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Extended model of the photoinitiation mechanisms in photopolymer materials

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In order to further improve photopolymer materials for applications such as data storage, a deeper understanding of the photochemical mechanisms which are present during the formation of holographic gratings has become ever more crucial. This is especially true of the photoinitiation processes, since holographic data storage requires multiple sequential short exposures. Previously, models describing the temporal variation in the photosensitizer (dye) concentration as a function of exposure have been presented and applied to two different types of photosensitizer, i.e., Methylene Blue and Erythrosine B, in a polyvinyl alcohol/acrylamide based photopolymer. These models include the effects of photosensitizer recovery and bleaching under certain limiting conditions. In this paper, based on a detailed study of the photochemical reactions, the previous models are further developed to more physically represent these effects. This enables a more accurate description of the time varying dye absorption, recovery, and bleaching, and therefore of the generation of primary radicals in photopolymers containing such dyes. © 2009 American Institute of Physics. [doi:10.1063/1.3262586]

I. INTRODUCTION

Holographic techniques are widely expected to provide the basis for the next generation of data storage devices. Photopolymer materials are proving to be the recording media of choice due to their ability to record low loss, environmentally stable and high diffraction efficient volume gratings. In any attempt to further develop the potential of photopolymer-based applications, a more accurate model of the photochemical processes is necessary.

Extensive work in this area has already been carried out to describe the time varying photoabsorptive behaviour of various dyes.^{1–4} The resulting models attempt to take account of the effects of (i) the photon absorption, (ii) the regeneration or recovery of absorptive photosensitizer, and (iii) photosensitizer bleaching. In this paper, the photoinitiation mechanisms involved during holographic recording in a polyvinyl alcohol/acrylamide (PVA/AA) based photopolymer^{5–11} is studied. The aim is to precisely predict the number of photons that are absorbed by the photosensitizer, which result in the generation of primary radicals, ED[•] (or R[•]). In this way, the initiation of photopolymer chains can be more accurately quantified. Eventually, incorporating an accurate photoinitiation model, which includes the major photochemical reactions, into the nonlocal photopolymerization driven diffusion (NPDD) model, will allow accurate predictions regarding the formation of the recorded holographic gratings.

In order to systematically present the results of this

study, the paper is structured as follows: In Sec. II the photochemical reactions involved in photoinitiation are discussed and a resulting set of governing rate equations are proposed. In Sec. III, the photoabsorptive behavior of two types of photosensitizer: Methylene blue (MB) and Erythrosine B (EB), of the same molarity in equivalent PVA/AA layers, are experimentally examined. Work done to analyze the recovery and bleaching processes are then presented. The improved model is applied to fit the experimental results using a numerical least squares fitting algorithm. The physical parameter values estimated in this way are then discussed. Finally, in Sec. IV, the limitations of the model are reviewed and a brief conclusion is given.

II. PHOTOINITIATION MECHANISM ANALYSIS

During holographic exposure of a PVA/AA photopolymer material, when the photosensitizer is illuminated with light of a suitable wavelength, the ground state dye molecule, Dye, absorbs a photon of light and is promoted to a singlet excited state,^{1,2,4–7,12} $^1\text{Dye}^*$,

where k_a (cm³/mol) is the rate constant of photon absorption in the ground state. The excited singlet state can return to its ground state by radiationless energy transfer to another molecule such as triethanolamine, which acts as an electron donor (ED), and by the emission of a photon by fluorescence.^{1,2,4–7,12} We assume that these processes take place at an overall rate of recovery, r_1 .

The resulting singlet state dye can also undergo intersystem crossing into the more stable and longer-lived triplet state,^{1,2,4–7,12} $^3\text{Dye}^*$,

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Independently estimating the rate of intersystem crossing, k_{st} , is very complex. In order to simplify our analysis we therefore assume that every Dye molecule which is excited can be directly converted into either $^1\text{Dye}^*$ or $^3\text{Dye}^*$. This is discussed in more detail below.

The triplet state can undergo *three* main reactions.

- (i) With an overall rate r_2 , it can return to ground state by either radiationless energy transfer or through collision with a ground state dye molecule,

- (ii) The transparent or clear (Leuco) dye^{13,14} can be formed when $^3\text{Dye}^*$ molecules react with the initially dissolved inhibitor Z, i.e., molecular oxygen O_2 ,¹⁵ with an inhibition rate constant k_z ($\text{cm}^3/\text{mol s}$).

- (iii) The production of free radicals takes place when the $^3\text{Dye}^*$ molecule accepts an electron from the electron donor ED. ED donates an electron to the excited triplet state of the dye, $^3\text{Dye}^*$, leaving the dye with one unpaired electron and an overall negative charge,¹⁻⁷ $\text{Dye}^{\cdot-}$,

where k_d ($\text{cm}^3/\text{mol s}$) is the rate constant of electron donation.

Based on Eqs. (1)–(4), we now wish to propose a set of rate equations governing the evolutions of the photosensitizer concentrations (Dye, $^1\text{Dye}^*$, and $^3\text{Dye}^*$) with time t . For simplicity, as stated in relation to Eq. (2), we assume that at any instant the fraction of dye molecules which are converted into the two excited dye states are constant values. We allow for this in the governing equations, Eqs. (5)–(7), by introducing the parameter, Ψ , such that $\Psi[\text{Dye}]$ molecules are available to be converted into the $^1\text{Dye}^*$ state, while $(1 - \Psi)[\text{Dye}]$ molecules are available to be converted into the $^3\text{Dye}^*$ form. Therefore,

$$\frac{d[\text{Dye}]}{dt} = -k_a \left(\frac{I'_0}{d} \right) [\text{Dye}] + r_1 [^1\text{Dye}^*] + r_2 [^3\text{Dye}^*], \quad (5)$$

$$\frac{d[^1\text{Dye}^*]}{dt} = k_a \left(\frac{I'_0}{d} \right) \{ \Psi[\text{Dye}] \} - r_1 [^1\text{Dye}^*], \quad (6)$$

$$\begin{aligned} \frac{d[^3\text{Dye}^*]}{dt} = & k_a \left(\frac{I'_0}{d} \right) \{ (1 - \Psi)[\text{Dye}] \} - r_2 [^3\text{Dye}^*] \\ & - k_z [^3\text{Dye}^*][Z] - k_d [^3\text{Dye}^*][\text{ED}], \end{aligned} \quad (7)$$

where I'_0 ($\text{Einstein}/\text{cm}^2 \text{ s}$) is the incident intensity corrected by the transmission fraction T_{sf} ,^{8,14} d is the thickness of the photopolymer material layer. The fraction Ψ differentiates between the concentration of $^1\text{Dye}^*$ molecules generated and the concentration of the more stable (longer-lived) triplet state molecules, $^3\text{Dye}^*$, simultaneously generated.

Since the primary radicals are generated in pairs,^{2-8,16} the rate equation governing $[\text{ED}]$ can be presented in the same fashion,

$$\frac{d[\text{ED}]}{dt} = -2k_d [^3\text{Dye}^*][\text{ED}]. \quad (8)$$

The unstable ED radical cation can then lose a proton to become a free radical,¹⁻⁷

which can undergo *two different reactions*. (a) The *first* is the initiation of the polymerization process in the presence of monomer,¹⁻⁷

where k_i ($\text{cm}^3/\text{mol s}$) is the initiation rate constant of polymerization associated with the reaction. (b) The *second* reaction involves the free radical undergoing dye bleaching.^{1-7,15,17} This occurs when the dye radical, see Eq. (4), abstracts the proton which the ED radical cation released at an earlier stage, see Eq. (9), and then abstracts a hydrogen molecule from the electron donor free radical, $\text{ED}^{\cdot}$. This results in the production of an unstable ED intermediate, ED_{int} , and the transparent dihydro dye,^{1,2,4,5} H_2Dye ,

where k_b ($\text{cm}^3/\text{mol s}$) is the rate constant of dye bleaching. Thus the transient state hydro dye radical concentration, $[\text{HDye}^{\cdot}]$, is governed by the rate equation,

$$\frac{d[\text{HDye}^{\cdot}]}{dt} = k_d [^3\text{Dye}^*][\text{ED}] - k_b [\text{HDye}^{\cdot}][\text{ED}^{\cdot}]. \quad (12)$$

It has also been reported^{2-4,7,8} that some of the free radicals produced, see Eq. (9), can be scavenged by reacting with inhibitor molecules to produce inactive or dead molecules, i.e., ED_{dead} . Thus

The rate equations governing the free radical, $\text{ED}^{\cdot}$, and the inhibitor, Z, concentrations are

$$\begin{aligned} \frac{d[\text{ED}^{\cdot}]}{dt} = & 2k_d [^3\text{Dye}^*][\text{ED}] - k_i [M][\text{ED}^{\cdot}] \\ & - k_b [\text{HDye}^{\cdot}][\text{ED}^{\cdot}] - k_z [Z][\text{ED}^{\cdot}] \end{aligned} \quad (14)$$

and

$$\frac{d[Z]}{dt} = -k_z [^3\text{Dye}^*][Z] - k_z [\text{ED}^{\cdot}][Z]. \quad (15)$$

As stated, two of the main reactions undergone by $^3\text{Dye}^*$ lead to bleaching: (i) production of Leuco dye, (ii) production of primary radicals subsequently leads to dihydro dye. Neglecting the contribution of $^3\text{Dye}^*$ which recovers, we can write that

$$k_a \left(\frac{I'_0}{d} \right) \{ (1 - \Psi)[\text{Dye}] \} \rightarrow [^3\text{Dye}^*] \rightarrow \text{bleached}. \quad (16)$$

The total bleached dye concentration at time t , $A_b(t)$, is given by the sum of the concentrations of the two transparent state species, i.e., Leuco and dihydrodye. Therefore,

$$\frac{dA_b(t)}{dt} = k_z[^3\text{Dye}^*][Z] + k_b[\text{HDye}^*][\text{ED}]. \quad (17)$$

The regenerated (or recovered) dye concentration, $A_r(t)$, is a combination of the recovered singlet and triplet dye concentrations, which are generated at rates r_1 , r_2 . $^3\text{Dye}^*$ has a longer lifetime than $^1\text{Dye}^*$,^{1-7,15} i.e., $r_1 > r_2$, and we assume that its contribution to the recovery process is negligible. As a result of this, in Eq. (5), $r_2[^3\text{Dye}^*]$ is neglected, i.e., $^1\text{Dye}^*$ dominates the recovery process. Therefore

$$k_a \left(\frac{I'_0}{d} \right) \{ \Psi[\text{Dye}] \} \rightarrow [^1\text{Dye}^*] \rightarrow \text{recovered} \quad (18)$$

and

$$\frac{dA_r(t)}{dt} = r_1[^1\text{Dye}^*] + r_2[^3\text{Dye}^*] \approx r_1[^1\text{Dye}^*]. \quad (19)$$

For any particular exposure time t_{exp} , once the exposing light is turned off, the dye concentration starts recovering from the value $A(t_{\text{exp}})$. A long time postexposure, i.e., $t \rightarrow \infty$, once the recovery process is complete, the amount recovered for that particular exposure is $A_r(t \rightarrow \infty)$. Thus the difference between the initial dye concentration, A_0 , and the dye concentration at $t \rightarrow \infty$, i.e., $A(t \rightarrow \infty)$, is the amount of dye that has been bleached, $A_b(t \rightarrow \infty)$. This description is further discussed in Sec. III. Based on this description, we substitute into Eqs. (5)–(7), from Eqs. (17) and (19), and an approximate expression for Ψ is derived,

$$\Psi \approx \frac{A_r(t \rightarrow \infty)}{A_r(t \rightarrow \infty) + A_b(t \rightarrow \infty)}. \quad (20)$$

This expression is used with our experimental data to provide the estimates for Ψ in Sec. III.

The combined effects of the photochemical reactions are governed by the set of first-order coupled differential equations, i.e., Eqs. (5)–(8), (12), (14), (15), (17), and (19), derived and presented above. Therefore, these equations govern the evolution of the concentrations of each chemical species during the photoinitiation process. In Sec. III, this model is experimentally examined.

III. EXPERIMENTAL VALIDATION

In a previous study in Ref. 1, experiments were carried out to characterize the recovery and bleaching processes of two types of photosensitive dye, i.e., MB and EB, in a PVA/AA layer.¹⁻⁸ In order to demonstrate the advantages and improvements arising from the use of the developed model presented here, it is applied to almost identical experimental data to that examined in Ref. 1 for MB and EB.

A. Photon absorption

Before characterizing the recovery and bleaching processes, the photon absorptivity of these two types of photosensitive dye needs to be determined at first. Starting with the examination of MB ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), the values of the rate constants, which determine the photochemical reactions discussed in Sec. II, are estimated. The absorbed intensity $I_a(t)$ is described using the Lambert–Beer law,^{1,2,8,14,18}

$$I_a(t) = I_0 T_{\text{sf}} \{ 1 - \exp[-\varepsilon A(t)d] \}, \quad (21)$$

where $\varepsilon = 7.89 \times 10^7 \text{ cm}^2/\text{mol}$ is the molar absorption coefficient of MB previously estimated in Ref. 1, and $A(t)$ is the varying concentration of ground state dye, i.e., $[\text{Dye}]$, available for photon absorption. The light incident upon the photopolymer material layer, after correcting for scattering and Fresnel losses, can be broken down into (i) the light that is absorbed, $I_a(t)$, and (ii) the light that is transmitted, $I_T(t)$, i.e., $I_0 T_{\text{sf}} = I_a(t) + I_T(t)$. Rearranging Eq. (21), the normalized transmittance $T(t) = I_T(t)/I_0$, can be expressed as

$$T(t) = T_{\text{sf}} \exp[-\varepsilon A(t)d]. \quad (22)$$

Using this relationship between $T(t)$ and $A(t)$, and recalling that $A(t)$ can be found using Eq. (5), a normalized transmission curve can be generated to fit the experimental data. Such a result is presented in Fig. 2(a) of Ref. 1. It shows a typical experimental transmittance curve with an initial value of $T_0 \approx 0.2$ which eventually, following constant exposure, saturates at a steady state value of $T_{\text{sf}} \approx 0.74$. To generate this result, a material layer thickness of $d \approx 100 \mu\text{m}$ was exposed normally with a beam of incident intensity, $I_0 = 4 \text{ mW}/\text{cm}^2$, at a wavelength $\lambda = 633 \text{ nm}$, for $t_{\text{exp}} = 150 \text{ s}$ exposure, with an initial photosensitizer concentration of $A_0 = 2.11 \times 10^{-6} \text{ mol}/\text{cm}^3$. Following fitting, the rate constant of the absorption in the ground state is estimated to be $k_a = 3 \times 10^4 \text{ cm}^3/\text{mol s}$.

As observed and discussed in Ref. 1, the transmittance curves of the second dye, EB ($\text{C}_{20}\text{H}_6\text{I}_4\text{Na}_2\text{O}_5$) are almost identical to those of MB, for similar experimental conditions, except the exposure wavelength is $\lambda = 532 \text{ nm}$ with $A_0 = 1.22 \times 10^{-6} \text{ mol}/\text{cm}^3$ and $\varepsilon = 1.415 \times 10^8 \text{ cm}^2/\text{mol}$.^{1,2,8} Once again, $A(t)$ is calculated using Eq. (5) and substituted into Eq. (22). The rate constant of photon absorption for EB is then estimated to be $k_a = 3.5 \times 10^4 \text{ cm}^3/\text{mol s}$.

B. Photochemical species

1. Dye molecule (MB)

When the ground state MB dye molecules, Dye, become excited, a fraction Ψ of them are promoted to $^1\text{Dye}^*$, Eqs. (6) and (7). These molecules do not react with any other species, but rapidly recover to the ground state at the rate r_1 . Under the same experimental conditions described in Sec. III A, and based on the results from fits to the transmittance curve data, the generation of $^1\text{Dye}^*$ during exposure is illustrated in Fig. 1(a). Figure 1(b) shows a simulation of the removal of $^1\text{Dye}^*$ postexposure due to the recovery effect which takes place over many hours.^{1,2} The chosen recovery rate of $^1\text{Dye}^*$ for a 150 s exposure $r_1 = 7.6 \times 10^{-4} \text{ s}^{-1}$. This mechanism is discussed in more detail later in Sec. III C.

FIG. 1. (Color online) (a) The generation of MB $^1\text{Dye}^*$ during exposure and (b) the removal of $^1\text{Dye}^*$ postexposure.

The remaining quantity of excited Dye molecules, $(1 - \Psi)$ become excited to the more stable triplet state of the photosensitizer, $^3\text{Dye}^*$.^{1-7,15} As the $^3\text{Dye}^*$ molecules are generated, during the early stages of exposure, they are rapidly consumed by reacting with ED and Z and by recovering to the ground state Dye, see Fig. 2. As can be seen in Fig. 2(a), during the very early stages of the exposure, i.e., $0 \leq t_{\text{Th}} \leq t_{\text{exp}}$, the generation of $^3\text{Dye}^*$ concentration is very fast, as a result of the large initial concentration of Dye, and hence the large number of photons absorbed. However, simultaneously this causes a rapid removal of Dye concentration which results in a reduction in the quantity of $^3\text{Dye}^*$ generated. Shortly after this point the removal mechanisms begin to dominate, until the maximum concentration of $^3\text{Dye}^*$ is reached at time t_{G1} , see Fig. 2(b). After the time t_{G1} , the concentration of $^3\text{Dye}^*$ decreases sharply. Since appreciable recovery occurs over long periods, the remaining $^3\text{Dye}^*$ molecules will eventually recover to the ground state, Dye, by relaxation postexposure the rate chosen for the simulation in Fig. 2 is $r_2 = 1.2 \times 10^{-4} \text{ s}^{-1}$. We recall that

FIG. 2. (Color online) The generation and removal of $^3\text{Dye}^*$ of MB as a function of time: (a) The initial stage, for $0 < t \leq 5$ s and (b) the full exposure for $0 < t \leq t_{\text{exp}}$.

FIG. 3. (Color online) (a) The generation of EB $^1\text{Dye}^*$ during exposure and (b) the removal of $^1\text{Dye}^*$ postexposure.

$^3\text{Dye}^*$ is known to be more stable and longer-lived than $^1\text{Dye}^*$.^{1-7,15} This is consistent with our estimated recovery rate of $^3\text{Dye}^*$ which is discussed later in Sec. III C.

2. Dye molecule (EB)

As noted previously in Refs. 1 and 2, the excited MB dye molecules more readily react with the available inhibitor to recover to the ground state, than in the case of EB. As a result, more EB dye molecules are bleached, i.e., $A_b(t)$ in Eq. (17), increases up to A_0 as the exposure time increases. Based on the fit to the experimental transmission data, the temporal evolution of the EB singlet state dye molecules, $^1\text{Dye}^*$, is presented in Fig. 3. As can be seen in Fig. 3(a), at $t_1 \approx 70$ s, the generation of $^1\text{Dye}^*$ concentration reaches its maximum value, which is lower than for the corresponding MB case in Fig. 1(a). This is further analyzed below in Secs. III C and III D. The $^1\text{Dye}^*$ concentration then starts to decrease, at time $t_{\text{II}} \approx 90$ s, due to the recovery process, which takes place much earlier than in the case of MB. This is also indicated in Fig. 3(b), where the removal of $^1\text{Dye}^*$ postexposure, due to its return to the ground state, Dye, finishes much more rapidly (i.e., within 4500 s) than in the case of MB, see Fig. 1(b) (i.e., within 10 000 s). Therefore, for a 150 s exposure, the recovery rate of $^1\text{Dye}^*$ for EB is estimated, in Sec. III C, to have a much higher value than for MB, i.e., $r_1 = 1.3 \times 10^{-3} \text{ s}^{-1}$.

The concentration of $^1\text{Dye}^*$ generated, directly impacts the temporal evolution of $^3\text{Dye}^*$, the generation of which is assumed to also take places at a rate constant k_a (but from a fraction, $1 - \Psi$, of the Dye concentration). The generation and removal of $^3\text{Dye}^*$ during exposure in the EB photosensitizer is illustrated in Fig. 4. As observed in Fig. 4(a), it takes a longer time t_{Th} for the $^3\text{Dye}^*$ to reach its threshold point, but a higher concentration is achieved at t_{Th} , i.e., the value at time t_{G1} in Fig. 4(b). This result is not surprising, because of the following.

- The rate constant of photon absorption, $k_a(\text{EB}) = 3.5 \times 10^4 \text{ cm}^3/\text{mol s} > k_a(\text{MB}) = 3 \times 10^4 \text{ cm}^3/\text{mol s}$, which means that for the same exposing intensity, EB

FIG. 4. (Color online) The generation and removal of $^3\text{Dye}^*$ of EB as a function of time: (a) The initial stage, for $0 < t \leq 10$ s, and (b) the full exposure for $0 < t \leq t_{exp}$.

Dye molecules absorb more photons per second, and therefore have a higher absorptivity than the MB molecules. This was verified in Ref. 1, i.e., $\epsilon(\text{EB}) = 1.415 \times 10^8 \text{ cm}^2/\text{mol} > \epsilon(\text{MB}) = 7.895 \times 10^7 \text{ cm}^2/\text{mol}$.

- (ii) The excited EB dye molecules are more likely to undergo bleaching rather than to recover, i.e., Ψ , is smaller for EB than MB. Ψ is determined in Sec. III D.

For $t > t_{G1}$ in Fig. 4(b), the generated $^3\text{Dye}^*$ molecules are eventually removed following reactions with ED and Z, and postexposure returns to the ground state. The recovery rate of $^3\text{Dye}^*$ for EB is estimated to be $r_2 = 9 \times 10^{-4} \text{ s}^{-1}$.

3. Primary radical (MB)

The primary radical concentration, ED^* (or R^*), is governed by the reaction between $^3\text{Dye}^*$ and ED, which will directly depend on the available concentrations. We note that there is a high concentration of ED in the system, i.e., the initial concentration of the electron donor is $\text{ED}_0 = 3.18 \times 10^{-3} \text{ mol/cm}^3$. Every $^3\text{Dye}^*$ molecule requires two ED molecules to produce a pair of radicals, as described in Eq. (8). Fitting the experimentally obtained transmittance curve data and using Eq. (8), the rate constant governing the electron donations by ED to $^3\text{Dye}^*$ for MB is estimated to be $k_d = 2.82 \times 10^2 \text{ cm}^3/\text{mol s}$.

The temporal evolution of the concentration of the primary radicals, ED^* , shown in Fig. 5, is important as it ultimately determines how much monomer is polymerized,¹⁹ which in turn determines the refractive index modulation formed during holographic recording. We note that the initiation of polymer chains is not included in the above description of the photoinitiation kinetics. Thus Fig. 5 shows the concentration of ED^* when no monomer is present, i.e., no photopolymerization takes place. The result does, however, indicate the availability of ED^* to initiate photopolymerization. As can be seen from Fig. 5, during the initial

FIG. 5. (Color online) The concentration of ED^* as a function of time for MB.

stages of the exposure, i.e., $0 \leq t \leq t_i$, the generation of ED^* is significantly inhibited by the originally dissolved oxygen. Thus the *scavenging effect*, included in Eq. (13), takes place at a rate constant k_z . Following the resulting inhibition period t_i , the generation of ED^* starts to progressively increase towards a maximum value at time t_{G2} . After t_{G2} the concentration of ED^* molecules decreases. With no monomer present this is solely due to the formation of the transparent dihydro-dye, H_2Dye , as discussed in Eq. (11), which continues to take place postexposure, i.e., $t \geq t_{exp}$. As can be seen, when $t = t_p$ in Fig. 5, there is a significant amount of ED^* remaining, which is available to initiate photopolymerization.

4. Primary radical (EB)

For the same initial concentration, $\text{ED}_0 = 3.18 \times 10^{-3} \text{ mol/cm}^3$. Fitting the transmittance curve data, the rate constant associated with the reaction between ED and $^3\text{Dye}^*$ for EB is estimated to be $k_d = 1.06 \times 10^2 \text{ cm}^3/\text{mol s}$. The general behavior of the ED^* concentration in EB is almost identical to that for MB, see Fig. 5. However, because more $^3\text{Dye}^*$ molecules are available in EB to react with the electron donor, more ED^* is produced. Therefore, (1) the inhibitor scavenging effect takes longer to end, i.e., $t \leq t_i \approx 15$ s, (2) at the corresponding time t_p in Fig. 5, the amount of dihydrodye formed is greater, and (3) a larger concentration of the primary radicals remain available to initiate photopolymer chains.

5. Hydrodye radical

The hydrodye radical, HDye^* , is the transient state dye radical before it reacts with ED^* , to form the transparent state dye, H_2Dye . The concentration of HDye^* as a function of time (during and postexposure) is presented in Fig. 6. HDye^* is quite unstable and highly reactive,⁵ and as a result as soon as the generation reaches its maximum value at time t_{G3} , the removal by the bleaching reaction with ED^* becomes dominant. However, this reaction is not synchronized with the exposure, therefore the consumption of HDye^* can take place over a long period postexposure. The rate constant associated

FIG. 6. (Color online) The concentration of HDye* as a function of time for MB.

with this reaction in Eq. (11) is estimated to be $k_b = 4.5 \times 10^4 \text{ cm}^3/\text{mol s}$, from the fits to the bleaching process data, which is discussed in Sec. III D.

For the corresponding EB case, due to the greater production of ED*, a larger quantity of HDye* is also produced during exposure, which is clearly important when the formation of H₂Dye dominates the bleaching process. The rate constant for EB is also estimated to be $k_b = 2.79 \times 10^4 \text{ cm}^3/\text{mol s}$.

6. Inhibitor (MB)

Following the work previously presented,^{6,7,20–22} it was assumed that inhibition primarily arises due to the reaction of initially dissolved oxygen O₂ (within the photopolymer layer), with the ³Dye* molecules, causing the suppression of the production of the monomer radical, ED-M₁. In this study, the inhibition mechanism has been extended by taking account of the inhibitor scavenging effect on primary radicals, arising due to the strong reactivity of the oxygen. This effect is especially significant in our photopolymer system, because of the following.

- (i) There is a limited amount of oxygen initially dissolved in the material, i.e., the initial concentration of inhibitor is assumed to be $Z_0 = 1.6 \times 10^{-7} \text{ mol/cm}^3$.^{2,4,6,7} Therefore, as soon as ³Dye* molecules are formed, they rapidly react with the dissolved oxygen present at a rate constant which is estimated to be $k_z = 3.4 \times 10^7 \text{ cm}^3/\text{mol s}$ for MB, see Sec. III D. Thus the Leuco dye is primarily and rapidly formed during the initial stages of exposure.
- (ii) Similarly the inhibitor scavenging effect also takes place over a very short period, $0 < t \leq t_i$, as indicated in Fig. 5. This is due to the limited initial inhibitor concentration Z_0 and the fast inhibition rate constant k_z , which is almost 30 times typically estimated values of the propagation rate of the growing polymer chains,^{3,7,8,16} i.e., $k_z \approx 30 k_p$.

Therefore, as expected, the inhibitor species Z is rapidly con-

sumed up by time t_i . If the material is not cover plated then new inhibiting oxygen can also diffuse into the layer from the atmosphere, but at a rate slower than k_z .^{20–22} The resulting effect is negligible under continuous exposure because the reaction between ³Dye* and ED* occurs at a much higher rate constant k_d than the oxygen can diffuse in to react with either of these two species. However, the effect of oxygen diffusing into the layer can have significant postexposure effects, as it can provide a means by which the excited dye molecules can recover to their ground state. This behavior was previously analyzed by examining the effects of cover plating^{1,6} on recovery.

7. Inhibitor (EB)

For EB, we note that the resulting inhibition period is longer. This is explained as follows.

- (i) The inhibitor is less reactive with the excited EB molecules than with the corresponding MB molecules, i.e., $k_z(\text{EB}) < k_z(\text{MB})$.¹ This is verified by the values extracted for the two rate constants of inhibition: $k_z(\text{EB}) = 1 \times 10^6 \text{ cm}^3/\text{mol s}$ and $k_z(\text{MB}) = 3.4 \times 10^7 \text{ cm}^3/\text{mol s}$.
- (ii) There is more ³Dye* available to react with the inhibitor due to the larger value of Ψ .

C. Recovery process (MB)

In this subsection the solution for $A_r(t)$, see Eq. (19), is used to describe the recovery process for a particular exposure. Following Ref. 1 Figs. 7(a) and 7(b) contain the sets of experimental data describing the evolutions of photosensitizer recovery of MB for four different short exposure times. In all cases examined the uncovered layers, of thickness $d \approx 100 \mu\text{m}$, were illuminated with a normally incident intensity of 4 mW/cm^2 . Four fractions of the maximum intensity transmitted through the layer at saturation are examined, these are $T_1 \approx T_{\text{sf}}/4$, $T_2 \approx T_{\text{sf}}/2$, $T_3 \approx 3T_{\text{sf}}/4$, and $T_4 \approx T_{\text{sf}}$. These correspond to four dye concentrations in the ground state: $A(t_1)$, $A(t_2)$, $A(t_3)$, and $A(t_4)$. The transmittances of the layers were then measured for a wide range of recovery times, i.e., $1 \text{ min} \leq t_{\text{off}} \leq 90 \text{ min}$. The resulting decreases in the transmittance being converted into the corresponding increases in the dye concentrations. The temporal evolutions of the recovery for the four cases can then be compared. As can be seen in Fig. 7(a), during exposing, i.e., up to t_1 , t_2 , t_3 , and t_4 the consumptions of the dye concentration predicted by the model for each case, i.e., the decaying part of each curve, agree well with the experimental data. In each of the four cases the predicted results overlapped with the full continuous exposure case, i.e., the full decaying curve for $0 < t \leq t_{\text{exp}} = 150 \text{ s}$. Once the exposures end the transmittances decrease as the concentration of Dye slowly increases, by recovery. In Fig. 7(a) this recovering is illustrated by four data points at $t_{\text{off}} = 60 \text{ s}$. Thus, at $t_{\text{off}} = 60 \text{ s}$ the first data points appear, indicating recovery for the four exposure times. See the full curves shown in Fig. 7(b).

Terminating the exposure involves setting the incident intensity appearing in Eqs. (5)–(7) to zero, i.e., $I'_0(t > t_{\text{exp}})$

FIG. 7. (Color online) (a) Combination of fits to experimental data of MB photosensitizer concentration during and postexposure for four varying exposure times: $t_1 = 5$ s (solid curve), $t_2 = 10$ s (long dashed curve), $t_3 = 20$ s (dashed curve), and $t_4 = 50$ s (short dashed curve), the full continuous exposure for $t_{\text{exp}} = 150$ s (shorter dashed curve), and the initial stage of postexposure from $t_{\text{off}} = 60$ s. (b) Extended postexposure version of (a) showing recovery of the MB photosensitizer concentration vs postexposure time off (t_{off}).

$= 0$. This enables the experimental data to be fit using the numerical solution of $A(t)$, both during, Fig. 7(a), and postexposure, Fig. 7(b). In this way, the recovery of MB over the entire postexposure period, i.e., for $t_{\text{off}} \gg t_{\text{exp}}$, can be examined for the four exposure times. This is a significant improvement on the previous dye models,^{1,2} which assumed that recovery was negligible during exposure and that the process could be treated in two separate limiting regimes,^{1,2}

i.e., during and postexposure. Consequently the previous results could only be presented in a schematic fashion, i.e., see Fig. 5 in Ref. 1. As can be observed in Fig. 7(b), appreciable recovery does occur over long periods. Going from Case 1 to Case 4, the longer the photosensitizer is exposed, the greater the number of MB dye molecules that become excited. However, these excited dye molecules then react strongly with any oxygen initially dissolved in the material layer and/or which diffuses into the unsealed layers from the air.^{1,23} The availability of oxygen, which can diffuse into the layer, allows the MB to almost recover to its initial concentration postexposure with only a small amount being bleached, i.e., the differences between the saturated values and the initial concentration A_0 . The larger the number of excited dye molecules, the longer the time required for the dye to recover even if oxygen is available (i.e., the uncover plated case). In Table I, the estimated rates of recovery for each particular exposure are presented. As previously observed,¹ for longer exposure times the estimated recovery rates become slower, i.e., both r_1 and r_2 systematically decrease from Case 1 to Case 4, as more excited dye molecules are created.¹ We also note that as expected, $r_1 > r_2$, because $^1\text{Dye}^*$ has a shorter lifetime than the corresponding $^3\text{Dye}^*$.^{1-7,15}

It is necessary to generate a value of Ψ to be used in the model during the fitting procedures. Assuming that the recovery process has fully taken place postexposure, i.e., when $t = 90$ min. We insert the values for $A_r(t = 90 \text{ min})$ and $A_b(t = 90 \text{ min})$ into Eq. (20), where $A_r(t = 90 \text{ min}) = A_0 - A_b(t = 90 \text{ min}) - A(t_{\text{exp}})$. The corresponding values of Ψ for each exposure, i.e., t_1 to t_4 , are presented in Table I, with the mean square error (MSE) values⁶⁻⁸ achieved for each fit.

D. Recovery process (EB)

Applying the same experimental procedures as for MB, but with $\lambda = 532$ nm, the analogous recovery experiments were performed for EB. The temporal evolution of $A(t)$ (or $[\text{Dye}]$) during and postexposure is presented in Fig. 8(a). For different exposure times, the predictions of $A(t)$, generated using Eq. (5), agree well with the experimental data for both short (i.e., t_1 , t_2 , t_3 , and t_4) and long exposures (i.e., $t_{\text{exp}} = 150$ s). Good agreement between the model and experimental data, both during and postexposure, is again simultaneously observed in Fig. 8(b), the extended version of Fig. 8(a). As can be seen, the longer the EB photosensitizer is initially exposed, the lower the maximum concentration to which it can recover. Fitting the experimental data allows the rates of recovery r_1 and r_2 to be estimated for each case, i.e., t_1 to t_4 . The Ψ values are also calculated in the same manner

TABLE I. Rates of recovery produced by fitting the experimental data of MB.

MB	t_{exp} (s)	$A(t_{\text{exp}})$ (mol/cm^3) ($\times 10^{-6}$)	r_1 (s^{-1}) ($\times 10^{-3}$)	r_2 (s^{-1}) ($\times 10^{-4}$)	Ψ (—)	MSE (—) $\times 10^{-14}$
Case 1	$t_1 = 5$	1.486	3.00	1.01	0.84	1.24
Case 2	$t_2 = 10$	1.120	2.20	0.71	0.86	5.23
Case 3	$t_3 = 20$	0.626	1.30	0.43	0.85	2.20
Case 4	$t_4 = 50$	0.118	0.89	0.30	0.85	6.38

FIG. 8. (Color online) (a) Combination of fits to experimental data of EB photosensitizer concentration during and postexposure for four varying exposure times: $t_1 = 5$ s (solid curve), $t_2 = 10$ s (long dashed curve), $t_3 = 20$ s (dashed curve), and $t_4 = 50$ s (short dashed curve), the full continuous exposure for $t_{\text{exp}} = 150$ s (shorter dashed decaying curve), and the initial stage of postexposure from $t_{\text{off}} = 60$ s. (b) Extended postexposure version of (a) showing the recovery of the EB photosensitizer concentration vs postexposure time off (t_{off}).

as before for MB. These extracted parameters and corresponding MSE values are presented in Table II.

We note that in agreement with the results presented in Ref. 1 for EB (and unlike the MB case, see Table I), the

estimated recovery rates are very similar for the different exposure times. This is assumed to be primarily due to the weak reactivity between the excited EB dye molecules and oxygen.¹ Another possible explanation might be the diffusion of dye molecules in from surrounding unexposed regions. However, in all the experiments discussed (EB and MB), the total layer area is exposed by the illumination beam therefore no dye concentration gradients are expected to be present within the layer. Furthermore, even if this was not the case, it is extremely unlikely that a significant number of the heavy EB dye molecules could diffuse into any substantial exposed area.^{1,2,5}

E. Bleaching process (MB)

In this section, the bleached MB dye concentration as a function of the exposure time, $A_b(t)$ in Eq. (17), is calculated and used to fit the experimental data.

To achieve a physical description of the bleaching process, the recovery process discussed above must first be well understood. As illustrated in Fig. 7(b), the amount of photosensitizer bleached depends on the exposure time. As a result of the bleaching process, 100% recovery cannot be achieved, which means that a certain amount of the dye is unable to return to its ground state. Thus, for the exposure times examined, we can predict that as t_{off} approaches infinity, i.e., once the recovery processes are complete, the dye concentration cannot recover to its initial value A_0 .

The amount of dye bleached is then found for each particular exposure time. The resulting experimental data sets give the bleached photosensitizer concentration as a function of the exposure times, i.e., $5 \text{ s} \leq t_{\text{exp}} \leq 250 \text{ s}$, for a fixed postexposure time off, i.e., $t_{\text{off}} \approx 12$ hours. Once again, an exposure intensity of 4 mW/cm^2 , normally incident on an uncoversplated photopolymer material layer of thickness $d \approx 100 \text{ }\mu\text{m}$, was used. Figure 9 contains the prediction of the model for $A_b(t)$, which was fit to the experimental data.

As discussed in Eq. (17), $A_b(t)$ is the sum of the transparent state dye concentrations, i.e., the bleached Leuco and dihydro forms. Since the initially dissolved inhibitor Z has a relatively low concentration but a very strong reactivity, i.e., $k_z = 3.4 \times 10^7 \text{ cm}^3/\text{mol s}$, the Leuco dye is immediately formed by the rapid reaction of $^3\text{Dye}^*$ and Z during the early stages of exposure, $t \leq t_{\text{Leuco}} \approx 12 \text{ s}$, see Fig. 9. This causes a rapid initial increase in the bleached dye concentration. Only once the inhibitors are consumed can a significant amount of dihydrodye formed. This is the dominant bleaching process

TABLE II. Rates of recovery produced by fitting the experimental data of EB.

EB	t_{exp} (s)	$A(t_{\text{exp}})$ (mol/cm^3) ($\times 10^{-6}$)	r_1 (s^{-1}) ($\times 10^{-3}$)	r_2 (s^{-1}) ($\times 10^{-4}$)	Ψ (-)	MSE (-) ($\times 10^{-14}$)
Case 1	$t_1 = 5$	1.096	1.30	9.00	0.24	1.61
Case 2	$t_2 = 10$	0.894	1.26	8.71	0.34	3.14
Case 3	$t_3 = 20$	0.810	1.28	8.89	0.42	2.89
Case 4	$t_4 = 50$	0.338	1.31	9.06	0.48	6.88

FIG. 9. (Color online) The bleached MB concentration as a function of the exposure time.

which occurs until all the hydrodye radicals, HDye^{*}, have reacted at an estimated rate constant of $k_b = 2.66 \times 10^4 \text{ cm}^3/\text{mol s}$.

As can be observed in Fig. 9 $A_b(t)$ increases with increased exposure. Examining the parameters extracted from the data, a maximum bleached dye concentration of $A_0/6$ tends to provide an asymptotic limit toward which $A_b(t)$ saturates, i.e., $A_b(t \rightarrow \infty) = A_0/6$. This appears to be the case because, as noted, MB strongly reacts with oxygen.^{1,23} Thus more excited MB dye molecules are continually recovering to the ground state following the reaction with the oxygen present (both during exposure and postexposure), than are transformed into the transparent bleached states. In this case, $\Psi = 1 - A_b(t \rightarrow \infty)/A_0 = 5/6$.

F. Bleaching process (EB)

Analyzing the EB recovery process, it can be seen that during exposure the amount of photosensitizer bleached increases, and thus less of the excited dye is available to recover. In the cases examined, more bleaching occurs in the EB than in the MB case. The same experiments were performed with an exposing wavelength of $\lambda = 532 \text{ nm}$. The resulting fit to the experimental data, $A_b(t)$, is shown in Fig. 10. The formation of the EB Leuco dye takes place at a relatively slower inhibition rate constant, $k_z = 1 \times 10^6 \text{ cm}^3/\text{mol s}$, over a longer period, $t_{\text{Leuco}} \approx 24 \text{ s}$, and with a higher concentration eventually being formed than for the equivalent MB case. After t_{Leuco} , the formation of dihydrodye, H₂Dye, begins to dominate the bleaching process, with $A_b(t)$ continuing to increase toward its asymptotic limit A_0 (the initial dye concentration) at an estimated rate constant of $k_b = 2.79$

FIG. 10. (Color online) The bleached EB concentration as a function of the exposure time.

$\times 10^4 \text{ cm}^3/\text{mol s}$. Therefore, in this case, 100% bleaching of the EB dye appears possible, with all recovered dye being eventually bleached if the layer is exposed for a sufficiently long time. Applying our methodology Ψ is found using Eq. (20). In this case $\Psi = 1 - A_b(t \rightarrow \infty)/A_0 \approx 0$, i.e., the bleached EB dye concentration: $A_b(t \rightarrow \infty) \rightarrow A_0$. This clearly indicates that Ψ , although assumed constant within this paper, is a temporally varying parameter, which depends on the amount of ground state dye available at any given time.

IV. DISCUSSIONS AND CONCLUSIONS

In this paper, the photochemical reactions, which occur during the photoinitiation mechanisms in a simple PVA/AA based photopolymer material have been analyzed in detail. These effects were analysed both during and postexposure. The concentration of each photochemical species is described as being governed by the coupled rate equations derived from the corresponding chemical reactions, i.e., Eqs. (5)–(8), (12), (15), (14), (17), and (19). The rates of the photochemical reactions of each species have been estimated for equivalent PVA/AA layers containing identical molarities of the MB and EB photosensitizers, by fitting the experimental data sets describing transmittance, photosensitizer recovery, and bleaching, see Tables I–III.

Several significant advances on the existing models in the literature have been indicated.

- (1) It was previously assumed that the main process responsible for the consumption of photosensitizer was by absorption.^{1–8,17,19} This was described^{1,2} by the quantum yield, ϕ , i.e., a fraction of the absorbed intensity $I_a(t)$ for

TABLE III. Parameter values from fits to experimental data for MB and EB.

Dye	k_a ($\text{cm}^3/\text{mol s}$) ($\times 10^4$)	k_d ($\text{cm}^3/\text{mol s}$) ($\times 10^2$)	k_z ($\text{cm}^3/\text{mol s}$) ($\times 10^7$)	k_b ($\text{cm}^3/\text{mol s}$) ($\times 10^4$)	Ψ (–)	MSE (–) ($\times 10^{-9}$)
MB	3.00	2.82	3.40	2.66	5/6	3.08
EB	3.50	1.06	0.10	2.79	0	2.62

a layer thickness d that causes the total removal of the ground state dye molecules.^{1,2} This approximation is now eliminated. The photon absorption is modeled by assuming the incident light interacts with the available photosensitizer concentration in its ground state, with a physical rate constant of absorption k_a .

- (2) Likewise, the rate of generation of primary radicals, $ED^{\cdot}$, was previously described using the following equation: $R_i = 2\Phi I_a(t)$, where Φ is the number of primary radicals initiated per photon absorbed and the factor of 2 indicates that radicals are created in pairs.^{2-8,16} However, in this paper, this process is more accurately described using Eq. (14), which includes all the major reactions involved in the generation and removal of primary radicals.
- (3) The previous models^{1,2} assumed that recovery was negligible during short exposure times and that a linear relationship existed between the rate of bleaching and the incident intensity. Making these assumptions two separate limiting regimes, i.e., during and postexposure, were identified and two corresponding descriptions of the time evolutions of recovery and bleaching derived.¹ In this paper, based on the proposed recovery mechanisms, $A_r(t)$ is calculated using Eq. (19). Applying this model, satisfactory fits to the experimental data have been found and the two rates r_1 and r_2 have been estimated. Moreover, the model presented in this paper enables a continuous fit of the data, during and postexposure, see Figs. 7(a), 7(b), 8(a), and 8(b).
- (4) $A_b(t)$ is calculated using Eq. (17) by combining the Leuco and dihydrodye concentrations. The fits to the experimental data in Figs. 9 and 10 are significantly improved from our previous work, i.e., see Figs. 6 and 9 in Ref. 1. This improvement is particularly obvious during the initial stages of the bleaching process.
- (5) Finally, the inhibition effects are now more physically described.

While significant progress has been made in the work presented here,^{1-8,11,13,14} much remains to be done. Most obviously, the process of intersystem crossing must be more physically modeled and the fraction parameter Ψ must be eliminated. An accurate description of photoinitiation must be incorporated into the NPDD model,^{3,4,7,8,24-27} allowing a more complete modeling of free radical photopolymerization. Such a model can then be applied to the study of photopolymer based holographic data storage^{26,27} and hybrid optoelectronics fabrication.^{28,29}

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