Mechanisms of the refractive index change in DO11/PMMA due to photodegradation

Benjamin Anderson and Mark G. Kuzyk
Department of Physics and Astronomy, Washington State University, Pullman, WA 99164-2814

Abstract
Using a white light interferometric microscope (WLIM) we measure the photodamage induced change in the complex index of refraction of disperse orange 11 (DO11) dye-doped (poly)methyl-methacrylate. We find that the change in the imaginary part of the refractive index is consistent with previous measurements of photodamage-induced absorbance change. Additionally, we find that the change in the real refractive index can be separated into a component due to damage to the dye molecules and a component due to irreversible damage to the polymer.

Keywords: Optical Damage; Polymers; Disperse Orange 11; Refractive Index Change; White Light Interferometry; Reversible Photodegradation

1. Introduction

Disperse orange 11 (DO11) is an organic laser dye [1, 2, 3] which when doped into (poly)methyl-methacrylate (PMMA) is found to exhibit reversible photodegradation [1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Previously, DO11/PMMA’s decay and recovery have been characterized using linear absorptive measurements (such as absorbance spectroscopy [4, 5, 13] and transmittance imaging [6, 11, 4, 10, 12, 13]), nonlinear optical measurements (specifically amplified spontaneous emission (ASE)[1, 2, 4, 7]), and photoconductivity [9, 10, 12].

From these measurements a model of reversible photodegradation – the extended correlated chromophore domain model (eCCDM) [2, 12, 13] – has been developed. The eCCDM proposes that dye molecules form one-dimensional aggregates with the polymer host; where interactions between molecules result in a mitigation of photodegradation and recovery of damaged molecules. While the exact mechanisms of the eCCDM are still under investigation, the model is found to predict all observed experimental data.

One of the fundamental questions still to be addressed arises from the observation of both a reversibly damaged and irreversibly damaged species in linear optical measurements [2, 12, 4, 10, 11, 12, 13], while amplified spontaneous emission (ASE) measurements observe full recovery [1, 2, 4, 5, 6, 8]. As a possible explanation we proposed the hypothesis that the irreversibly damaged species is due to damage to the polymer host [12, 13], as ASE probes only the dye molecules. If the irreversibly species is due to polymer damage, we would expect the refractive index change to be the most sensitive probe as the polymer has the largest contribution to the sample’s refractive index, given the typically low concentration of dye (≈ 0.8 wt %).

2. Method

To measure the refractive index change of DO11/PMMA we use a white light interferometric microscope (WLIM) which uses white light in a Michelson interferometer and CCD camera to image the interferograms. The WLIM allows for the resolution of a sample’s complex index of refraction as a function of position in the plane of a thin film sample. The procedure to measure the change in refractive index using the WLIM is as follows. Images, as a function of arm length difference, are first taken with the empty interferometer to measure the reference white light interferograms at each pixel. Nearly identical samples are then placed in each of the interferometer’s arms and the interferometer is adjusted to take into account the change in optical path length and phase distortion introduced by the samples. Another set of images is then taken, as a function of arm-length difference, to measure the pristine sample’s interferograms at each pixel. After taking the white light and pristine interferograms, the sample in the stationary arm is burned using an ArKr laser operating at 488 nm and focused to a line spot with a peak intensity of 5 W/cm². The x-axis is defined to be the short axis, and the y-axis is the long axis. The sample is photodegraded for 4 hours, at which point the pump beam is turned off and another set of images are taken to measure the damaged sample interferograms at each pixel. After several days a final set of images is taken to determine changes due to recovery.

Email: benjamin.r.anderson@gmail.com

Preprint submitted to Elsevier

January 22, 2014
Once all the interferograms – white light, pristine sample, damaged sample, and recovered sample – are measured for each pixel, they are Fast Fourier Transformed to give spectral amplitude, $I(k_0; x, y)$, and complex phase, $\Phi(k_0; x, y)$ as a function of wavenumber and pixel position. We then calculate the change in absorbance due to photodegradation (and recovery) using

$$\Delta A = A_2 - A_1,$$

$$= -\ln \left( \frac{I_2}{I_0} \right) + \ln \left( \frac{I_1}{I_0} \right),$$

$$= -\ln \left( \frac{I_1}{I_2} \right),$$

where $A_2$ is the absorbance after degradation/recovery, $A_1$ is the pristine absorbance, $I_0$ is the spectral amplitude of the white light, $I_1$ is the spectral amplitude of the pristine sample, and $I_2$ is the spectral amplitude of the degraded sample. After determining the change in absorbance as a function of wavenumber and pixel position, we then calculate the change in phase:

$$\Delta \Phi(k_0; x, y) = \Phi_2(k_0; x, y) - \Phi_1(k_0; x, y),$$

where $\Phi_1(k_0; x, y)$ is the pristine phase and $\Phi_2(k_0; x, y)$ is the phase after degradation/recovery.

A complication arises when computing the change in phase as a function of position, as the process of unwrapping a noisy phase signal results in arbitrary constant offsets in the phase signal. These offsets are found to be random from pixel-to-pixel with the average over a large number of pixels being zero. However, using only a few pixels for averaging results in a non-zero phase offset. Therefore, in order to accurately calculate the effect of photodegradation, we enforce a constraint that the phase change be zero at the wavenumber corresponding to peak absorbance change. This constraint is consistent with the Kramers-Kronig relations between the real and imaginary parts of the refractive index.

After correcting for the random phase offset, the phase change is then converted to the scaled refractive index difference (SRID): \[\xi = \frac{\Phi_2 - \Phi_1}{2k_0} \] \[= d_1 \Delta n \]

where $d_1$ is the thickness of the damaged sample, and $\Delta n$ is the change in refractive index due to photodegradation (or recovery).

3. Results and discussion

As an example, consider the change in the complex index of refraction at nine points along the beam’s $x$ axis.
Figure 2: Scaled refractive index difference for several doses with two-peak Gaussian fits for reference. Also shown is the peak change in absorbance.

Figure 3: Scaled refractive index change at $k_0 = 11.55 \mu m^{-1}$ (circles) and change in absorbance at $k_0 = 13.27 \mu m^{-1}$ (triangles) with Gaussian fits (curves). The Gaussian widths of each fit are within experimental uncertainty of each other, and of the pump profile, as expected.

Figure 4: Scaled refractive index change as measured by the WLIM at peak intensity (points), KK of absorbance data (blue curve), and residual between the two (red curve).

Given that the difference is found to monotonically increase with wavenumber starting near $k_0 = 14 \mu m^{-1}$ ($\lambda \approx 450 nm$), the measured SRID and KK calculation begin diverging. However, starting above $k_0 = 14 \mu m^{-1}$ ($\lambda \approx 450 nm$), the measured SRID and KK calculation begin diverging. Therefore by not including the absorbance change in the UV regime, the KK calculation misses the effect of polymer damage.

To understand why the KK calculation is insensitive to the contribution of polymer damage, we consider two limitations of the KK calculation. First, the Hilbert transform integral spans a limited range of wavenumbers (corresponding to $390 nm < \lambda < 800 nm$). This wavenumber domain leaves out the spectral region in which the polymer’s absorbance change is greatest ($\lambda < 350 nm$) [18, 19, 22, 20, 21], but includes the region of peak absorbance change for DO11. Therefore by not including the absorbance change in the UV regime, the KK calculation misses the effect of polymer damage.

As an estimate of the effect of irreversible polymer damage on the SRID, we approximate the change in absorbance in the UV regime, shown in Figure 3 and perform the KK calculation again. We assume that the change in absorbance in the UV regime is of the same form as the change in absorbance for neat PMMA [18, 20, 19]. By performing the Hilbert transform on the extended change in absorbance we find the estimated SRID, as shown by the red curve in Figure 4. We find that by including a change in the UV absorption similar to that of neat
PMMA our KK calculation is consistent within experimental uncertainty of the measured SRID. This suggests that irreversible polymer damage is indeed responsible for the deviation between the truncated KK calculation and the measured SRID.

The second limitation to the KK calculation of the SRID is that the KK relations require the measured change in absorbance to be solely due to changes in the system’s electric susceptibility. However, irreversible photodegradation of PMMA is known to form scattering sites [23], whose effect on absorption and refractive index does not follow the KK relations [24, 25, 26]. The change in refractive index due to scattering sites is known to be proportional to $k^4$ [24, 25, 26], which is consistent with the observation of the divergence from the KK calculation. Though the absorption peak of PMMA is in the UV spectral range and thus requires an UV photon to cause and excitation and damage, absorption of a photon near the dopant’s absorbance may lead to damage of the polymer through energy transfer [27, 28, 29, 30, 31].

4. Conclusions

In conclusion, we spatially resolve the change in complex index of refraction due to photodegradation finding that the change in absorbance is consistent with previous measurements [4] while the measured change in refractive index is inconsistent with predictions using KK relations. Given the form of the residual, as shown in Figure 4, we conclude that the difference is due to irreversible polymer damage as the KK calculation primarily considers the effect of photodegradation on the dye molecules alone. This result supports the proposed nature of irreversible photodegradation in DO11/PMMA being due to polymer damage [12, 13]. Further research is currently underway to test this hypothesis including UV spectroscopy, scattering experiments, and FTIR.

5. Acknowledgments

We would like to thank Elizabeth Bernhardt for help with sample preparation and would like to thank Wright Patterson Air Force Base and Air Force Office of Scientific Research (FA9550- 10-1-0286) for their continued support of this research.
References

[1] B. Howell and M. G. Kuzyk, “Amplified Spontaneous Emission and Recoverable Photodegradation in Disperse-Orange-11-Doped-Polymer,” J. Opt. Soc. Am. B 19, 1790 (2002).

[2] B. Howell and M. G. Kuzyk, “Lasing Action and Photodegradation of Disperse Orange 11 Dye in Liquid Solution,” Appl. Phys. Lett. 85, 1901–1903 (2004).

[3] B. Abbas and M. A. Khalil, “Dichroism of poly(methyl methacrylate) thin films doped with disperse orange 11 molecules,” ACTA Physica Polonica A 115, 837 (2009).

[4] N. 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).

[5] S. K. Ramini, B. R. Anderson, and M. G. Kuzyk, “Recent progress in reversible photodegradation of disperse orange 11 when doped in pmma.” in “SPIE Laser Damage Symposium Proc.”, G. Exarhos, ed. (SPIE, Boulder CO, 2011), [8190-18].

[6] B. Anderson, S. K. Ramini, and M. G. Kuzyk, “Imaging studies of photodamage and self-healing in disperse orange 11 dye-doped pmma,” J. Opt. Soc. Am. B 28, 528–32 (2011).

[7] S. K. Ramini and M. G. Kuzyk, “A self healing model based on polymer-mediated chromophore co relations,” J. Chem Phys. 137, 054705 (2012).

[8] S. K. Ramini, B. R. 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,” Polymer Chemistry 4, 4948 (2013).

[9] B. R. Anderson, S. T. Hung, and M. G. Kuzyk, “Testing theories of self-healing using photoconductivity as a probe of photodegradation and recovery.” in “SPIE Optics and Photonics: Optical Engineering + Applications,” E. W. Taylor, ed. (San Diego, CA, 2012), 8519-16.

[10] B. R. Anderson, S. T. Hung, and M. G. Kuzyk, “Electric field dependent decay and recovery of do11 doped into pmma thin films: beyond 100% recovery.” in “Laser-Induced Damage in Optical Materials: 2012.”, vol. 8530, G. J. Exarhos, T. Tamaki, J. Nishii, and K. Itoh, eds. (Boulder, CO, 2012), vol. 8530.

[11] B. R. Anderson, S.-T. Hung, and M. G. Kuzyk, “The influence of an electric field on photodegradation and self healing in disperse orange 11 dye-doped pmma thin films.” arXiv:physics/1309.3037 (2013).

[12] B. R. Anderson and M. G. Kuzyk, “Generalizing the correlated chromophore domain model of reversible photodegradation to include the effects of an applied electric field,” arXiv:1309.5176v1 (2013).

[13] B. Anderson, S. Hung, and M. Kuzyk, “The effect of pump absorption on reversible photodegradation.” arXiv:physics (2013).

[14] B. R. Anderson, S. K. Ramini, and M. G. Kuzyk, “Imaging studies of photodamage and self-healing of anthraquinone derivative dye doped polymers.” in “SPIE Laser Damage Symposium Proc.”, G. Exarhos, ed. (SPIE, Boulder, CO, 2011), [8190-16].

[15] B. R. Anderson, E. Bernhardt, and M. G. Kuzyk, “A white light interferometric microscope for measuring dose-dependent reversible photodegradation,” J. Apl. Phys. (2013).

[16] B. R. Anderson, E. Bernhardt, and M. G. Kuzyk, “Studies of mechanisms of decay and recovery in organic dye-doped polymers using spatially-resolved white light interferometry,” in “Optical Processes in Organic Materials and Nanostructures,” vol. 8474, R. Jakubiak, ed. (2012), vol. 8474.

[17] V. Lucarini, J. Saarinen, K. Peiponen, and E. Vartiainen, Kramers-Kronig Relations in Optical Materials Research (Springer, 2005).

[18] A. Baum, P. J. Scully, W. Perrie, D. Liu, and V. Lucarini, “Mechanisms of femtosecond laser-induced refractive index modification of poly(methyl methacrylate),” JOSA B 27, 107 (2010).

[19] A. Baum, P. J. Scully, M. Basanta, C. L. P. Thomas, P. R. Fielden, and N. J. Goddard, “Photochemistry of refractive index structures in poly(methyl methacrylate) by femtosecond laser irradiation,” Optics Lett. 32, 190 (2007).

[20] R. Ahmed, “Optical study on poly(methyl methacrylate)/poly(vinyl acetate) blends,” International Journal of Photoenergy 2009, 150389 (2009).

[21] S. Murase and K. Horie, “Large photoinduced refractive index changes of transparent polymer films containing photoeliminable diazo and azido groups,” Macromolecules 32, 1103–1110 (1999).

[22] S. Sowa, W. Watanabe, T. Tamaki, J. Nishii, and K. Itoh, “Symmetric waveguides in poly(methyl methacrylate) fabricated by femtosecond laser pulses,” Optics Express 14, 291–297 (2006).

[23] W. Watanabe, K. Matsuda, S. Hiroino, and H. Mochizuki, “Fabrication of diffraction optical elements in polymers by 400 nm femtosecond laser pulses,” Journal of Laser Micro/Nano engineering 7, 58 (2012).

[24] J. Cabannes, “La diffusion moleculaire de la lumineure,” Ann. de physique 15, 5 (1921).

[25] B. H. Zimm and W. B. Dandliker, “Theory of light scattering and refractive index of solutions of large colloidal particles,” J. Chem. Phys. 58, 644–648 (1954).

[26] M. Nakagaki and W. Heller, “Effect of light scattering upon the refractive index of dispersed colloidal spheres,” J. Appl. Phys. 27, 975 (1956).

[27] R. S. Moshrefzadeh, D. K. Misemer, M. D. Radcliffe, C. V. Francis, and S. K. Mohapatra, “Nonuniform photobleaching of dyed polymers for optical waveguides,” Appl. phys. lett. 62, 16–18 (1993).

[28] A. Galvan-Gonzalez, M. Canva, G. J. Stegeman, R. Twieg, K. P. Chan, T. C. Kowalczyk, X. Q. Zhang, H. S. Lackritz, S. Marder, and S. Thayumanavan, “Systematic behavior of electro-optic chromophore photostability,” Optics Lett. 25, 322–324 (2000).

[29] S.-C. Chang, G. He, F.-C. Chen, T.-F. Guo, and Y. Yang, “Degradation mechanism of phosphorescent-dye-doped polymer light-emitting diodes,” App. Phys. Lett. 79, 2088 (2001).

[30] P. Annieta, L. Joseph, L. Irimpan, P. Radhakrishnan, and V. Nampoori, “Photosensitivity of laser dye mixtures in polymer matrix a photoacoustic study,” .

[31] J. F. Rabek, Polymer Photodegradation: Mechanisms and experimental methods (Springer-Science+Business Media, 1995).