



The effect of pump depletion on reversible photodegradation



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ABSTRACT

We model the effect of pump depletion on reversible photodegradation using the extended domain model [Anderson and Kuzyk, arXiv:1309.5176v1, 2013] and the Beer–Lambert law. We find that neglecting pump absorption in the analysis of the linear optical transmittance leads to an underestimate of the degree and rate of photodegradation. The model is used to accurately measure the molecular absorbance cross sections of the three species involved in photodegradation of disperse orange 11 dye in (poly)methyl-methacrylate polymer (DO11/PMMA). Finally we find that the processing history of a dye-doped polymer affects reversible photodegradation, with polymerized monomer solutions of DO11 being more photostable than those prepared from solvent evaporated dye-polymer solutions.

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1. Introduction

Reversible photodegradation of dye-doped polymers is a relatively new phenomena reported in dye polymer combinations of disperse orange 11 (DO11) doped into PMMA [1–12], DO11 doped into polystyrene [13], various anthraquinone derivatives doped into PMMA [14], AF455 doped into PMMA [15,16], pyrro-methene and rhodamine doped PMMA [17], and 8-hydroxy-quinoline aluminum (Alq3) doped into PMMA [18]. Quantitative measurements of reversible photodegradation assume that samples are sufficiently thin for the pump intensity to be constant throughout the sample [15,3,14,6–8,12]. In this study we use the extended correlated chromophore domain model (eCCDM) [12] and the Beer–Lambert law to account for pump depletion. Additionally, we use this model to find the absorbance cross sections of the three species involved in reversible photodegradation.

2. Theory

The effect of pump absorption on *irreversible* photodegradation has been studied extensively with the degradation mechanism assumed to be the conversion of undamaged molecules into a different molecular species [19–25]. For a monochromatic pump beam, the degradation process is described by a simple rate equation

$$\frac{dn}{dt} = -\frac{c\varepsilon_0(\omega_p)}{\hbar\omega_p B(\omega_p)} n I_p, \quad (1)$$

$$\frac{dn}{dt} = -\alpha n I_p, \quad (2)$$

where n is the fractional population of undamaged molecules, c is the concentration of absorbers, $\hbar\omega_p$ is the pump photon energy, B is the frequency-dependent bleaching rate [26–29], ε is the molecular absorptivity of the undamaged species, $\alpha = c\varepsilon_0/\hbar\omega_p B$ is the intensity-independent decay rate, and I_p is the pump intensity. The pump intensity as a function of depth follows the differential Beer–Lambert law,

$$\frac{dI_p}{dz} = -n(t)\sigma_0 I_p - [1 - n(t)]\sigma_1 I_p, \quad (3)$$

where σ_0 is the absorbance per unit length of the undamaged species and σ_1 is the absorbance per unit length of the damaged species.

Eqs. (2) and (3) have been used to model photodegradation in three cases: (1) neglecting pump absorption ($\sigma_0 = \sigma_1 = 0$) [27,30], (2) assuming a transparent damaged species ($\sigma_1 = 0$) [19,20,31] and (3) assuming an absorbing damaged species [21–25]. Cases 1 and 2 are found to have analytic solutions, while case 3 requires numerical solution methods.

In this study we use the three-species eCCDM model [12] with the assumption that all three species absorb pump light. The eCCDM proposes that domains of correlated chromophores are responsible for self-healing after photodegradation. These domains are found to be described by a linear aggregation model with the distribution of domains size N being $\mathcal{Q}(N)$ [6,7,12,32,33]. For a domain of size N , the population dynamics at depth z are modeled by a three-species “parallel” degradation model, with rate equations given by [12]

$$\frac{\partial n_0(z, t; N)}{\partial t} = -\left(\frac{\alpha}{N} + \varepsilon N\right) I_p(z, t) n_0(z, t; N) + \beta N n_1(z, t; N), \quad (4)$$

$$\frac{\partial n_1(z, t; N)}{\partial t} = \frac{\alpha I_p(z, t)}{N} n_0(z, t; N) - \beta N n_1(z, t; N), \quad (5)$$

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$$\frac{\partial n_2(z, t; N)}{\partial t} = \epsilon N I_p(z, t) n_0(z, t; N), \quad (6)$$

where $n_0(z, t; N)$ is the undamaged population, $n_1(z, t; N)$ is the reversibly damaged population, $n_2(z, t; N)$ is the irreversibly damaged population, α is the intensity independent reversible decay rate, ϵ is the intensity independent irreversible decay rate, $I_p(z, t)$ is the pump intensity at depth z , and β is the recovery rate. Eqs. (4)–(6) describe the microscopic dynamics, while the macroscopic dynamics are determined by an ensemble average over all domains

$$\bar{n}_i = \sum_{N=1}^{\infty} n_i(z, t; N) \Omega(N), \quad (7)$$

where $\Omega(N)$ is the density of domains of size N .

To describe the effect of pump absorption on decay and recovery we use the differential Beer–Lambert law to describe the pump and probe intensity depth profiles:

$$\frac{\partial I_p(z, t)}{\partial z} = -I_p(z, t) \sum_{N=1}^{\infty} [n_0(z, t; N) \sigma_0(\omega_p) + n_1(z, t; N) \sigma_1(\omega_p) + n_2(z, t; N) \sigma_2(\omega_p)] \Omega(N), \quad (8)$$

$$\frac{\partial I(z, t; \omega)}{\partial z} = -I(z, t; \omega) \sum_{N=1}^{\infty} [n_0(z, t; N) \sigma_0(\omega) + n_1(z, t; N) \sigma_1(\omega) + n_2(z, t; N) \sigma_2(\omega)] \Omega(N), \quad (9)$$

where $\sigma_i(\omega)$ is the absorbance per unit length at frequency ω of the i th species with $i=0$ being the undamaged species, $i=1$ the reversibly damaged species, $i=2$ the irreversibly damaged species, and ω_p is the pump frequency.

3. Experimental method

We measure the effect of pump depletion on photodegradation using several thin films with differing thickness of (poly)methylmethacralte (PMMA) doped with disperse orange 11 (DO11) to a concentration of 9 g/l. Several different preparation methods are used to produce a wide range of thickness. Thickness measurements are performed using absorbance spectroscopy, and transmittance imaging microscopy is used to measure photodegradation.

3.1. Samples prepared from monomer

The thickest samples are prepared using bulk dye-doped polymer as follows. Filtered methyl-methacralate (MMA) is mixed with DO11 dye in the correct proportions to obtain 9 g/l. The solution is then sonicated for half an hour, at which point initiator (butanethiol) and a chain transfer agent (Tert-butyl peroxide) are added in amounts of 33 μ l per 10 ml of MMA, and the solution is sonicated for another 30–60 min. After sonication the solution is filtered through 0.2 μ m disk filters to remove particulates, and put into glass vials. The vials of solution are placed in a 95 °C oven for 48 h to complete polymerization.

Small pieces of the bulk dye-doped polymer are removed and thermally pressed between two glass substrates to form a thick film. A custom oven/sample press applies an uniaxial stress of 90 psi at a temperature of 150 °C for 1 h, allowing the polymer melt to uniformly flow from the center, at which point the stress is gradually removed while the sample is allowed to cool. Typical thicknesses for this preparation method range from 60 to 100 μ m.

3.2. Samples prepared from polymer solution

To form thinner samples we add dye to PMMA/solvent solution, which is then either spun coated or thermally pressed after a drop

is placed on a substrate. The dye-doped PMMA/solvent solution is prepared as follows. DO11 and PMMA in a ratio of 9 g/l are dissolved into a solution of 33% γ -butyrolactone and 67% propylene glycol methyl ether acetate (PGMEA) with a ratio of 15% solids to 85% solvents. The solution is stirred for 72 h to dissolve the dye and polymer, after which the solution is filtered with 0.2 μ m disk filters into vials to remove any remaining solids.

1.5 cm \times 1.5 cm glass substrates are flooded with solution and then spun at 1200 rpm for 30 s/layer, with thicker films requiring multiple layers. After spin coating, the samples are placed in an 85 °C oven for 24 h to force solvent evaporation and remove other volatilities, after which they are allowed to cool. Spin coating typically results in films between 1 and 10 μ m.

To get thicknesses between 10 μ m and 60 μ m we use the method of drop pressing. Drop pressing involves heating a glass substrate at 50 °C for 10 min, at which point DO11/PMMA/solvent solution is dropped onto the substrate, and the temperature is raised to 95 °C for half an hour to induce solvent evaporation. The sample is then placed in a vacuum oven at room temperature overnight to ensure that the sample is dry. Once dried, the sample is used to make a sandwich structure with another clean glass substrate and placed in the thermal press oven for 135 min at a uniaxial stress of 72 psi and a temperature of 130 °C.

3.3. Thickness measurements

Sample thickness is measured using the pristine absorbance, A , of each sample, which is related to the thickness, L , by

$$A = \epsilon_0 c L \quad (10)$$

where c is the concentration and ϵ_0 is the molecular absorbance cross section of undamaged DO11/PMMA which is extrapolated from the absorption spectrum of DO11/MMA [32,33].

The absorption spectra of DO11/PMMA prepared by different methods and normalized to have the same peak heights all have, within the resolution limit of the spectrometer, the same peak position and width as that of DO11/MMA. As such, the absorption cross-section of the dye in these two hosts is the same and can be used to determine the thickness from the amount of light extinction. The contribution of the substrate is determined by measuring the absorption spectrum of the glass substrate and a non-doped PMMA thin film sandwiched between two glass slides in the wavelength range from 450 to 750 nm. The measured offset is the same for both the substrate and the PMMA sandwich structure (PMMA is transparent in this spectral range), indicating that it is due to surface reflection and scattering. The constant offset for a dye-doped sample is obtained from the average offset in the long wavelength regime where DO11/PMMA is transparent and subtracted from the spectrum when using the absorbance to determine the thickness of the dye-doped polymer layer.

The absorbance measurements are performed at six different locations on the samples to determine the average thickness, with the average thicknesses for the four samples used in these studies of 8 ± 2 μ m, 22 ± 3 μ m, 35 ± 5 μ m, and 83 ± 8 μ m.

3.4. Degradation measurements

A CW Ar:Kr laser, operating at 488 nm, focused to a line with a peak intensity of 120 W/cm² induces degradation, which is probed using a blue LED and transmittance imaging microscopy [8,14]. The transmittance imaging microscope measures the change in absorbance due to photodegradation, which we denote as the scaled damaged population, $n'(t)$. The scaled damaged population

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