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# Ultraviolet absorbers and singlet oxygen

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## Abstract

Photooxygenation of 9,10-dimethylanthracene (DMA) was carried out with eosine as photosensitizer in ethyl cellulose films to investigate the behaviour of the three UV absorbers, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (M-OH-P), 2-(2-hydroxy-4-methoxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine (M-OH-X) and 2-(2-hydroxy-5-methylphenyl)benzotriazole (Tinuvin P, TIN P), in the presence of singlet oxygen $O_2$ ($^1\Delta_g$). None of the UV absorbers displays significant reaction with singlet oxygen after 50 h of irradiation with a 500 W mercury lamp. Quenching experiments in ethanol reveal that these UV absorbers do not attenuate the reaction of DMA with singlet oxygen, i.e. there is no detectable physical quenching of singlet oxygen. M-OH-P produces a minute amount of singlet oxygen with either M-OH-X or TIN P, no measurable quantities of singlet oxygen are generated. These UV absorbers, therefore, have no significant capacity for generating singlet oxygen. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* UV absorbers; Singlet oxygen; 2-(2-Hydroxy-4-methoxyphenyl)-4,6-diaryl-1,3,5-triazines; 2-(2-Hydroxy-5-methylphenyl)benzotriazole (Tinuvin P, TIN P); $^1O_2$ ($^1\Delta_g$) production; Eosine as photosensitizer; Photooxygenation of 9,10-dimethylanthracene; Tetramethylethylene; Ethyl cellulose

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## 1. Introduction

UV absorbers with an intramolecular hydrogen bond (IMHB), such as 2-(2-hydroxyaryl)benzotriazoles or 2-(2-hydroxyaryl)-1,3,5-triazines, are widely employed for protecting polymers against photodegradation [1,2]. The variety of materials to be protected, e.g. different types of plastics and varnishes, demands a high standard for the photophysical properties of the UV absorbers, such as photostability and extinction coefficient [1–10]. A good UV absorber should strongly absorb in the 300–400 nm wavelength range, though, ideally, none at all in the visible range in order to prevent any unwanted colouration. Numerous investigations have been reported on the deactivation mechanism of intramolecularly hydrogen-bridged UV absorbers. It has been established that photoexcitation of these compounds is followed by an excited-state intramolecular proton transfer (ESIPT) and subsequent rapid, mainly radiationless deactivation, including a proton back-transfer to the original $S_0$ ground state [8,10–18]. This process constitutes a classic intramolecular Förster Cycle [19,20] and ensures that the absorbed ultraviolet radiation is rapidly transformed into vibrational energy. This is essential for the high photostability required from an efficient UV absorber. While the ESIPT process itself does not appear to be an absolute prerequisite for effective energy transformation, an intact IMHB in the excited state is indispensable since it offers the plenitude of vibrational modes needed to trigger rapid radiationless deactivation processes [21].

Another important requirement is sufficient miscibility of the photostabilizer with the polymer which is achieved by introducing alkyl, polar, or even polymerizable substituents into the UV absorber molecule [6,13,22,23].

In practice, UV absorbers are used in combination with other additives, e.g. antioxidants, radical scavengers, or pigments. By favourable synergistic effects, the protective effect of the stabilizer combination may exceed the sum of the protecting capacities of the individual components [3–5,24]. A UV absorber may, for instance, protect the polymer as well as an added antioxidant molecule from photodegradation. This same antioxidant may, on the other hand, prevent oxidation of the UV absorber. Antagonistic effects, however, are also known for additive mixtures [2]. Additionally, certain dyes, as well as other additives, are capable of generating singlet oxygen ($^1\Delta_g$), and thus can act as

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sensitizers [7,25–30]. Singlet oxygen produced in this way, as a rule, is deactivated by the addition of quenchers such as Ni-dibutyldithiocarbamate (Q in Scheme 2) [31]. A really good UV absorber, however, should be resistant to singlet oxygen to conserve its protective effect as long as possible.

Catalán et al. [32] have found that the singlet oxygen quenching and generating properties of the UV absorber 2-(2-hydroxy-5-methylphenyl)benzotriazole (TIN P, trade name of Ciba SC, formerly of Ciba–Geigy) depend on the nature of the solvent. In non-polar solvents, TIN P exists solely as a conformer with intact intramolecular hydrogen bond [9,11,12,33]; this form does not interact with singlet oxygen when using rubrene as sensitizer [32]. In polar solvents, the intramolecular hydrogen bond is partially opened [9,11,12], and the 'open' form of TIN P is able to physically quench singlet oxygen. TIN P anions, finally, formed in basic solutions, undergo chemical reaction with singlet oxygen [32].

We now report on the stability of some intramolecularly hydrogen-bridged UV absorbers towards singlet oxygen (structures are given in Scheme 1). These compounds are also probed for any singlet oxygen quenching activity. Detection of phosphorescence from some UV absorbers [14,34] has motivated us to further test whether they can act as singlet oxygen sensitizers.

(1) $^1D \longrightarrow {}^1D^*$ (hν)

(2) $^1D^* \longrightarrow {}^3D^*$ ($k_{ISC}$)

(3) $^1D^* \longrightarrow {}^1D$ ($k_d + k_F$)

(4) $^3D^* + {}^3O_2 \longrightarrow {}^1D + {}^1O_2$ ($k_{sens}$)

(5) $^1O_2 + {}^1Q \longrightarrow {}^3O_2 + {}^1Q$ ($k_{PQ}$)

(6) $^1O_2 + {}^1A \longrightarrow AO_2$ ($k_{reac}$)

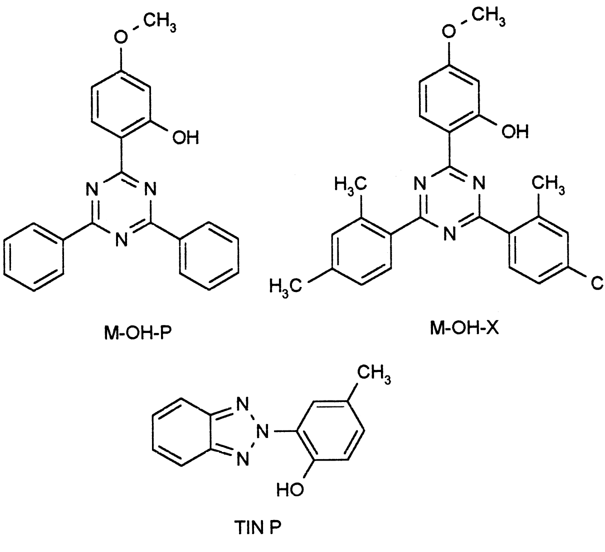
(7) $^1O_2 \longrightarrow {}^3O_2$ ($k_D$)

Scheme 2. Reactions relevant to photosensitized photooxygenation: D, dye; Q, quencher; and A, acceptor.

## 2. Experimental section

### 2.1. Materials

2-(2-Hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (M-OH-P), 2-(2-hydroxy-4-methoxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine (M-OH-X), and 2-(2-hydroxy-5-methylphenyl)benzotriazole (Tinuvin P, TIN P) were synthesized in the laboratories of Ciba Specialty Chemicals (Marly, now Basle, Switzerland) and recrystallized twice from cyclohexanol or methylcyclohexane. 9,10-Dimethylanthracene (DMA) and eosine, purchased from Aldrich–Chemie (Steinheim, Germany), and ethyl cellulose, obtained from Merck (Darmstadt, Germany), were employed as supplied. Solvents (ethanol, butanol, 1,1,2-trichlortrifluorethane) from Merck (spectrophotometric grade, Uvasol) were used without further purification.



Scheme 1. Structures of the UV absorbers.

### 2.2. Apparatus

For photoirradiation, the light of a 500 W mercury lamp was passed through a water-cooled solution of copper sulphate as a cut-off filter for wavelengths <300 nm. Selective excitation was assured by combining a Schott 546 nm interference with a Schott 455 nm cut-off filter. Progress of photodegradation was monitored by recording the absorption spectra with a Perkin–Elmer Lambda 7 UV-VIS-spectrometer.

### 2.3. Singlet oxygen production and detection

Both, eosine [35–37] and fluorenone [38,39] were employed as sensitizers for singlet oxygen formation which was monitored indirectly by its reaction with 9,10-dimethylanthracene [40,41] or 2,3-dimethyl-2-butene (tetramethylethylene, TME) [29,42–44]. Whenever possible, thin ethyl cellulose films were used for the experiments to mimic practical conditions, and also because the lifetime of singlet oxygen is higher in polymers than in most solvents [45]. Otherwise ethanol or 1,1,2-trichlortrifluorethane (TCTFE) solutions were employed.

Additionally, singlet oxygen was detected directly by measuring the singlet oxygen phosphorescence at 1270 nm under continuous irradiation [46–48]; singlet oxygen was produced by photosensitization with rose bengal in acetonitrile. These measurements, carried out at the Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe, corroborate the findings from indirect detection [49].

### 2.4. Sample preparation

Thin films of ethyl cellulose were prepared by dissolving the components (e.g. UV absorber, ca. 1–2 mg; DMA, ca. 2 mg, eosine, ca. 4 mg) and 800 mg ethyl cellulose in 10 ml of a 1 : 1 (v : v) ethanol/butanol mixture under gentle heating and stirring. The cooled suspension was spread on a quartz plate, and the solvent allowed to evaporate overnight. A transparent film was obtained. The respective experiments were carried out under air to allow oxygen to diffuse into the film sample.

In the liquid solution experiments, where no oxygen diffusion was allowed to prevent solvent evaporation, the oxygen concentration was not constant due to oxygen consumption. Ethanol solution concentrations were $1.6 \times 10^{-4}$ M (DMA), $1.6 \times 10^{-5}$ M (eosine), and $1.1 \times 10^{-5}$–$6.7 \times 10^{-5}$ M (UV absorber).

## 3. Results and discussion

### 3.1. Reactivity towards singlet oxygen

In order to check the effectiveness of eosine as sensitizer and DMA as singlet oxygen acceptor, a thin ethyl cellulose film containing both, eosine and DMA was irradiated at 546 nm to ensure selective photoexcitation of eosine. The reaction of DMA was monitored by absorption spectroscopy. As shown in Fig. 1, DMA was degraded after a few minutes of irradiation (light intensity attenuated to 10% by a neutral density filter) due to conversion to the corresponding endoperoxide [40,41].

In order to investigate the resistance of the UV absorbers to singlet oxygen, DMA was replaced by the respective UV absorber. The films were irradiated for 50 h at 546 nm without attenuation of the light intensity. As the UV absorbers do not absorb at the chosen irradiation wavelength, eosine is excited selectively. With 250–280 kJ/mol [14,34], the triplet energies of all three UV absorbers are much higher than that of eosine (178.4 kJ/mol [50]). Triplet–triplet energy transfer from eosine to the UV absorber can, therefore, be excluded. Under comparable conditions, but in the absence of eosine, the UV absorbers have been proven as stable [51]; any degradation of the stabilizer in the presence of eosine thus can be attributed to reaction of the UV absorber with singlet oxygen produced by eosine. Eosine itself underwent substantial photodegradation [37] during 50 h of irradiation with the mercury lamp. For a proper interpretation of the results, the fact that eosine also shows absorption in the same spectral region as the UV absorbers must be taken into account. The absorption spectra of M-OH-P before, and after, 50 h of irradiation, corrected for the bleaching of eosine, show no significant change (see Fig. 2). The same holds for M-OH-X. A reaction of the UV-absorber chromophore with singlet oxygen can, therefore, be excluded within experimental error. Considering all results, an upper limit of $10^{-6}$ is calculated for the yield of the reaction of M-OH-P and M-OH-X with singlet oxygen relative to that of the reaction of DMA.

With TIN P, somewhat different results are obtained. After correction for eosine absorption, a small difference remains between the spectra of TIN P before, and after,

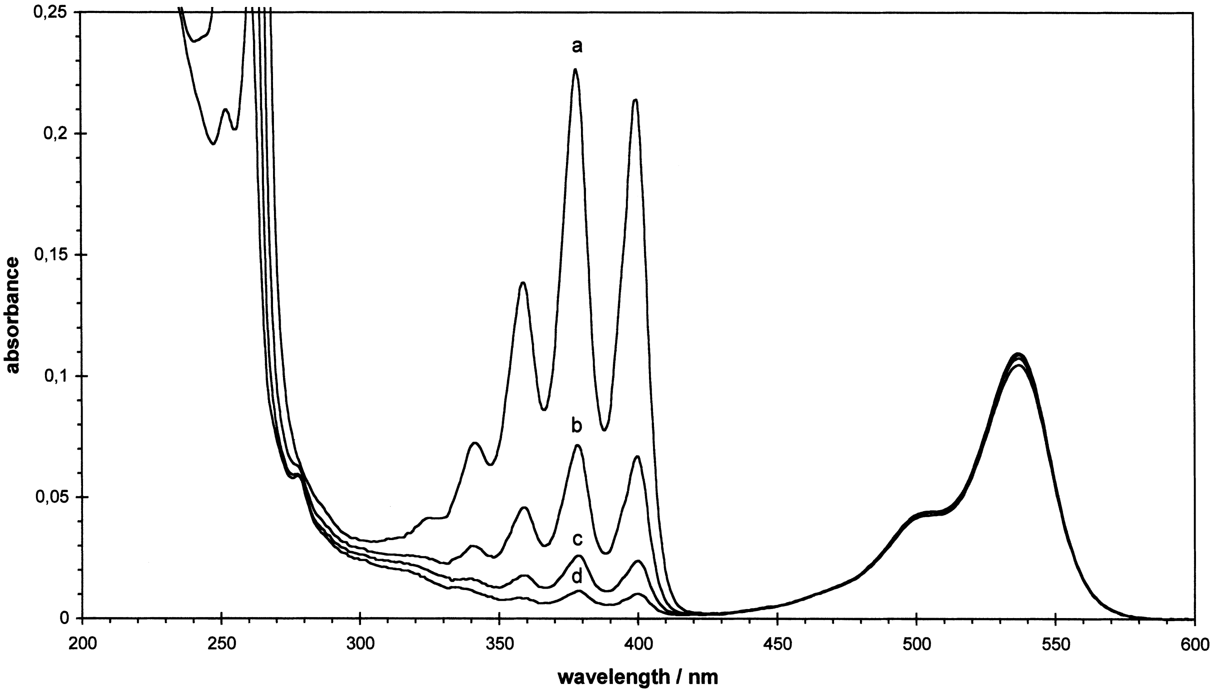


Fig. 1. Absorption spectra of DMA and eosine in ethyl cellulose after (a) 0 min, (b) 1 min, (c) 2 min, and (d) 4 min of irradiation at 546 nm (light intensity of the 500 W mercury lamp attenuated to 10% by a neutral density filter).

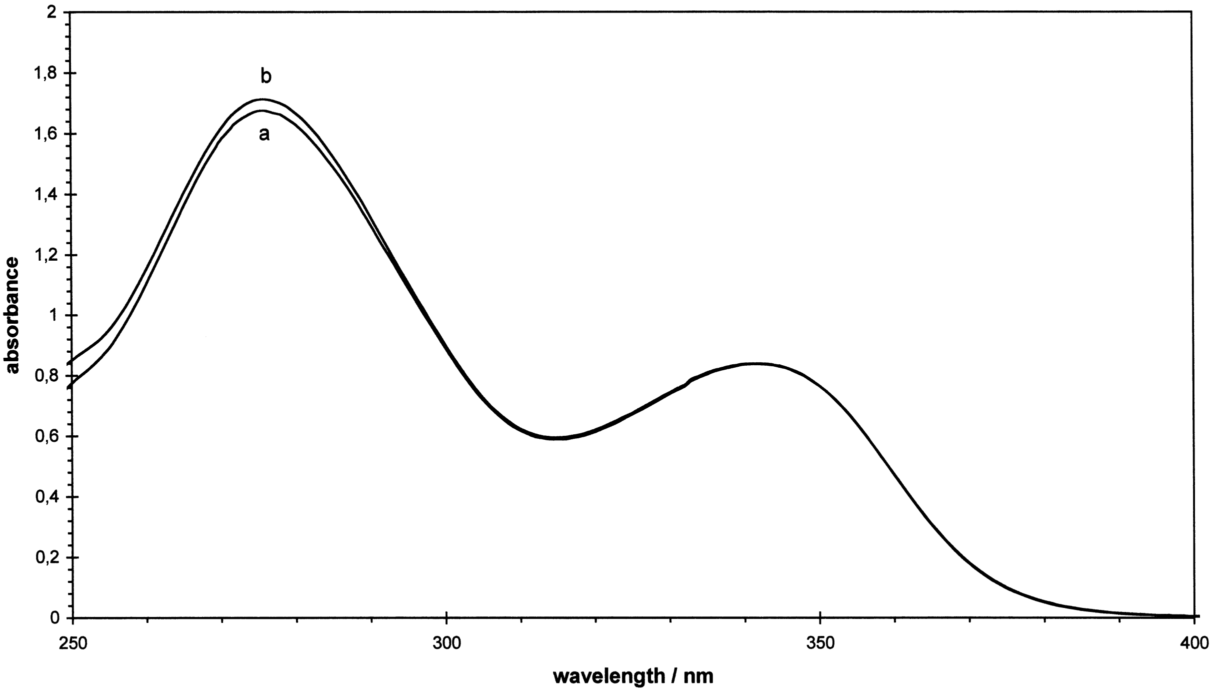


Fig. 2. Absorption of M-OH-P in ethyl cellulose (a) before and (b) after 50 h of irradiation at 546 nm in the presence of eosine (spectra corrected for eosine absorption).

irradiation for 50 h, respectively (see Fig. 3). However, this is not necessarily due to reaction with singlet oxygen. The observed decrease of the long-wavelength absorption band might also arise from a light-induced opening of the intramolecular hydrogen bridge of part of the TIN P molecules as found earlier for comparable compounds, e.g. methyl salicylate and *o*-hydroxybenzophenone [52–55]. These ‘open-form’ molecules are expected to be non-planar with a concomitant loss of the long-wavelength absorption band [11–13]. There is experimental evidence in support of this interpretation [49] which will be discussed in detail in a forthcoming paper.

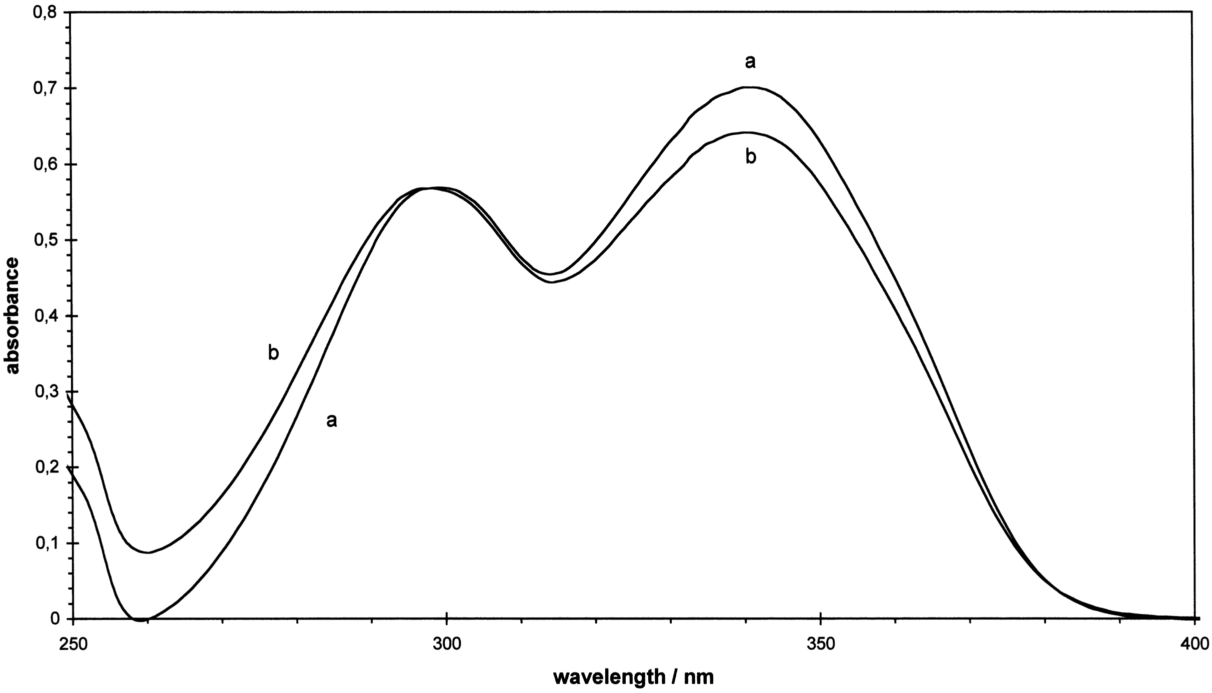


Fig. 3. Absorption of TIN P in ethyl cellulose (a) before, and (b) after 50 h of irradiation at 546 nm in the presence of eosine (spectra corrected for eosine absorption).

### 3.2. Physical quenching of singlet oxygen

According to Catalán et al. [32], TIN P can quench singlet oxygen physically in its ‘open’ form with an intermolecular hydrogen bridge to the solvent. These authors used DMSO for their experiments, a polar solvent with pronounced proton-accepting capacity. We at first employed ethyl cellulose but the results suffered from insufficiently reproducible sample thickness and concentrations. Ethanol solutions, in contrast, proved suitable to quantitatively evaluate the ability of the UV absorbers to quench singlet oxygen produced by eosine in the presence of DMA (see Section 2). Similar results were obtained for all three UV absorbers: none of them was able to compete with DMA for singlet oxygen within experimental error. The dependence of DMA absorbance ($\lambda_{obs} = 397$ nm) upon irradiation time is shown in Fig. 4. For all UV absorbers and at all concentrations, the curves exhibit the same shape. The rate of DMA bleaching does not even change with a tenfold increase in TIN P concentration. The rate constant for the reaction of DMA with singlet oxygen in ethanol, with eosine as sensitizer, is very high though, $k_q = 4.4 \times 10^7\,l\,mol^{-1}\,s^{-1}$ [56]. Therefore, it cannot be decided from these experiments if M-OH-P and M-OH-X are, in principle, unable to quench singlet oxygen physically or if their quenching constants are just too low to compete with that of the exceptionally good singlet-oxygen acceptor DMA.

The question remains, however, why TIN P showed no physical quenching of singlet oxygen in ethanol solution, which Catalán et al. [32] observed when studying TIN P in DMSO, with a quenching rate constant $k_q = 2.8 \times 10^6\,l\,mol^{-1}\,s^{-1}$. As outlined above, only the ‘open’ form of TIN P is able to quench singlet oxygen. Woessner et al. [11] have determined the ratio ‘open’ to ‘closed’ form of TIN P in DMSO as 1.25, whereas in ethanol, this value is only 0.09. The absence of physical quenching of singlet oxygen by TIN P in our experiments can thus be explained by the fact that there are simply too few ‘open’ TIN P molecules in ethanol.

### 3.3. Sensitizing singlet oxygen

The ability of the UV absorbers to produce singlet oxygen by photosensitization cannot be investigated with ethyl cellulose films, containing DMA as the singlet-oxygen acceptor, for several reasons. Since DMA absorbs in the same region as the UV absorbers, selective excitation of the UV absorber is not feasible. Furthermore, DMA undergoes photosensitized autoxidation [30,40,41,51]. Any potential photooxygenation of DMA, sensitized by the UV absorber, thus cannot be distinguished from this autoxidation. Consequently, tetramethylethylene (TME) [29,42,44] was chosen as the singlet-oxygen acceptor since it does not absorb between 300 and 400 nm, but due to its high vapour pressure cannot be used in ethyl cellulose films. Therefore, 1,1,2-trichlortrifluorethane (TCTFE) was employed as solvent where singlet oxygen lifetime is in the range of $\tau = 0.02$–$0.099$ s [38]. TME absorption has its maximum at 230 nm; the low transparency of TCTFE at this wavelength permits only qualitative investigations. In the absence

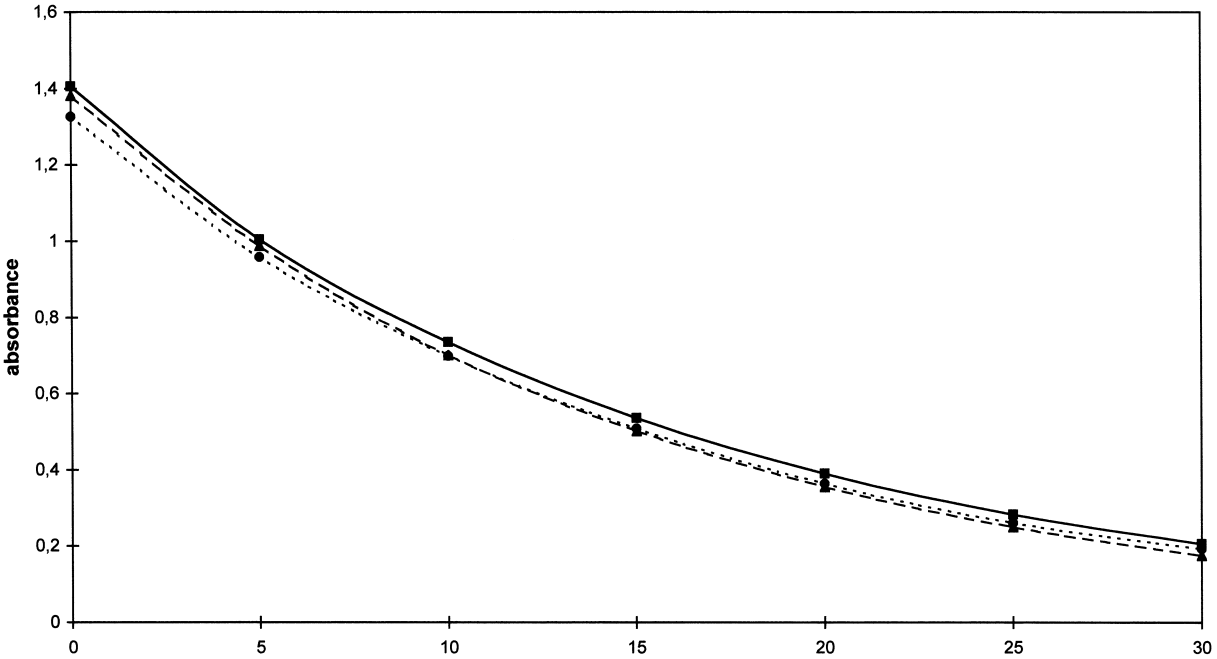


Fig. 4. Irradiation–time dependence ($\lambda_{irr} = 546$ nm) of DMA absorbance ($\lambda_{obs} = 397$ nm) in ethanol for the reaction of DMA ($1.6 \times 10^{-4}$ M) with $^1O_2$ ($^1\Delta_g$) produced by eosine ($1.6 \times 10^{-5}$ M) in the presence of M-OH-P: (———) 0 M; (- - -) $3.35 \times 10^{-5}$ M; and (· · ·) $6.7 \times 10^{-5}$ M.

of a sensitizer, a solution of TME in TCTFE did not show any changes in the absorption spectrum after 5 h of irradiation. In the presence of M-OH-P ($c \approx 10^{-4}$ mol/l), TME suffered a minor bleaching after 5 h which can be attributed to reaction of TME with singlet oxygen produced by the M-OH-P triplet state. The same kind of bleaching, although with a higher rate, was observed after a few minutes of irradiating a TME solution containing fluorenone as sensitizer. Upon replacing M-OH-P by M-OH-X or TIN P no bleaching of TME was observed within experimental error. Of the three UV absorbers investigated here, only M-OH-P produces a small amount of singlet oxygen. This might be related to the slightly different phosphorescence quantum yields of M-OH-P and M-OH-X [51] which will also be discussed in detail in a forthcoming paper.

The triplet energies of these UV absorbers (cf. Section 3.1) are much higher than the energy of the $^1\Delta_g$ and even the $^1\Sigma_g^+$ state of $^1O_2$ (94 kJ/mol and 157 kJ/mol [57], respectively). Bodesheim et al. [58] have reported the yield of singlet oxygen to decrease when the triplet energy of the sensitizer exceeds a limit of ≈240 kJ/mol, and proposed a different deactivation channel, mediated by a charge-transfer state, finally producing oxygen in its triplet ground state. Thus, no substantial yield of singlet oxygen is expected for the UV absorbers investigated here.

## 4. Conclusions

M-OH-P, M-OH-X, and TIN P have been shown not to react significantly with singlet oxygen. This result is highly favourable with respect to their function as UV absorbers. Since more than one additive, as a rule, is employed to protect a polymer [1,2], it is possible that singlet oxygen is produced by one or more of these additives or by dyes or pigments which might also be present. Therefore, UV absorbers should be resistant to singlet oxygen to ensure that their effectivity is not reduced by photooxidation.

No physical quenching of singlet oxygen by TIN P, M-OH-P or M-OH-X was observed in ethanol solution. In DMSO, however, a solvent of high proton-accepting capability, where TIN P forms *inter*- rather than *intra*molecular hydrogen bonds, physical quenching of singlet oxygen by TIN P was reported [32].

No singlet oxygen is generated by M-OH-X or TIN P, and just a small yield of singlet oxygen was detected for M-OH-P, in agreement with findings of Bodesheim et al. [58] who predict a decrease of singlet-oxygen production for sensitizers with a triplet energy >240 kJ/mol. This criterion holds for all three UV absorbers investigated here.

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