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Transient products in the photoreduction of benzophenone derivatives in poly(ethylene-vinyl alcohol) film

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Abstract

The formation, stability, and reactivity with oxygen of the so-called light-absorbing transient (LAT) photoproducts formed on photoreduction of benzophenone and several benzophenone derivatives in poly(ethylene-vinyl alcohol) (EVOH) films were investigated. The maximum total yield of LAT photoproducts on photoreduction of benzophenone was estimated to be approximately 50%, which was found to comprise around 75% of the *para*-LAT isomer with the remainder being attributed to the *ortho*-LAT isomer. The concentrations of these LAT isomers were found to decay over a period of weeks at room temperature in the absence of oxygen, with the decay of the *para*-LAT isomer being substantially slower than the *ortho*-LAT isomer. Furthermore, the decay rate of the *para*-LAT isomer was found to increase markedly in the presence of oxygen. Mechanisms for the decay of the LAT isomers that are consistent with available data are postulated. The presence of alkyl, alkoxy, or aryloxy moieties on the phenyl rings of benzophenone appears to have little effect on the efficiency of formation, stability, and reactivity with oxygen of the LAT photoproducts in EVOH films, for the benzophenone derivatives studied in this work.

Keywords: Benzophenone derivatives; Photoreduction; Light-absorbing transient; Poly(ethylene-vinyl alcohol)

1. Introduction

The photoreduction of benzophenone in solution is one of the most extensively investigated photochemical reactions, having been studied using a wide range of reductants, solvent systems, reactant concentrations, and irradiation conditions [1–13]. It is now well established that exposing de-oxygenated solutions containing benzophenone and a suitable reductant, such as 2-propanol, to ultraviolet (UV) light results in the reduction of electronically excited benzophenone molecules to form hydroxydiphenylmethyl radicals (also referred to as diphenylketyl radicals), and the concomitant oxidation of the reductant (to form 2-hydroxy-2-propyl radicals when 2-propanol is the reductant). As illustrated in Scheme 1, the resulting hydroxydiphenylmethyl radicals (**1**) can then undergo several possible subsequent competing reactions, including hydrogen abstraction to re-form benzophenone, coupling with another hydroxydiphenylmethyl radical to form benzopinacol (**2**), a second hydrogen abstraction by the hydroxydiphenylmethyl radical to form benzhydrol (**3**), or coupling with an hydroxyalkyl radical to form an asymmetrical pinacol (**4**).

It is also known that the photoreduction of benzophenone in hydrogen-donating solvents usually results in the formation of a transient photoproduct displaying an absorption maximum at around 330 nm. This meta-stable photoproduct decays over a period of days [8,12] when stored at room temperature in the absence of oxygen and so is usually referred to as the “light-absorbing transient” (LAT). A range of possible chemical structures for this oxygen-sensitive LAT product have been proposed, and although definitive elucidation of its structure has proved elusive, the evidence available is consistent with the LAT being the product of the coupling of an hydroxyalkyl radical at the *para* (**5**) or *ortho* (**6**) position of the hydroxydiphenylmethyl radical.

Poly(ethylene-vinyl alcohol) (EVOH) is used widely as a polymeric oxygen-barrier layer in materials used for packaging

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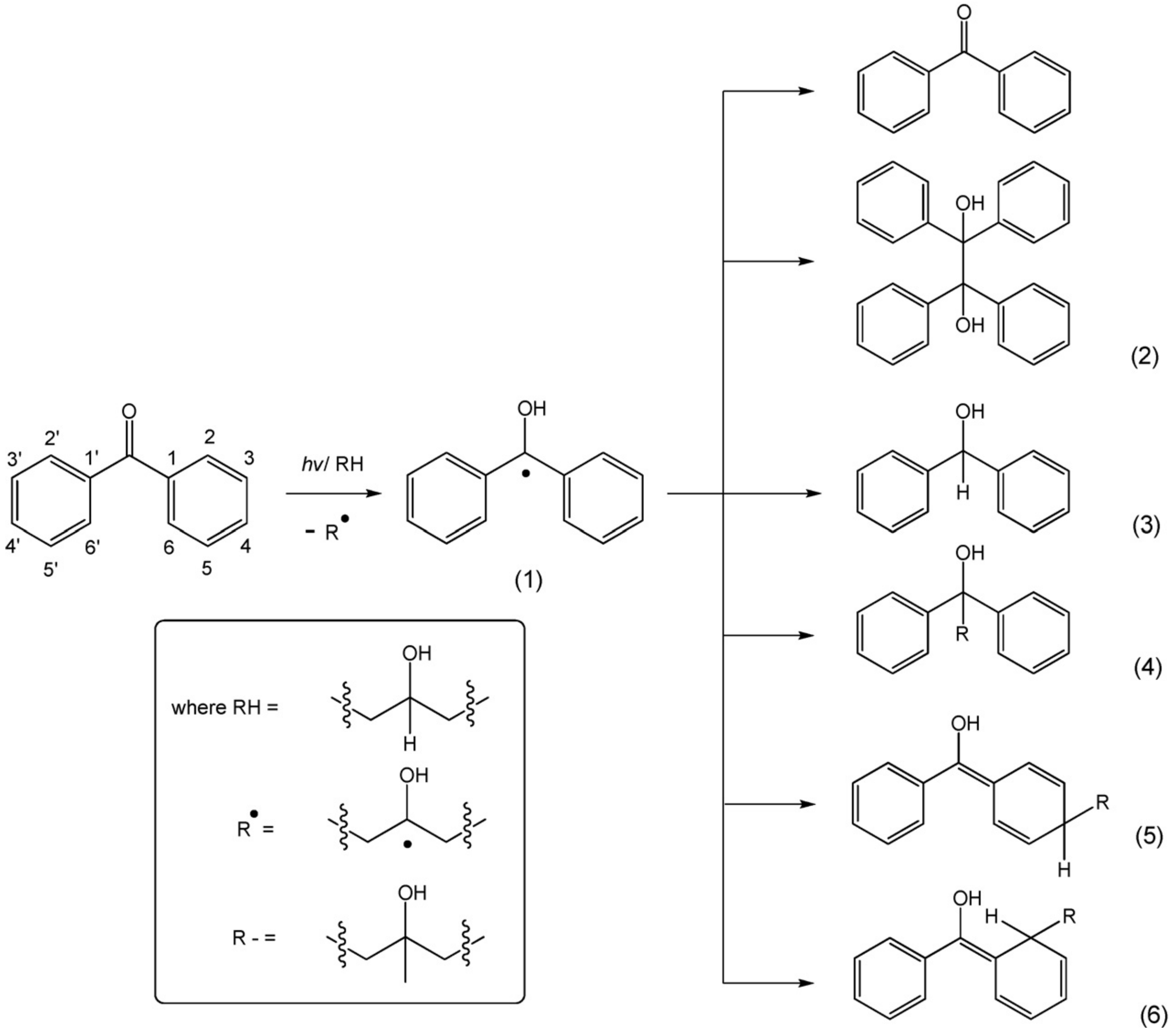


Scheme 1. Proposed fate of the hydroxydiphenyl radical (**1**) on photoreduction of benzophenone in EVOH film in the absence of oxygen.

oxygen sensitive products such as foods and pharmaceuticals. One method of enhancing the oxygen barrier performance of EVOH and other polymeric packaging materials is to incorporate into these materials additives that are capable of reacting irreversibly with oxygen permeating through the polymer matrix from the external atmosphere, resulting in materials that are often referred to as "oxygen scavengers" [14]. Of particular interest are oxygen-scavenging polymeric materials that can be activated at a pre-determined point in time, for example by a brief exposure of the material to UV light, in order to minimize any loss in the oxygen-scavenging material's capacity to react with oxygen prior to the time of filling the package. The oxygen sensitivity of the LAT photoproducts produced on photoreduction of benzophenone and its derivatives makes these compounds of potential interest for use in this application.

Although detailed investigations of LAT formation on the photoreduction of benzophenone in fluid solutions have been conducted, relatively limited information is available about LAT formation on photoreduction of benzophenone in organized media such as micellar solutions [15] and cyclodextrins [16], or in rigid polymeric materials [17–20]. The aim of the present work was to investigate the formation, stability, and reactivity with oxygen of the LAT photoproducts formed on photoreduction of benzophenone in EVOH films, where the vinyl alcohol groups of EVOH represent a polymeric equivalent of 2-propanol and so are expected to be capable of acting as effective hydrogen-donating groups for the photoreduction of benzophenone. The effect of incorporation of electron-donating substituents onto the phenyl groups of benzophenone on the efficiency of formation and stability of the LAT photoproducts in EVOH was also investigated.

2. Experimental details

Poly(ethylene-vinyl alcohol) (EVOH) comprising 32 mol% ethylene (Soarnol® DC3212) was obtained from Nippon Gohsei. Benzophenone, 2-methylbenzophenone (2-MeBP), 3-methylbenzophenone (3-MeBP), 4-methylbenzophenone (4-MeBP), 4,4′-dimethoxybenzophenone (4,4-di-MeOBP), and all other reagents were obtained from Aldrich, and were used as received unless stated otherwise. 3-Methoxybenzophenone (3-MeOBP), 4-methoxybenzophenone (4-MeOBP), and 2,4-dimethoxybenzophenone (2,4-di-MeOBP) were prepared from 3-hydroxybenzophenone, 4-hydroxybenzophenone, and 2-hydroxy-4-methoxy-benzophenone, respectively, using an adaptation of a method described by Fromantin [21] for the *O*-alkylation of 3-hydroxybenzophenone. All of the methoxylated products were isolated by flash column chromatography using 230–400 Mesh silica gel (BDH) and an isocratic elution (20% ethyl acetate (BDH-AnalAR)/petroleum ether 60–80 °C (BDH-AnalAR)).

2-Benzyloxy-4-methoxy-benzophenone (2-BzO-4-MeOBP) and 2,2′-dibenzyloxy-4-methoxybenzophenone (2,2′-di-BzO-4-MeOBP) were prepared from 2-hydroxy-4-methoxybenzophenone and 2,2′-dihydroxy-4-methoxybenzophenone, respectively, using a procedure adapted from that described in the literature for the preparation of 2,2′-dibenzyloxybenzophenone [22]. The benzyloxylated products were purified by re-crystallisation from ethanol.

The structures of the benzophenone derivatives synthesized in the present work were confirmed using ^{1}H NMR spectroscopy (200 MHz; Bruker AMX spectrometer). 4-Methoxybenzophenone (200 MHz, acetone-d_6): δ 7.48–7.85 (7H, m), 7.02–7.12 (2H, m) and 3.92 (3H, s) ppm; 3-methoxybenzophenone (acetone-d_6): δ 7.74–7.82 (2H, m), 7.4–7.7 (4H, m), 7.15–7.35 (3H, m) and 3.88 (3H, s) ppm; 2,4-dimethoxybenzophenone ($CDCl_3$): δ 7.74–7.79 (2H, m), 7.26–7.52 (4H, m), 6.50–6.57 (2H, m), 3.86 (3H, s) and 3.69 (3H, s) ppm; 2-benzyloxy-4-methoxybenzophenone ($CDCl_3$): δ 7.74–7.82 (2H, m), 7.3–7.6 (4H, m), 7.15–7.22 (3H, m), 6.90–7.00 (2H, m), 6.55–6.63 (2H, m), 4.97 (2H, s) and 3.85 (3H, s) ppm; 2,2′-dibenzyloxy-4-methoxybenzophenone ($CDCl_3$): δ 7.55–7.63 (1H, m), 7.35–7.50 (2H, m), 7.15–7.24 (6H, m), 6.90–7.10 (6H, m), 6.60–6.70 (2H, m), 4.95 (4H, s) and 3.88 (3H, s) ppm.

EVOH films containing approximately 2% (w/w) of the benzophenone derivatives and having thicknesses in the range 40–60 μm were prepared by melt-compression molding using an hydraulic press constructed in-house. Each film was prepared using three melt-compression cycles, comprising a first cycle in which the solid benzophenone compound was melted between two pieces of previously melt-compressed EVOH (1 g), and then two subsequent cycles in which the film was cut into pieces and then melt-compressed. All melt-compression was conducted at 200 °C, and there was no evidence of residual undissolved matter in the final films.

UV exposure of the films was performed using a commercial bench-top high-power UV-curing system (FusionUV Systems; F300) fitted with a ‘D’ bulb having a spectral output centered at a wavelength of around 365 nm. Each film was sandwiched between two layers of transparent polypropylene film (or EVOH-based transparent oxygen barrier film for samples subsequently stored in vacuum) and vacuum-sealed to form a flat package containing essentially no headspace prior to UV irradiation. The film samples were placed on the conveyor belt, and passed under the lamp at a speed of 10.5 m/min. Unless otherwise stated, each side of the EVOH films was passed under the UV lamp the same number of times, until there was no further measurable change in the UV–vis absorption spectrum of the film. The EVOH films were removed from the polypropylene packages after UV exposure. The UV dose received by the EVOH films in a single pass under the focussed output of the UV curing lamp was measured to be approximately 0.8 J/cm^2 using the UV-A bandwidth of a UV Power Puck® (EIT Inc.). Since the width of the focussed line at the sample was ∼3 cm, it is estimated that the average irradiance at the sample was approximately 5 W/cm^2.

Film samples for storage in vacuum were transferred into a foil-lined multilayer bag immediately after UV exposure, and this bag was then vacuum-sealed to form a flat package containing essentially no headspace. This foil-lined pouch prevented ingress of oxygen into the inside of the pouch. The EVOH film samples were removed from the foil-lined pouch for UV–vis spectral measurements, and were then immediately re-packed under vacuum into the foil-lined pouch. All UV–vis absorption spectra were recorded using a Cary 3E spectrophotometer.

The EVOH film samples used to measure efficiency of reaction with oxygen after UV exposure were removed from the polypropylene package and then transferred immediately into a foil-lined multilayer bag together with 1 ml of water to increase the rate of permeation of oxygen into the EVOH, and this bag was then vacuum-sealed to form a flat package containing essentially no headspace. A known volume of air was then injected into the foil-lined pouches, and the pouches were stored at 40 °C. The oxygen content of the headspace inside the pouch was measured periodically by inserting a syringe needle through a silicon septum to extract 0.3 ml of the headspace gas, and then analysing the oxygen content in the extracted gas using a gas chromatograph (Shimadzu, GC-8A).

3. Results and discussion

3.1. Transient product formation on benzophenone photoreduction

The change in the absorption spectrum of benzophenone dissolved in EVOH film on UV exposure is shown in Fig. 1. The

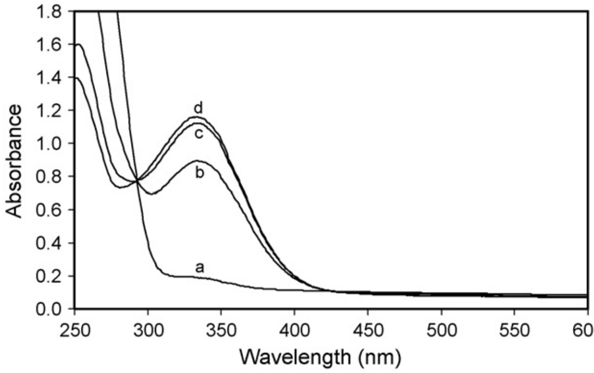


Fig. 1. Change in the absorption spectrum of an EVOH film containing benzophenone, as a function of UV exposure: (a) prior to UV exposure, (b) 1 pass/side, (c) 2 passes/side, (d) 3 passes/side.

decrease in the benzophenone absorption band centred at a wavelength of around 250 nm on exposure of the film to UV light is accompanied by a concomitant appearance of an absorption band having a maximum absorbance at around 330 nm. This new absorption band decays with time, even in the absence of oxygen, and is attributed to absorbance by the meta-stable reduced forms of benzophenone known as the light-absorbing transient (LAT) photoproducts.

Demeter and Bérces proposed [12] that, on the basis of the results of spectral and kinetic analysis of the photoreduction of benzophenone in fluid solution, the *para*-coupled isomeric reaction product (**5**) dominates the initial LAT photoproduct population, with the *ortho*-coupled isomer (**6**) being present as only a minor component. The clear isosbestic point observed at a wavelength of around 290 nm in the spectra shown in Fig. 1 indicates that the sum of the extinction coefficients at this wavelength of the LAT photoproducts formed on photoreduction of benzophenone in EVOH film are the same as that of benzophenone.

3.2. *Effect of substituent on transient photoproduct formation*

Benzophenone derivatives containing substituents capable of increasing the stability of the resonance forms of (**1**) having the radical center located at the 2-, 2′-, 4-, or 4′- positions, relative to other possible resonance forms, might be expected to contribute to an enhancement in the efficiency of LAT photoproduct formation. For example, the bonding of electron-donating substituents, such as alkyl and alkoxy groups, to carbon radicals is well known to increase the stability of the radicals. Furthermore, the presence of these substituents appears to have little effect on the photochemical properties of these benzophenone derivatives compared with benzophenone, with the lowest excited triplet-state retaining a predominantly nπ* nature [23] and the formation of the hydroxydiphenylmethyl radicals of the benzophenone derivatives being readily detected [24].

3.2.1. *Benzophenone derivatives containing one alkyl or alkoxy group*

The absorption spectra of EVOH films containing benzophenone or various mono-substituted derivatives containing one alkyl or alkoxy substituent were measured before and after UV exposure, and representative spectra of benzophenone, 4-MeBP and 4-MeOBP in EVOH film are shown in Fig. 2.

The absorption spectra of 3-MeBP (not shown) and 4-MeBP before and after UV exposure were found to be essentially identical to those of benzophenone, with clear spectral evidence for the formation of the LAT photoproducts after UV exposure. This result suggests that alkyl substitution in these positions has little effect on the yield of LAT photoproduct formation, compared with benzophenone. The absorption spectrum of 2-MeBP (not shown) indicated a complete absence of LAT photoproduct formation on UV exposure, which is consistent with reports [25–27] that formation of the hydroxydiphenylmethyl radical from this molecule is almost completely suppressed by the highly efficient excited-state intra-molecular hydrogen abstraction from the *ortho*-methyl group yielding the corresponding enol tautomer.

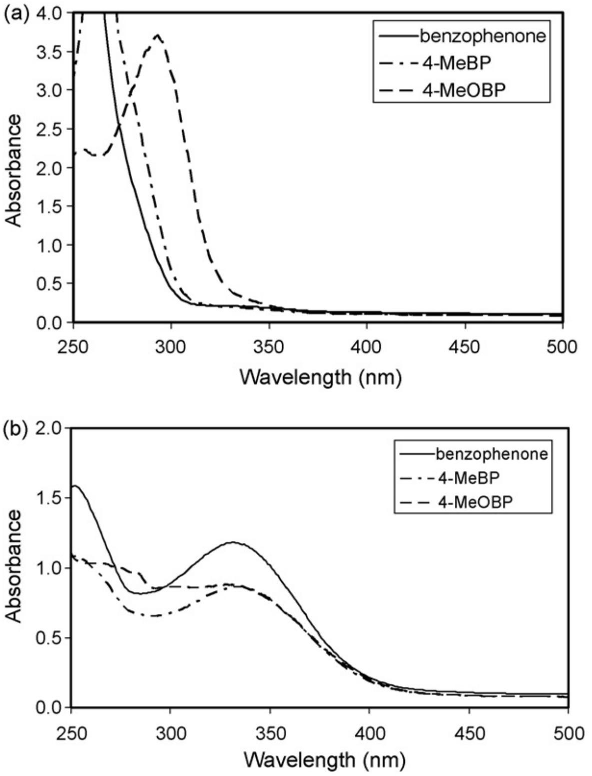


Fig. 2. Absorption spectra of EVOH films containing benzophenone derivatives: (a) prior to UV exposure, (b) after UV exposure (3 passes/side).

As shown in Fig. 2(a), the symmetry allowed absorption band of 4-MeOBP is substantially red-shifted compared with benzophenone and its mono-substituted methyl derivatives. The absorption spectra of the 3-MeOBP before and after UV exposure (not shown) are essentially identical to that of 4-MeOBP, indicating that the photoreduction mechanism for these compounds is independent of position of substitution. Although the shape of the absorption spectrum of 3-MeOBP and 4-MeOBP after UV exposure differ somewhat from that of 3-MeBP and 4-MeBP, the similarity in spectral position and intensity is sufficiently strong to suggest similar efficiencies of LAT photoproduct formation for these mono-substituted benzophenone derivatives.

3.2.2. *Benzophenone derivatives containing two or more alkoxy or aryloxy groups*

The effect of substitution of benzophenone with multiple alkoxy or aryloxy groups on the efficiency of LAT formation was also investigated. The absorption spectra for these compounds in EVOH films before and after UV exposure are shown in Fig. 3(a) and (b), respectively. It can be seen from these spectra that benzophenone derivatives substituted with multiple alkoxy or aryloxy groups display a more structured absorbance in the 290–320 nm wavelength range than benzophenone and the mono-substituted benzophenone derivatives described above. As was the case for the other benzophenone derivatives investigated in this work, the absorption spectra measured after UV

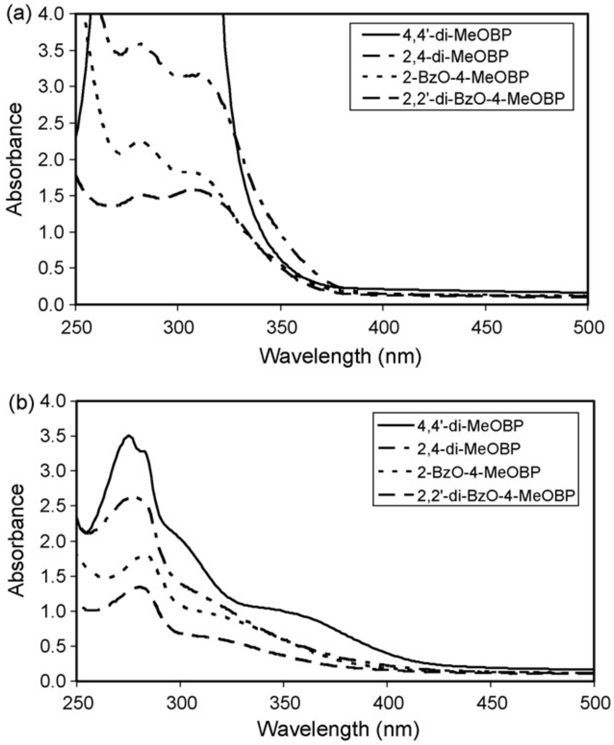


Fig. 3. Absorption spectra of EVOH films containing benzophenone derivatives: (a) prior to UV exposure, (b) after UV exposure. 4,4′-Di-MeOBP (2.6%, w/w), 3 passes/side; 2,4-di-MeOBP (2.6%, w/w), 8 passes/side; 2-BzO-4-MeOBP (2.0%, w/w), 1 pass/side; 2,2′-di-BzO-4-MeOBP (1.9%, w/w), 1 pass/side.

exposure of EVOH films containing the substituted benzophenone derivatives comprising multiple alkoxy or aryloxy groups show the presence of a new absorption band centred in the wavelength range 330–350 nm (Fig. 3(b)), suggesting the formation of LAT photoproducts having the same general structure as the other benzophenone derivatives investigated in this work. However, no compelling evidence was found for any substantial enhancement in the yield of LAT photoproduct formation for any of the substituted benzophenone derivatives investigated in this work compared with benzophenone.

3.3. Decay of transient photoproducts in the absence of oxygen

As shown in Fig. 4, on storage in the dark and in the absence of oxygen, the absorption band associated with the LAT photoproducts slowly decays. The change in absorbance at ∼330 nm with time shown in Fig. 5 indicates that the decay of this absorption band in the absence of oxygen (i.e. vacuum) comprises a rapid component and a slower component. This bi-component decay behaviour has also been reported by others [8,12] and has been used as supporting evidence for the proposed formation of the two abovementioned LAT isomers.

Therefore, the decay of the total absorbance measured at 330 nm, A, was analysed according to the bi-exponential function shown in Eq. (1), where k_1 and k_2 represent the rate constants associated with the two decay processes, and the pre-exponential factors, A_1 and A_2, represent the initial absorbance of each of the two decaying components. The parameter BL is the baseline residual absorbance after decay of the photoproducts, and its value was fixed at a value of 0.20 which is the absorbance at 330 nm immediately prior to UV exposure.

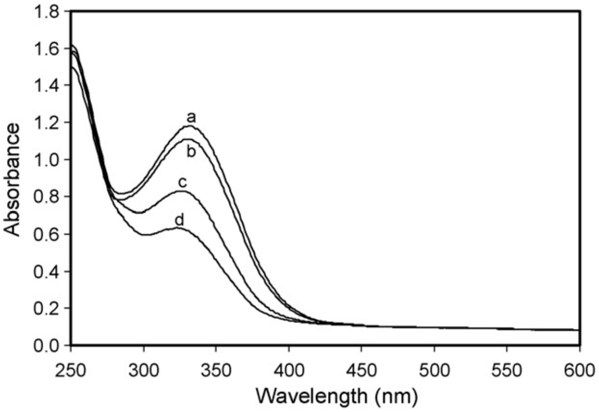


Fig. 4. Change in absorption spectrum during storage in vacuum of EVOH film containing benzophenone, after UV exposure (3 passes/side): (a) 0 h (immediately after UV exposure), (b) 1.2 h, (c) 120 h and (d) 264 h.

$$A(t) = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) + \mathrm{BL} \qquad (1)$$

The best-fit curve obtained from analysis using this equation is shown in Fig. 5, and the associated values for the adjustable parameters were found to be $A_1 = 0.193$, $k_1 = 0.385\,\mathrm{h}^{-1}$, $A_2 = 0.783$, and $k_2 = 2.3 \times 10^{-3}\,\mathrm{h}^{-1}$.

From a comparison of the absorption spectrum of the LAT photoproduct with model compounds, Demeter and Bérces [12] proposed that the LAT population formed on photoreduction of benzophenone in a solution of 2-propanol/acetonitrile is comprised predominantly of the *para*-LAT isomer. These authors also reported that the extinction coefficients of the *ortho-* and *para*-LAT isomers at 330 nm are very similar in magnitude, and so the pre-exponential factors obtained in the present work can be used to estimate the relative concentrations of each isomeric form of the LAT. The result of this calculation indicates that the

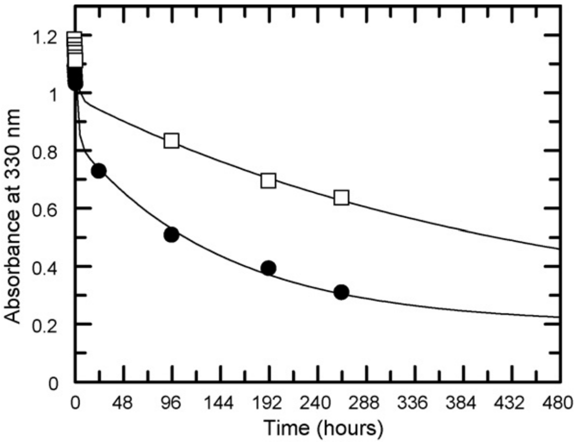


Fig. 5. Change in absorbance by LAT photoproduct on photoreduction of benzophenone in EVOH films, and storage in vacuum (□) or air (●) at 25 °C. The solid lines are the best-fit bi-exponential curves calculated using Eq. (1) (vacuum) or Eq. (2) (air).

LAT population immediately after UV exposure of the EVOH film comprises around 80% of the long-lived component. Therefore, we attribute the longer-lived LAT photoproduct to the *para* isomer, and the proportion of the initial LAT photoproduct comprising the *para*-LAT isomer found in the present work is in very good agreement with the range reported by Demeter and Bérces of 75–85% [11,12].

The value for the decay rate of the longer-lived *para*-LAT isomer, k_2, obtained in the present work of $2.3 \times 10^{-3}\ \mathrm{h}^{-1}$ is in excellent agreement with the reported value of $2.4 \times 10^{-3}\ \mathrm{h}^{-1}$ ($6.7 \times 10^{-7}\ \mathrm{s}^{-1}$) in 2-propanol/acetonitrile [12], although a much faster decay rate in isooctane of $2.6 \times 10^{-2}\ \mathrm{h}^{-1}$ has been reported [8]. Demeter and Bérces [12] found that, in contrast to the decay of the *para* isomer, the decay rate of the *ortho* isomer is dependent on the concentration of benzophenone. Using the parameters reported by Demeter and Bérces [12] for the decay of the *ortho* isomer in 2-propanol/acetonitrile, the decay rate of the *ortho* isomer at the benzophenone concentrations in the EVOH films ($\sim$0.1 mol dm^{-3}) is calculated to be about 1.1 h^{-1}, which is substantially faster than the value for k_1 of 0.385 h^{-1} obtained in the present work. Demeter and Bérces [12] speculated that the decay of the *ortho* isomer proceeds *via* an activated complex involving benzophenone, which is unable to form in the case of the *para* isomer for steric reasons. If this is the case, then the slower decay of the *ortho*-LAT isomer found in the present work could be attributed to the rate of formation of this type of complex being substantially slower in the solid EVOH matrix than in fluid solutions.

The absorbance decay results shown in Fig. 6 for monosubstituted benzophenone derivatives indicate that the presence of the substituent appears to have little impact on the anaerobic stability of the LAT photoproducts formed on photoreduction of benzophenone.

3.4. Decay of transient photoproducts in the presence of oxygen

It has been reported [1,8] that the decay of the LAT photoproducts is accelerated on exposure to oxygen. As seen from the spectra shown in Fig. 7, and a comparison of the rate of decay of the LAT photoproducts in the EVOH film exposed to air or vacuum shown in Fig. 5, the rate of decay of the LAT photoproducts in EVOH is accelerated substantially in the presence of oxygen.

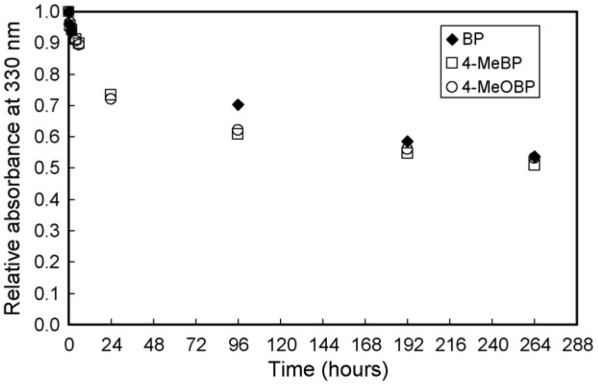


Fig. 6. Relative stability of the LAT photoproducts after photoreduction of benzophenone derivatives in EVOH film, on storage in vacuum at 25 °C.

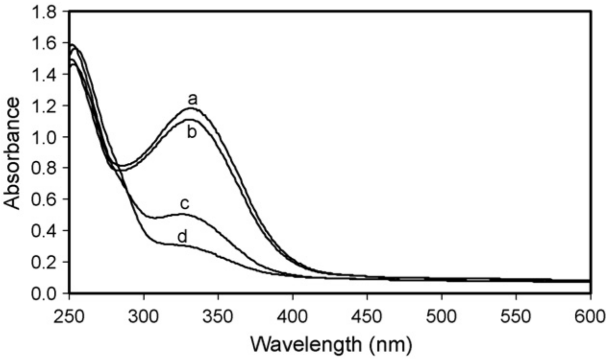


Fig. 7. Change in absorption spectrum of EVOH film containing benzophenone as a function of time after UV exposure (3 passes/side) during storage in air for: (a) 0 h (immediately after UV exposure), (b) 1.2 h, (c) 120 h and (d) 288 h.

The decay of absorbance at 330 nm shown in Fig. 7 was analysed according to the bi-exponential function given by Eq. (2). In this analysis, it was assumed that the two decay processes found to operate in the absence of oxygen also operate in the presence of oxygen, and that the new decay pathway involving reaction of the *para*-LAT photoproduct with oxygen is described by the pseudo first-order rate constant k_3. Therefore, in this analysis, the values of the two decay constants in Eq. (2), k_1 and k_2, were fixed at the abovementioned values of 0.385 h^{-1} and $2.3 \times 10^{-3}\ \mathrm{h}^{-1}$, respectively.

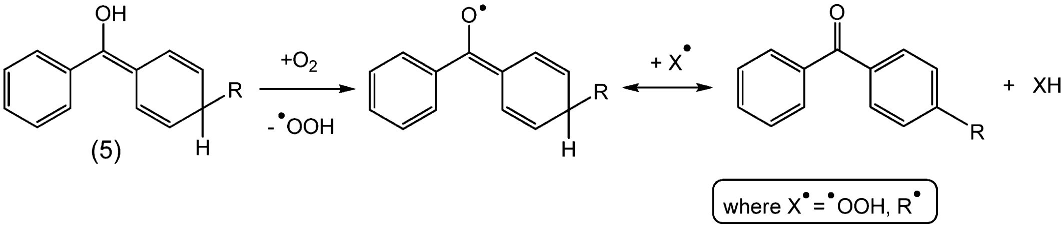
$$A(t) = A_1 \exp(-k_1 t) + A_2 \exp[-(k_2 + k_3)t] + \mathrm{BL} \qquad (2)$$

The best-fit curve obtained from analysis using this equation is shown in Fig. 5, and the associated values for the adjustable parameters were found to be $A_1 = 0.276$, $A_2 = 0.630$, with the pseudo first-order decay constant, k_3, associated with the reaction of the *para*-LAT isomer with oxygen, having a value of $4.5 \times 10^{-3}\ \mathrm{h}^{-1}$.

Assuming that extinction coefficients at 330 nm of the *ortho*- and *para*-LAT isomers are the same, the results of this analysis indicate that the initial LAT population comprises around 70% of the longer-lived *para* isomer, which is in satisfactory agreement with the value of 80% mentioned above for the reaction in the absence of oxygen. Therefore, we conclude that the proportion of *para* isomer in the initial LAT population is in the vicinity of 75%. Furthermore, the magnitude of the rate constant associated with the decay of the *para*-LAT isomer *via* reaction with oxygen, k_3, is almost double that of the decay process in vacuum, k_2, which indicates that approximately 66% of the initially formed *para*-LAT isomers decay *via* reaction with oxygen on exposure of the EVOH film to air immediately after UV exposure.

3.5. Transient photoproduct yields

The number of oxygen molecules that react with an EVOH film containing benzophenone after UV exposure can be used to determine the efficiency of conversion of photoreduced benzophenone into the LAT isomers, assuming that the extent of



Scheme 2. Proposed mechanism for the decay of the *para*-LAT isomer in EVOH film in the presence of oxygen.

reaction of the *ortho*-LAT isomer with oxygen is negligibly small. The efficiency of reaction with oxygen of an EVOH film containing benzophenone after UV exposure is defined as the number of oxygen molecules consumed through reaction with the EVOH film after UV exposure divided by the number of benzophenone molecules present in the film prior to UV exposure. According to the proposed reaction mechanisms shown in Schemes 1 and 2, this reaction efficiency can be used to estimate the efficiency of conversion of benzophenone to yield the oxygen-sensitive *para*-LAT isomer on UV exposure.

As seen in Fig. 8, the efficiency of reaction with oxygen of EVOH film containing benzophenone was found to be about 25%. Since, as mentioned above, 66% of the *para*-LAT isomers decay *via* reaction with oxygen, the initial yield of *para*-LAT isomer formed on photoreduction of benzophenone in EVOH film is estimated to be approximately 40%. Furthermore, since the *para* isomer represents around 75% of the total LAT population initially formed on photoreduction of benzophenone in EVOH film, it is estimated that the total yield of LAT photoproduct is approximately 50%. The films were exposed to a dose of UV light just sufficient to maximize the conversion of benzophenone to LAT photoproduct, as judged by the absorbance peak at around 330 nm, so it is concluded that, for the experimental conditions used in the present work, this value of around 50% represents the maximum possible yield of LAT photoproduct from photoreduction of benzophenone in EVOH film.

The quantum efficiency for LAT photoproduct formation on the photoreduction of benzophenone by 2-propanol in acetonitrile is reported to be in the range 10–20% (depending on benzophenone concentration and light intensity) [11,13]. The quantum efficiencies for the formation of the other likely major photoproducts, namely benzopinacol (**2**), benzhydrol (**3**), and the mixed pinacol (**4**), are also dependent on benzophenone concentration and light intensity, with reported values being 20–50, 2.4, and 9%, respectively [11]. Therefore, assuming that the quantum efficiencies for the system studied in the present work are similar to those reported for the photoreduction of benzophenone by 2-propanol in acetonitrile solution, the probability of each electronically excited benzophenone molecule yielding a photoproduct is estimated to be approximately 75% (for the benzophenone concentrations in the EVOH films used in the present work). Assuming a quantum efficiency for LAT formation of 15%, it is estimated that the maximum yield of LAT photoproducts on complete consumption of benzophenone through photoreduction would be around 20%, which is substantially smaller than the value of approximately 50% found in the present work.

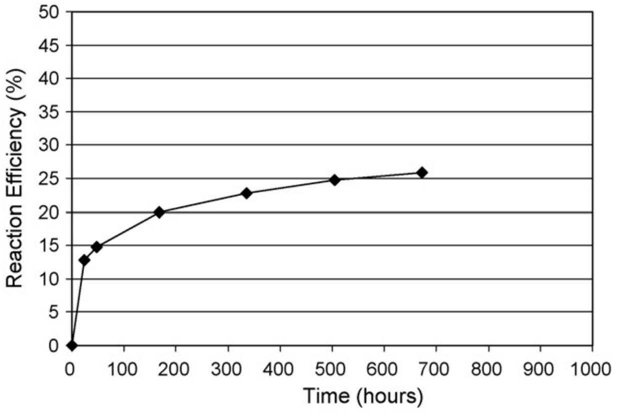


Fig. 8. Efficiency of reaction with oxygen of an EVOH film containing benzophenone, after UV exposure. Film stored in air at 40 °C.

Since the extent of benzopinacol (**2**) formation will be strongly dependent on the rate of diffusion of two hydroxydiphenylmethyl radicals to sufficiently close proximity for the coupling reaction to occur, it is likely that the probability of this reaction will be substantially lower in the glassy EVOH polymer matrix used in this work ($T_g = 61\,°C$) than in fluid solution, and that the predominant photoproducts will, therefore, be those arising from the reaction between geminate pairs of hydroxydiphenylmethyl radicals and hydroxyalkyl radicals (i.e. benzhydrol (**3**), mixed pinacol (**4**), LAT (**5**,**6**)). In this case, where the quantum efficiency of benzopinacol formation is assumed to be negligibly small, the maximum yield of LAT photoproducts on complete consumption of benzophenone through photoreduction estimated using the reported quantum efficiencies for the cross-coupling reactions is found to be in the range 50–60%, which is consistent with the value found in the present work.

Adam et al. reported [28] a significant increase in the yield of LAT photoproduct for the photoreduction of benzophenone in ethanol using the so-called laser jet technique. These authors reported that the spin density distribution of the first electronically excited state of the hydroxydiphenylmethyl radical is substantially shifted towards the carbon atom in the *para* position, and therefore proposed that sequential absorption of two photons to produce electronically excited hydroxydiphenylmethyl radicals was responsible for the increased yield of LAT photoproduct. However, any contribution of this type of sequential bi-photonic excitation process to the relatively high yield of

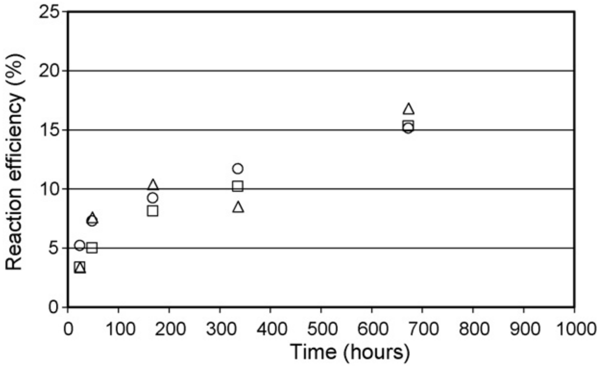


Fig. 9. Efficiency of reaction with oxygen of EVOH films containing benzophenone derivatives, after UV exposure. (○) 2,4-Di-MeOBP, (△) 2,2′,4-tri-MeOBP, (□) 4,4′-di-MeOBP. Films stored in air at 40 °C.

LAT photoproduct obtained in the present work is expected to be minimal given the comparatively low irradiance from the UV curing lamp.

The oxygen reaction efficiencies of EVOH films containing a selection of the benzophenone derivatives studied in this work are shown in Fig. 9, and are similar to that for benzophenone in an EVOH film. Since, as shown above, substitution of benzophenone with electron-donating groups such as alkyl and alkoxy groups appears to have little effect on the yield or anaerobic decay kinetics of the LAT photoproducts, the similarity of the oxygen reaction efficiencies implies that the yields of the LAT isomers on photoreduction of these benzophenone derivatives in EVOH film are similar to those for benzophenone.

3.6. Decay mechanism of transient photoproduct

The absorption spectrum of *para*-LAT reported by Demeter and Bérces [29] shows a close resemblance to the absorption spectrum of photoreduced benzophenone in EVOH (Fig. 1(d)). These authors also reported [12] that the extinction coefficient of the *para*-LAT at 317 nm is approximately 2.8×10^4 dm^3 mol^{-1} cm^{-1}. Since the absorbance by the *para*-LAT isomer at around 250 nm is similar to that at 317 nm [29], the extinction coefficient of *para*-LAT at the absorption maximum centered near 250 nm must also be approximately 2.8×10^4 dm^3 mol^{-1} cm^{-1}. This is somewhat larger than the extinction coefficient of benzophenone at the maximum of its absorption band centered at around 250 nm, which is reported to be approximately 2.2×10^4 dm^3 mol^{-1} cm^{-1} [30].

Although the products formed on decay of the LAT isomers in the absence of oxygen have not been identified unequivocally, if benzophenone (or a benzophenone derivative containing an alkyl substituent, which has absorbance properties similar to that of benzophenone) is the major product of the decay of *para*-LAT in the absence of oxygen, then decay of the *para*-LAT would be expected to result in a decrease in the absorbance at around 250 nm of around 20% due to the smaller extinction coefficient of the benzophenone derivative. However, of the 50% yield of LAT on photoreduction of benzophenone in EVOH, around 25% is proposed to be *ortho*-LAT. If this isomer also decays to form benzophenone (or a benzophenone derivative containing an alkyl substituent) in the absence of oxygen, then the overall absorbance at this wavelength after decay of the LAT isomers to re-form benzophenone (or an alkyl-substituted derivative) would remain relatively constant (as shown in Fig. 4) if the extinction coefficient of the *ortho*-LAT isomer at around 250 nm is approximately 4.0×10^3 dm^3 mol^{-1} cm^{-1}, and assuming the absorbance by the other minor photoproducts (**2**), (**3**), and (**4**) is negligible at this wavelength. Therefore, the re-formation of a benzophenone derivative *via* a radical reaction seems to be a plausible explanation for the observed lack of change in the absorption spectrum at around 250 nm in Fig. 4, although the reason for the faster rate of re-formation of benzophenone from *ortho*-LAT than for *para*-LAT is unclear at present.

It is postulated that the bi-exponential decay kinetics observed in the present work is the result of the different rates of the reactions for the two LAT isomers, where the reaction involving the *ortho* isomer may be the benzophenone-mediated process proposed by Demeter and Bérces [12]. The rate of decay of the *para*-LAT isomer in EVOH film is essentially the same as that in solution, suggesting that this reaction is sufficiently slow for the viscosity of the medium to have little effect on the rate constant.

The reaction of the LAT photoproducts with oxygen is also not well understood, but the similar lack of change in the intensity of the benzophenone absorbance band at around 250 nm on exposure to oxygen, as seen in Fig. 7, suggests that similar re-formation of benzophenone (and/or an alkyl-substituted benzophenone derivative) is also the primary product of the reaction in this case. On the basis of this observation, and the assumption that the relatively rapid decay of the *ortho*-LAT isomer is essentially unaffected by the presence of oxygen, we propose that the increase in the overall rate of loss of the absorption band at 330 nm is due primarily to a reaction between the *para*-LAT isomer and oxygen, and a possible mechanism for this reaction is shown in Scheme 2. The validity of this reaction scheme is supported by the results reported by Rubin [10], and the fact that hydrogen peroxide, a likely product of LAT oxidation, was readily detected by immersing in water a UV-exposed EVOH film containing benzophenone and then analyzing the water for hydrogen peroxide using a standard test-kit (Merck, Reflectoquant®).

4. Conclusions

The results of this work indicate that the maximum total yield of LAT photoproducts produced on photoreduction of benzophenone in EVOH films is approximately 50%, comprising around 75% of the *para*-LAT isomer with the remainder being attributed to the *ortho*-LAT isomer. The total yield of LAT photoproducts found in this work is substantially higher than that reported for the photoreduction of benzophenone in low viscosity fluid solutions such as 2-propanol, and it is proposed that the enhanced yield of LAT photoproducts in the rigid EVOH films used in this work is due mainly to the lower probability of benzopinacol formation resulting from the significantly slower diffusion of hydroxydiphenylmethyl radicals in the rigid EVOH polymer matrix.

The LAT isomers were found to decay over a period of weeks at room temperature in the absence of oxygen, with the decay of the *para*-LAT isomer being substantially slower than the *ortho*-LAT isomer, and the decay rate of the *para*-LAT isomer increasing markedly in the presence of oxygen. Mechanisms for the decay of the LAT isomers that are consistent with the available data were postulated.

The presence of alkyl, alkoxy, or aryloxy moieties on the phenyl rings of benzophenone was found to have little effect on the efficiency of formation, stability, and reactivity with oxygen of the LAT photoproducts in EVOH films, for the benzophenone derivatives studied in this work.

References

[1] J.N. Pitts, R.L. Letsinger, R.P. Taylor, J.M. Patterson, G. Recktenwald, R.B. Martin, J. Am. Chem. Soc. 81 (1959) 1068–1077.

[2] J.L.J. Bäckstrom, K.L. Appelgren, R.J.V. Niklasson, Acta Chem. Scand. 19 (1965) 1555–1565.

[3] G.O. Schenck, M. Cziesla, K. Eppinger, G. Matthias, M. Pape, Tetrahedron Lett. 2 (1967) 193–198.

[4] N. Filipescu, F.L. Minn, J. Am. Chem. Soc. 90 (1968) 1544–1547.

[5] S.G. Cohen, J.I. Cohen, Tetrahedron Lett. 9 (1968) 4823–4826.

[6] S.A. Weiner, J. Am. Chem. Soc. 93 (1971) 425–429.

[7] S.G. Cohen, G.C. Ramsay, N.M. Stein, S.Y. Weinstein, J. Am. Chem. Soc. 96 (1974) 5124–5130.

[8] J. Chilton, L. Giering, C. Steel, J. Am. Chem. Soc. 98 (1976) 1865–1870.

[9] P. Colman, A. Dunne, M.F. Quinn, J. Chem. Soc., Faraday Trans. I 72 (1976) 2605–2609.

[10] M.B. Rubin, Tetrahedron Lett. 23 (1982) 4615–4618.

[11] A. Demeter, B. László, T. Bérces, Ber. Bunsenges. Phys. Chem. 92 (1988) 1478–1485.

[12] A. Demeter, T. Bérces, J. Photochem. Photobiol. A: Chem. 46 (1989) 27–40.

[13] C. Viltres Costa, M.A. Grela, M.S. Churio, J. Photochem. Photobiol. A: Chem. 99 (1996) 51–56.

[14] M.L. Rooney, in: J.H. Han (Ed.), Innovations in Food Packaging, Elsevier Ltd., San Diego, 2005, pp. 123–137 (and references cited therein).

[15] J.C. Scaiano, E.B. Abuin, L.C. Stewart, J. Am. Chem. Soc. 105 (1982) 5673–5679.

[16] M. Barra, J.C. Scaiano, Photochem. Photobiol. 62 (1995) 60–64.

[17] K. Horie, H. Ando, I. Mita, Macromolecules 20 (1987) 54–58.

[18] Chr. Bräuchle, D.M. Burland, G.C. Bjorklund, J. Phys. Chem. 85 (1981) 123–127.

[19] F.W. Deeg, J. Pinsl, Chr. Bräuche, J. Phys. Chem. 90 (1986) 5715–5719.

[20] F.W. Deeg, J. Pinsl, Chr. Bräuchle, IEEE J. Quantum Elect. QE-22 (1986) 1476–1481.

[21] J.M.J. Fromantin, United States Patent 4,277,497 (1981).

[22] P.J. Wagner, M.A. Meador, B. Park, J. Am. Chem. Soc. 112 (1990) 5199–5211.

[23] H. Shimamori, H. Uegaito, K. Houdo, J. Phys. Chem. 95 (1991) 7664–7667.

[24] R.W. Redmond, J.C. Scaiano, L.J. Johnston, J. Am. Chem. Soc. 114 (1992) 9768–9773;
L.J. Johnston, D.J. Lougnot, V. Wintgens, J.C. Scaiano, J. Am. Chem. Soc. 110 (1988) 518–524;
M. Sakamoto, X. Cai, M. Hara, S. Tojo, M. Fujitsuka, T. Majima, J. Phys. Chem. A 108 (2004) 8147–8150.

[25] P.G. Sammes, Tetrahedron 32 (1976) 405–422.

[26] T. Suzuki, U. Okuyama, T. Ichimura, Chem. Phys. Lett. 266 (1997) 107–110.

[27] T. Nakayama, K. Hamanoue, T. Hidaka, M. Okamoto, H. Teranishi, J. Photochem. 24 (1984) 71–78.

[28] W. Adam, F. Kita, R.S. Oestrich, J. Photochem. Photobiol. A: Chem. 80 (1994) 187–197.

[29] A. Demeter, T. Bérces, J. Phys. Chem. 95 (1991) 1228–1232.

[30] S.L. Murov, Handbook of Photochemistry, Marcel Dekker, Inc., New York, 1973, p. 23.