. Rev. **109**, 190–212 (2008).
7. S. Luo, E. Zhang, Y. Su, T. Cheng, and C. Shi, "A review of nir dyes in cancer targeting and imaging," Biomaterials **32**, 7127–7138 (2011).
8. T. G. Pavlopoulos and P. R. Hammond, "Spectroscopic studies of some laser dyes," J. Am. Chem. Soc. **96**, 6568–6579 (1974).
9. K. H. Drexhage, "Fluorescence efficiency of laser dyes," J. Res. Nat. Stand. Sec. A **80A**, 421–428 (1976).
10. C. F. Zhao, R. Gvishi, U. Narang, G. Ruland, and P. N. Prasad, "Structures, spectra, and lasing properties of new (aminostyryl) pyridinium laser dyes," J. Phys. Chem. **100**, 4526–4532 (1996).
11. S. Cho, M. Humar, N. Martino, and S. H. Yun, "Laser particle stimulated emission microscopy," Phys. Rev. Lett. **117**, 193902 (2016).
12. M. Yamashita and H. Kashiwagi, "Photodegradation mechanisms in laser dyes: a laser irradiated esr study," IEEE J. Quant. Electron. **12**, 90–95 (1976).
13. G. Jones and W. R. Bergmark, "Photodegradation of coumarin laser dyes: an unexpected singlet self-quenching mechanism," J. Photochem. **26**, 179–184 (1984).
14. S. Sinha, S. Sasikumar, A. K. Ray, and K. Dasgupta, "The effect of dye photodegradation on the performance of dye lasers," Appl. Phys. B **78**, 401–408 (2004).
15. A. N. Fletcher, D. A. Fine, and D. E. Bliss, "Laser dye stability part 1. flash frequency and fluid filtration effects," Appl. Phys. A **12**, 39–44 (1977).
16. J. Widengren and R. Rigler, "Mechanisms of photobleaching investigated by fluorescence correlation spectroscopy," Bioimaging **4**, 149–157 (1996).
17. L. A. Deschenes and D. A. V. Bout, "Single molecule photobleaching: increasing photon yield and survival time through suppression of two-step photolysis," Chem. Phys. Lett. **365**, 387–395 (2002).
18. A. Kurian, N. A. George, B. Paul, V. P. N. Nampoori, and C. P. G. Vallabhan, "Studies on fluorescence efficiency and photodegradation of rhodamine 6g doped pmma using a dual beam thermal lens technique," Laser Chem. **20**,

99–110 (2002).
19. A. Dubois, M. Canva, A. Brun, F. Chaput, and J.-P. Boilot, "Photostability of dye molecules trapped in solid matrices," Appl. Opt. **35**, 3193–3199 (1996).
20. E. Yariv, S. Schultheiss, T. Saraidarov, and R. Reisfeld, "Efficiency and photostability of dye-doped solid-state lasers in different hosts," Opt. Mater. **16**, 29–38 (2001).
21. M. Ahmad, T. A. King, D.-K. Ko, B. H. Cha, and J. Lee, "Photostability of lasers based on pyrromethene 567 in liquid and solid-state host media," Opt. Commun. **203**, 327–334 (2002).
22. S. K. Ramini and M. G. Kuzyk, "A self healing model based on polymer-mediated chromophore correlations," J. Chem. Phys. **137**, 054705 (2012).
23. G. D. Peng, Z. Xiong, and P. L. Chu, "Fluorescence decay and recovery in organic dye-doped polymer optical fibers," J. Lightwave Technol. **16**, 2365 (1998).
24. B. F. Howell and M. G. Kuzyk, "Amplified spontaneous emission and recoverable photodegradation in polymer doped with Disperse Orange 11," J. Opt. Soc. Am. B **19**, 1790–1793 (2002).
25. S. K. Ramini, N. Dawson, and M. G. Kuzyk, "Testing the diffusion hypothesis as a mechanism of self-healing in disperse orange 11 doped in poly (methyl methacrylate)," J. Opt. Soc. Am. B **28**, 2408–2412 (2011).
26. S.-T. Hung, S. K. Ramini, D. G. Wyrick, K. Clays, and M. G. Kuzyk, "The role of the polymer host on reversible photodegradation in disperse orange 11 dye," in "SPIE Organic Photonics + Electronics," (2012), p. 84741A.
27. S. K. Ramini, *Experimental investigations of a proposed chromophore correlation model of self healing of Disperse Orange 11 doped in Poly(methyl methacrylate)* (Washington State University, Pullman, 2012).
28. B. Anderson, S.-T. Hung, and M. G. Kuzyk, "Influence of an electric field on photodegradation and self-healing in disperse orange 11 dye-doped pmma thin films," J. Opt. Soc. Am. B **30**, 3193–3201 (2013).
29. S. K. Ramini, B. Anderson, S.-T. Hung, and M. G. Kuzyk, "Experimental tests of a new correlated chromophore domain model of self-healing in a dye-doped polymer," Polym. Chem. **4**, 4948–4954 (2013).
30. N. B. Embaye, S. K. Ramini, and M. G. Kuzyk, "Mechanisms of reversible photodegradation in disperse orange 11 dye doped in pmma polymer," J. Chem. Phys. **129**, 054504 (2008).
31. B. R. Anderson, R. Gunawidjaja, and H. Eilers, "Photodegradation and self-healing in a rhodamine 6g dye and y_2o_3 nanoparticle-doped polyurethane random laser," Appl. Phys. B **120**, 1–12 (2015).
32. P. Dhakal and M. G. Kuzyk, "Molecular structure and reversible photodegradation in anthraquinone dyes," J. Photochem. and Photobiol. A **328**, 66–76 (2016).
33. W. Nie, J.-C. Blancon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, S. Tretiak, J. J. Crochet, G. Gupta, and A. D. Mohite, "Light-activated photocurrent degradation and self-healing in perovskite solar cells," Nature communications **7**, 11574 (2016).
34. B. R. Anderson and M. G. Kuzyk, "Mechanisms of the refractive index change in DO11/PMMA due to photodegradation," Opt. Mater. **36**, 1227–1231 (2014).
35. B. F. Howell and M. G. Kuzyk, "Lasing action and photodegradation of disperse orange 11 dye in liquid solution," Appl. Phys. Lett. **85**, 1901–1903 (2004).
36. J. H. Andrews, M. Crescimanno, K. D. Singer, and E. Baer, "Melt-processed polymer multilayer distributed feedback lasers: Progress and prospects," J. Polym. Sci. B **52**, 251–271 (2014).

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 pyrromethene-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] More recently DO11 was shown to degrade without recovery in polystyrene, and the degree of recovery increases for DO11-doped PMMA/polystyrene copolymers when the concentration of PMMA increases. [26] No recovery is also observed in DO11-doped methyl methacrylate (MMA) monomer. [27] Studies on DO11-doped PMMA since its discovery as a self-healing material seek to elucidate the effects of external electric fields, [28] temperature, [29] and concentration [30] on the rate of healing. PMMA was the only polymer matrix known to promote the healing of only a few dyes until 2015, when Anderson *et al*. showed that a degraded random laser with a rhodamine 6g dye-doped polyurethane gain medium also underwent self-healing as revealed via the restoration of the laser's output power. [31] Many anthraquinone dyes have recently been reported to either partially or fully recover their optical properties after being photodegraded by a pump beam. [32] Recently, the phenomenon of self-healing from photodegradation has been observed from photocurrent measurements in perovskite solar cells. [33]

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. 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. [34]

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 minutes, 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 spectrometer. We used an integration time of 0.9 s while collecting the data from the spectrometer's CCD array, 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 sparse intervals. Spectra were recorded for 30 s intervals during the degradation portion of the experiment. Spectra obtained during the recovery portion of the experiment were collected sparingly over varying time intervals, since the time between measurements was increased to avoid any systematic degradation during the recovery period.

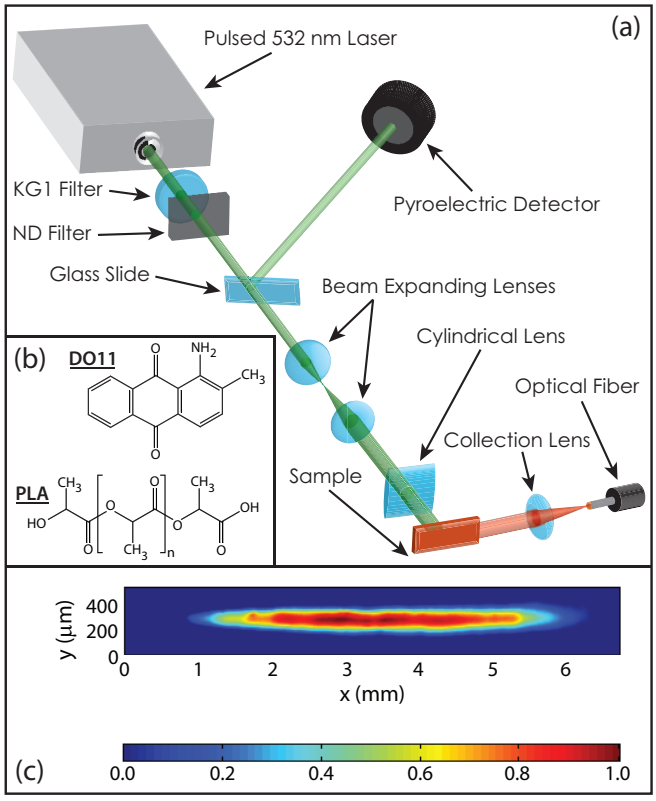

Fig. 1. (a) Diagram of photodegradation experiment. (b) Chemical structures for DO11 and PLA. (c) The pump beam profile captured from fluorescent imaging on the DO11-doped PLA sample.

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. [35] 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. [30] Device architectures employing high concentrations of dye molecules are ideal suited for self-healing materials. Organic microcavity lasers rely on relatively high concentration gain media. [36] Thus the focus of our attention here is the self-healing attributes of high concentration, dye-doped, thin films.

For a circular beam spot, we observed a broad fluorescent signal at low pump intensity. An ASE peak began to protruded 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. 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. %

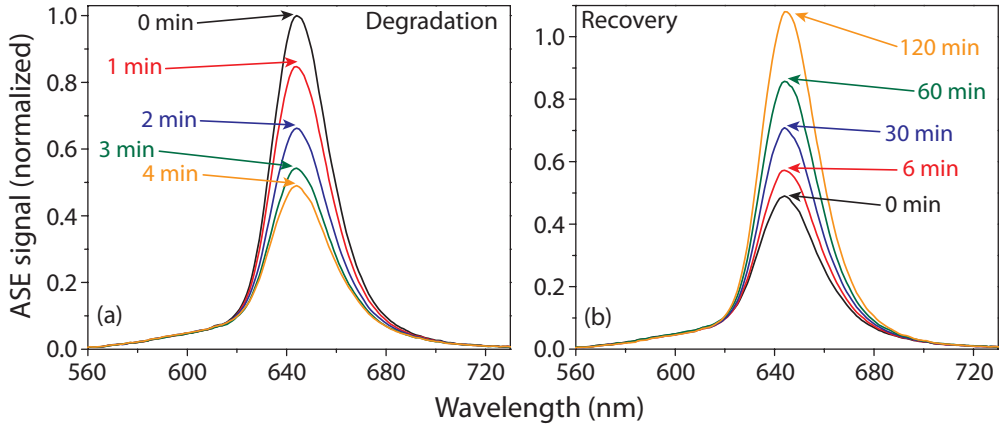

Fig. 2. The ASE spectra over time for the (a) degradation and (b) recovery of a 2 wt. % DO11-doped PLA sample.

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 these 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, atleast 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.

There are other contributing factors that may affect the rate of photodegradation and recovery in these samples. As described, the ASE intensity itself is a nonlinear function of the concentration of molecules in the excited state and so small changes in the pump beam's alignment could have resulted in large, spurious swings 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 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 recovery times are much shorter and appear to be less convolved with competing effects, and so measurements from thin films of dye-doped PMMA should be used to more rigorously compare with the recovery times in PLA reported above.

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 promotes healing of some classes

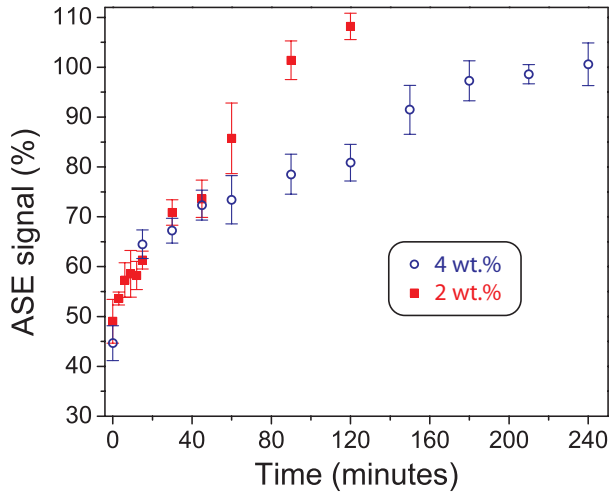

Fig. 3. The peak ASE signal as a function of time from probing of the degraded samples at short intervals during recovery.

of photodegraded laser dyes. Self-healing materials can significantly improve device lifetime, which can be used in next generation technologies. Furthermore, PLA is a biodegradable polymer. Thus, DO11-doped PLA not only has the advantages of being used in self-healing optical materials, but also is a step towards 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 polyurethane as another host matrix that promotes 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 polyurethane give insights for other potential candidates for creating materials that recover from photodegradation. 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 those polymers like polystyrene used in materials that do not show signs of recover from photodegradation. We expect to observe many more materials and some biomaterials with self-healing properties by taking note the dye and polymer structure.

Acknowledgments

NJD thanks the University of The Bahamas Annual Fund, MC acknowledges partial support from the YSU Office of Research, and MGK thanks the Meyer Distinguished Professorship of the Sciences.