Photodegradation of Polystyrene Films Containing UV-Visible Sensitizers[#]

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Abstract: The photodegradation of polystyrene films has been investigated in the presence of sensitizers such as benzophenone (BP) and thioxanthone (TX). The phototransformations were studied by infrared and UV-Vis spectroscopy. The results indicate that these photosensitizers accelerate and increase the efficiency of the photodegradation and the photo-oxidation processes in polystyrene and increase the formation of double bonds in the polymer. In all these process, TX showed a larger photosensitization efficiency than BP. Flash photolysis experiments indicate that the triplet reactivity of both sensitizers towards polystyrene are similar, so that the higher efficiency of thioxanthone when compared with benzophenone should be assigned to its larger absorptivity, as well as to the absorptivity of its degradation products in the irradiating region.

Keywords: Polymer membranes, photodegradation, benzophenone, thioxanthone, UV-Vis irradiation.

1. INTRODUCTION

The photo-induced degradation of polymers has been investigated extensively to clarify their reaction mechanisms. Polystyrene (PS) is one of the commercial polymers widely used in various industrial fields and its stabilization against light is also an important problem [1, 2]. Polymers can be degraded by illumination either directly or using a photosensitizer. Although direct irradiation of the polymer may be the simplest method, the introduction of a photosensitive structure to a polymer presents some advantages. The photosensitization method is preferred when there is a need of controlling the photodegradation, as well as when using light of wavelengths that are not absorbed by the polymer [3, 4]. The excitation of sensitizers by light usually results in the production of free radicals that initiate the polymer degradation processes [5-9]. In general, these radicals abstract a hydrogen atom from the macromolecule forming a polymeric alkyl radical that reacts with oxygen, initiating an oxidative chain reaction [10, 11]. Reactions of benzophenone (BP) and thioxanthone (TX) in polymers are also important as these sensitizers are also used as polymerization photoinitiators [12].

BP was first studied as a photodegradation additive in polystyrene by Geuskens [13]. When BP absorbs light it will be excited to an upper singlet state, which subsequently decays to the triplet state. The benzophenone triplet abstracts a hydrogen atom from the polymer to give a polystyryl radical and the ketyl radical of benzophenone. The polystyryl radical then reacts with oxygen to form a polystyryl peroxyradical [14-16]. The photodegradation of polystyrene films in air, containing benzophenone, was also studied by Torikai *et al*. [1] by electron spin resonance and infrared spectroscopy.

Continuing our research on the sensitized photodegradation of polymer films [17], we present here the results on the evaluation of the efficiency of the benzophenone and thioxanthone in the photodegradation of polystyrene films.

2. EXPERIMENTAL SECTION

2.1. Materials

Commercial polystyrene (Aldrich, $\overline{M}_w$ 500 000) was used as received. The photosensitizers were thioxanthone (97%, Aldrich) and benzophenone (99%, Aldrich). The solvents chloroform (99%, Mallinckrodt), benzene (99%, Merck), and tetrahydrofuran (Tedia, HPLC grade) were used without further purification.

2.2. Photodegradation

Solutions of 5% w/w polystyrene containing TX (1.0×10^{-3} M) or BP (5.0×10^{-3} M) were prepared in chloroform. Thin PS films (about 300 μm) containing the photosensitizers were obtained by evaporation of the solutions from a horizontal glass plate. After solvent evaporation, samples were dried in vacuum for 4 h. The films were exposed to sixteen 6W G5 XELUX UV-visible light lamps in an irradiation chamber. The

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temperature was kept at 40°C to assure a minimum contribution of the thermal process.

2.3. Analysis

The weight-average molecular weights ($\overline{M}_w$) of the starting and irradiated polymers were measured by GPC on a Shimadzu LC–10 AD chromatographic system with a Shimadzu RID–6A refractive index detector. 20 μL of the sample solutions were injected in a combination of two Styragel HR4 and two Styragel HR5 columns. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}. Narrow-distribution polystyrene standards (American Polymers Standards Corp.) were used for calibration.

Photodegradation kinetics were determined by infrared spectroscopy. Exposed and control samples were placed over a specular reflection accessory (Spectratec, Inc.) in the compartment of a FT-Infrared spectrophotometer (BOMEN 100 MS Series). The samples were analyzed for C=O, OOH and OH groups content by examining their IR spectra, and absorbance was recorded at different times.

Ground state absorption spectra of the films were recorded using a UV spectrophotometer (Shimadzu UV-2550) with a diffuse reflectance attachment. All the samples were irradiated for specified times, and the absorption spectra were taken after each time increment.

2.4. Flash Photolysis

Laser flash photolysis experiments were performed on a laser photolysis transient absorption spectrometer with a diffuse reflectance accessory (Luzchem LFP 112 /122). Excitation at 355 nm was provided by a Q-switched Nd:YAG laser (Quantel Brilliant, ≥20 mJ/pulse, 5 ns). The detection system consisted 175-W Xenon lamp, a monochromator and a photomultiplier. Signals from the photomultiplier were digitized by a programmable digital oscilloscope (Tektronix TDS 2012 digitizer).

Transient spectra were recorded using 10×10 mm quartz cells with 3 mL capacity. The absorbance of the samples was kept 0.3 at the laser wavelength. All experiments were carried out at room temperature and deareated by bubbling with ultra-dry nitrogen.

The diffuse-reflectance experiments were performed using a right-angle geometry between the excitation beam and the monitoring beam to prevent the laser light to enter into the monochromator by specular reflection of. The area irradiated by the laser beam was approximately 0.2 cm^2, and the cell was slightly displaced after each shot in order to irradiate a fresh area. The reported signals were the result of an average of 10 shots.

3. RESULTS AND DISCUSSION

3.1. Molecular Weight Analysis

The results obtained for the photodegradation of PS doped with thioxanthone and benzophenone are listed in Table **1**. Undegradated samples are characterized by molecular weights in the 500 000 D range. The molecular weights of the irradiated samples were determined by GPC [18-21], and all showed a

Table 1: Average Molar Mass ($\overline{M}_w$), Average Chain Scissions (*S*) and Number of Chain Scission Events (N_t) of Photodegradated Polystyrene Films Containing Thioxanthone and Benzophenone Sensitizers

System	Irradiation time / h	$\overline{M}_w$ (Da)	$\overline{M}_n$ (Da)	*S*	N_t
PS/TX	0	501 000	224 000	0	0
	20	411 000	180 000	0.24	1.09
	38	370 000	175 000	0.28	1.25
	80	320 000	161 000	0.40	1.75
	132	275 000	117 000	0.91	4.08
PS/BP	0	505 000	210 000	0	0
	20	478 000	178 000	0.18	0.85
	38	404 000	160 000	0.31	1.48
	80	340 000	147 000	0.43	2.04
	132	321 000	133 000	0.58	2.75

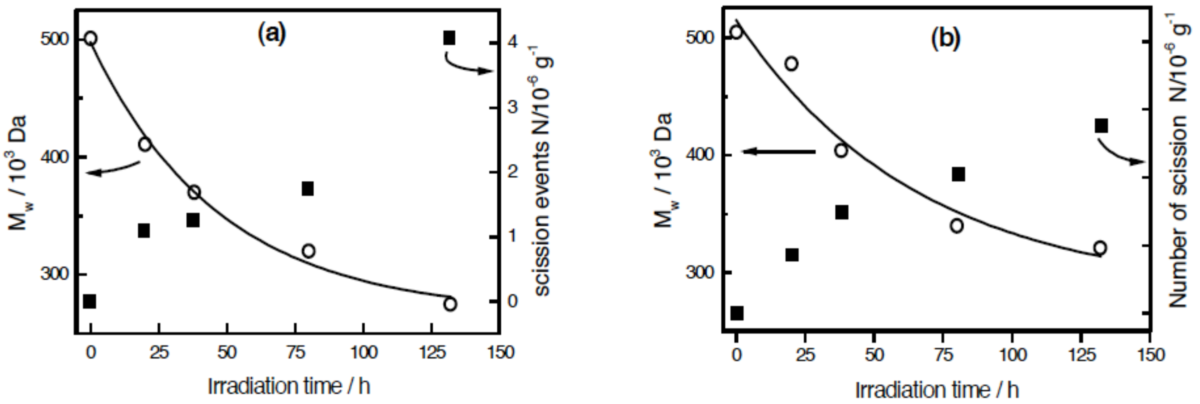

Figure 1: Variation of the molecular weight of PS during sensitized photodegradation and number of chain scissions per g of polymer. (**a**) Polystyrene films containing TX sensitizer and (**b**) containing BP sensitizer.

significant decrease after 132 h of irradiation, suggesting random chain scissions.

Figure **1** shows the variation of the molecular weight and the number of chain scissions of polystyrene films during irradiation.

The average number of chain scissions (*S*) per macromolecule, can be calculated using [22, 23]

$$S = \left[\left(\bar{M}_n\right)_0 \Big/ \left(\bar{M}_n\right)_t \right] - 1 \qquad (1)$$

where $\left(\bar{M}_n\right)_0$ and $\left(\bar{M}_n\right)_t$ are the number-average molecular weights of the polymer before and after *t* hours of irradiation, respectively. These values are shown in Table **1**.

The number of scission events per gram of polymer, N_t, is calculated using [24]

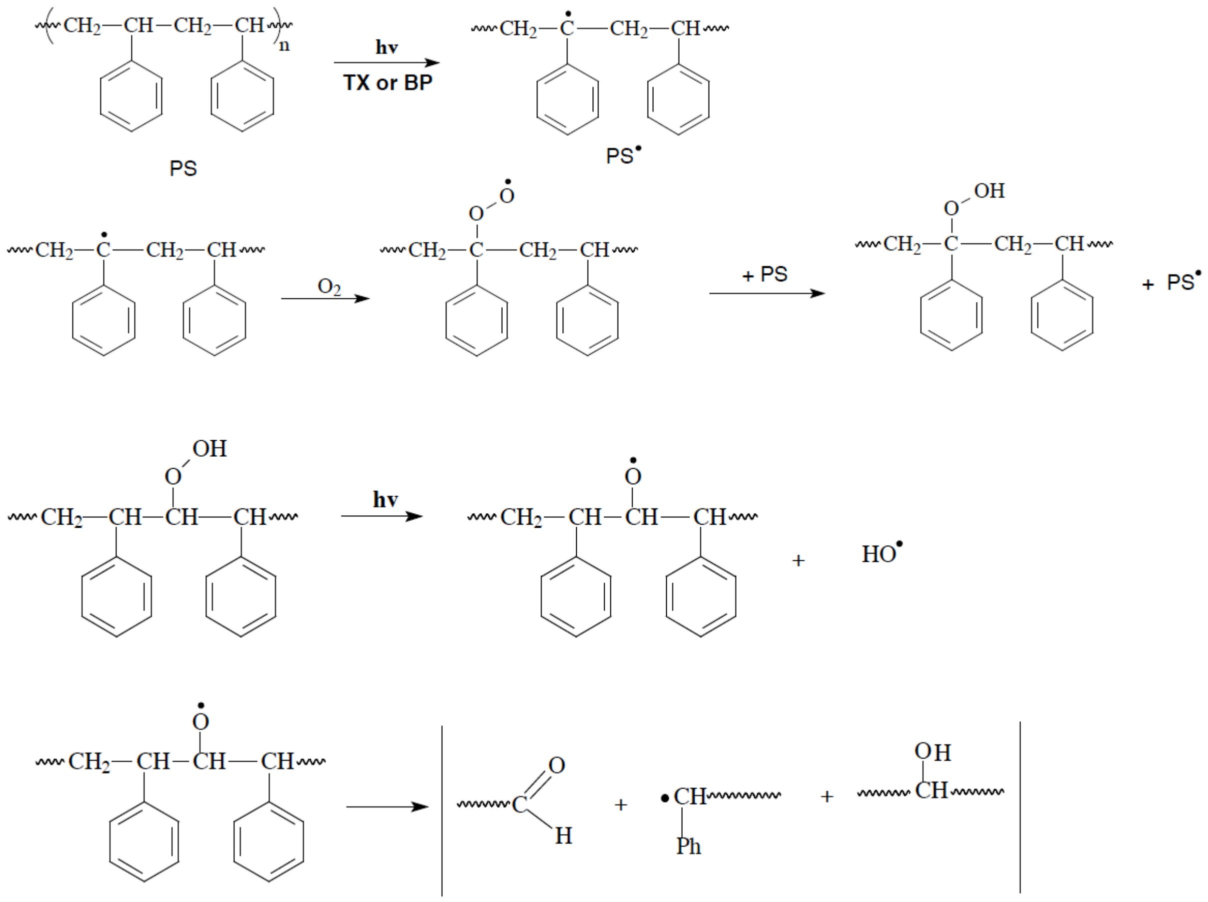

Figure 2: Photodegradation mechanism for polystyrene.

Table 2: Relative Intensity of the Absorption Bands at 1740 cm^{-1} (C=O Groups) and 3645 cm^{-1} (OH/OOH Groups) in PS/TX, PS/BP and PS Films During Irradiation

Films	ν, cm^{-1}	Irradiation time, h						
		0	1	2	5	10	15	20
PS/TX	1740	0	4.0	4.5	5.8	6.9	7.2	7.7
	3645	0	3.0	3.2	3.3	3.9	4.0	4.3
PS/BP	1740	0	3.4	3.3	4.0	4.5	5.3	6.1
	3645	0	0.4	0.6	0.8	1.0	1.1	1.5
PS	1740	0	0	0	0	0	0	0
	3645	0	0	0	0	0	0	0

$$N_t = \left[\frac{1}{(M_n)_t}\right] - \left[\frac{1}{(M_n)_0}\right] \qquad (2)$$

These data indicates that both sensitizers induce the photodegradation of polystyrene films. It can be seen from Figure **1** that the decrease in molecular weight of the polymer parallels the number of scission events. Films containing thioxanthone showed more chain scissions and faster molecular weight loss than those with benzophenone, indicating a higher photodegradation efficiency for the TX sensitizer.

3.2. FTIR Spectra Analysis

During irradiation significant changes are observed over practically the whole IR region. Macroradicals, which are the primary species formed during the photodegradation, will react with oxygen forming macroperoxy radicals, which abstract hydrogen to form hydroperoxides. The (thermal) dissociation of hydroperoxides in alkoxy and hydroxyl radicals, leads to the formation of the C=O and OH groups on the polymer chain, as shown in the Scheme in Figure **2** [6].

The results for the formation of carbonyl groups (IR peak at ~1740 cm^{-1}) during the photodegradation of the films are shown in Table **2**. As can be seen, the rate of formation of the C=O groups is larger in PS/TX. Results were normalized in order to facilitate the comparison between the films [1, 7, 25, 26].

The absorption due to the band at 3645 cm^{-1} (Table **2**) also increased during irradiation of the sensitized PS films. This band is typical for hydroxyl and/or hydroperoxide groups, which cannot be distinguished between them [27]. As show in Figure **3**, the formation of hydroxyl/hydroperoxide groups (3645 cm^{-1} absorption) and carbonyl groups (1740 cm^{-1} absorption) during irradiation of films is more efficient for films containing TX.

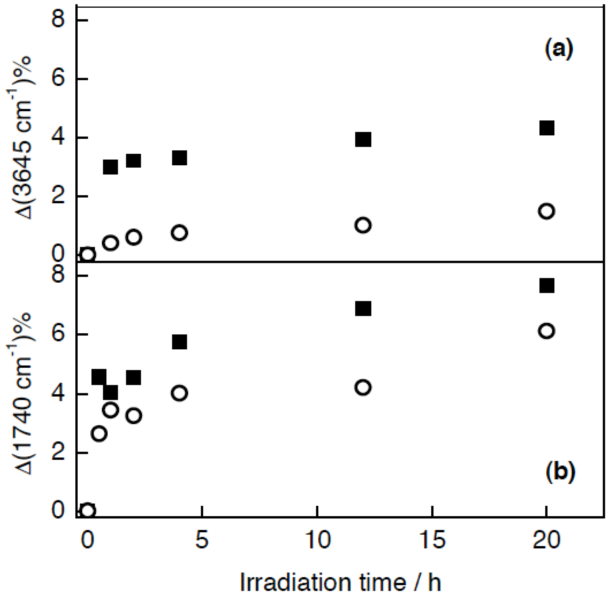

Figure 3: Normalized absorptions at 1740 cm^{-1} and 3645 cm^{-1} of irradiated (**a**) PS/BP and (**b**) PS/TX films.

3.3. UV-Vis Absorption

The changes in the UV-Vis absorbance of PS films containing BP or TX submitted to photodegradation are shown in Figure **5**.

It can be seen that in the films containing TX the absorption due to the sensitizer decreases during the photodegradation of the polymer, which indicates that the sensitizer is also being degraded. After practically 5 hours the thioxanthone is completely bleached. This process can be approached by first-order kinetics with a half-life around 1 h, under the conditions used in this experiment.

Noteworthy, the photodegradation process continues, even when all the TX has been degraded. This may be due to the presence of TX photodegradation products that absorb in the 320-360

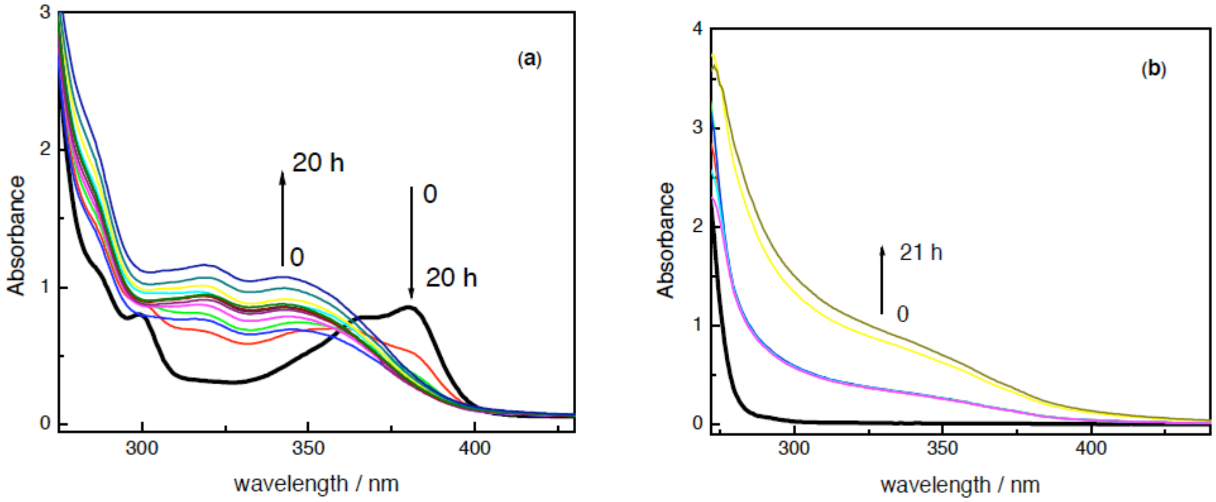

Figure 4: Changes in the UV-visible spectra of PS films sensitized with (**a**) thioxanthone, and (**b**) benzophenone, during irradiation.

nm range [28], as well as of photoproducts of the polymer degradation absorbing in the same region.

This effect is also observed for the BP-containing film, in which there is a continuous increase in the absorption at this wavelength range during photodegradation (Figure **4b**).

The increase of the absorption of the bands of degraded polymer in the 318-345 nm region can be assigned to the formation of conjugated double bonds [27, 29]. Thioxanthone is a well known sensitizer for photochemical reactions that yields ketyl radicals by abstracting a tert-hydrogen from the polymer [30], as shown in the Scheme in Figure **5** [31].

These polystyrene macroradicals will add an oxygen molecule forming the corresponding peroxyradical that abstracts an hydrogen atom from another polymer site to form the hydroperoxide which decomposes to yield a radical placed on the oxygen and a hydroxyl radical. These species will carry the propagation of the photooxidative chain, as shown in Figure **2**.

When excited, the polystyrene peroxide may decompose promoting chain scission and forming an aldehyde and a polystyrene with an end styrene entity (Figure **6**).

According to Geuskens *et al.* [13] polymers with excited unsaturated end groups will decompose by a molecular mechanism to yield conjugated dienes and hydrogen (Figure **7**) [32].

Figure **8** shows the evolution of the absorption at 312 nm (assigned to conjugated double bonds) during the photodegradation of polystyrene sensitized by benzophenone. On the other hand, it is not possible to evaluate the degree of formation of double bonds in the

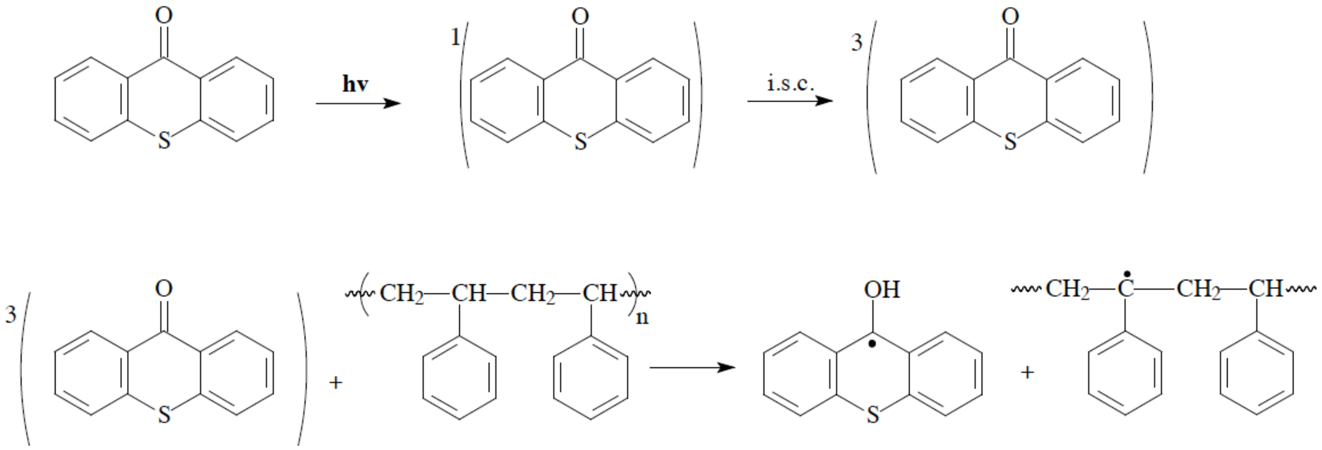

Figure 5: Photodegradation initiation using thioxanthone as sensitizer.

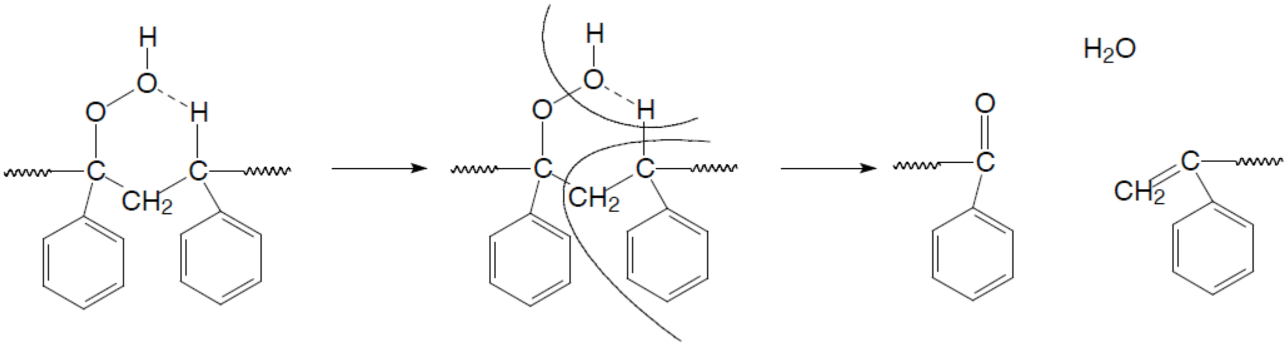

Figure 6: Decomposition of the hydroperoxy group on polystyrene.

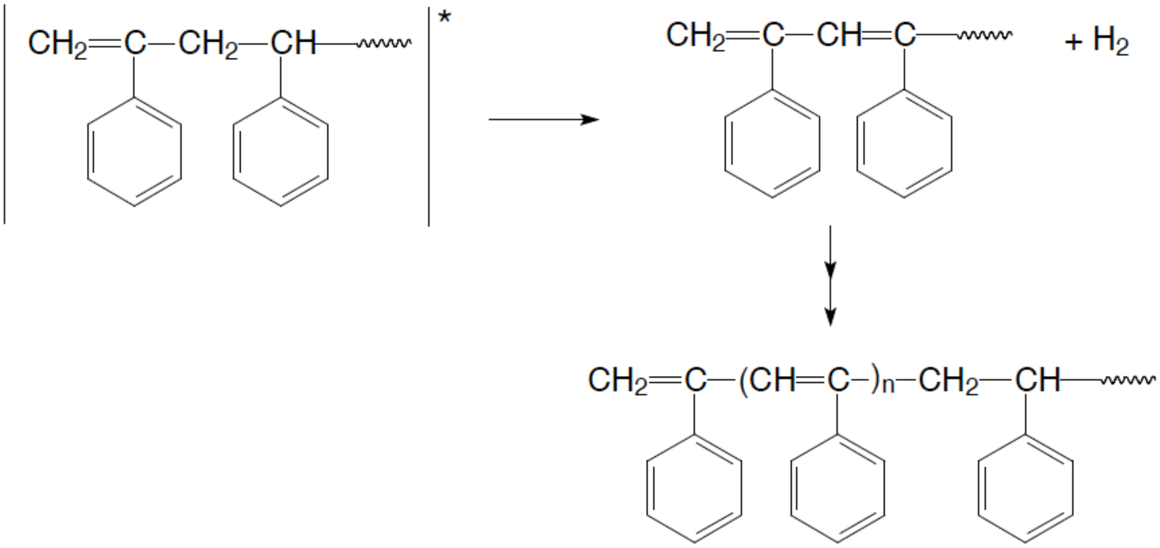

Figure 7: Mechanism for the formation of conjugated double bonds.

PS/TX films due to the degradation of the dye that forms products that also absorb in that region [17].

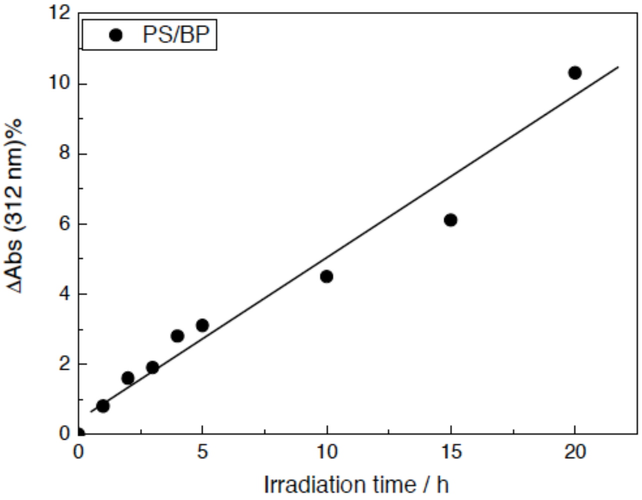

Figure 8: UV-Vis absorption at 312 nm (conjugated double bond region) of irradiated BP-containing PS films (calculated as the percentage of the differences between the initial absorption and the absorption at time *t*).

3.4. Flash Photolysis Studies

The triplet state lifetimes of both sensitizers, TX and BP, were determined by flash photolysis under different conditions, in an attempt to understand the difference in their sensitizing behaviour.

The transient spectrum of TX in PS powder shows an intense peak at 650 nm and that of BP shows a peak at 540 nm. These peaks, assigned to the triplet-triplet absorption of the sensitizers, show first-order decay kinetics (Figures **9A** and **B**). The lifetimes of the triplet states of the sensitizers absorbed on polystyrene powder were 12 and 5 μs for thioxanthone and benzophenone, respectively. When compared with the lifetimes of the same compounds in solution (6.4 and 6.9 μs, respectively), it can be seen that there is no great change for benzophenone, whereas for TX the lifetime increases considerably. This might be justified assuming that TX is absorbed more strongly than BP, hindering its mobility and, thus, increasing the triplet

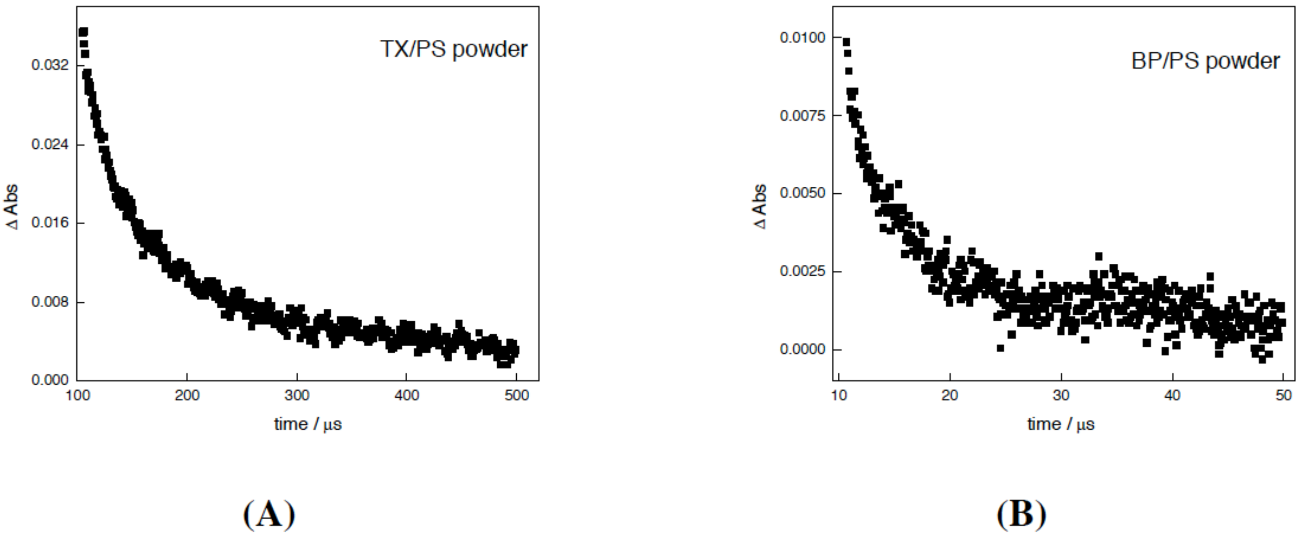

Figure 9: Decay of the transient absorption of (**A**) TX (0.3 %) at 650 nm and of (**B**) BP (1.2 %) at 540 nm in the presence of PS powder.

lifetime. I any case, there seems to be no effect than can be traced to a higher reactivity of the TX triplets.

Furthermore, the comparison of the lifetimes of both sensitizers in a solution of polystyrene in benzene, shows similar reductions in the lifetimes (0.6 and 0.8 μs, respectively. See Figure **10**). The overall rate constant for the disappearance of the sensitizers' triplets in PS solution can be assumed to be

$$k = k_o + k_Q C \qquad (3)$$

where k, k_o and k_Q are, respectively, the rate constants for the overall decay of the transient, the decay in the absence of PS and the quenching by the polymer, and C is the concentration of the polymer. Using the experimental lifetimes for the decay of the transients in the presence an absence of polymer (τ and τ_o), the ratio between the quenching rate constants of both sensitizers will be

$$R = \frac{\tau_o^{Bz}}{\tau_o^{TX}}\left(\frac{\tau_o^{TX}/\tau^{TX}}{\tau_o^{Bz}/\tau^{Bz}}\right) \qquad (4)$$

Using the lifetimes in Table **3**, the ratio is 0.98, indicating that both sensitizers will have the same initiation efficiency for the photodegradation process.

Therefore, the better efficiency for sensitized photodegradation of polystyrene films using thioxanthone as compared with benzophenone has to be traced merely to its larger extinction coefficient in the irradiation region, yielding more excited initiating species.

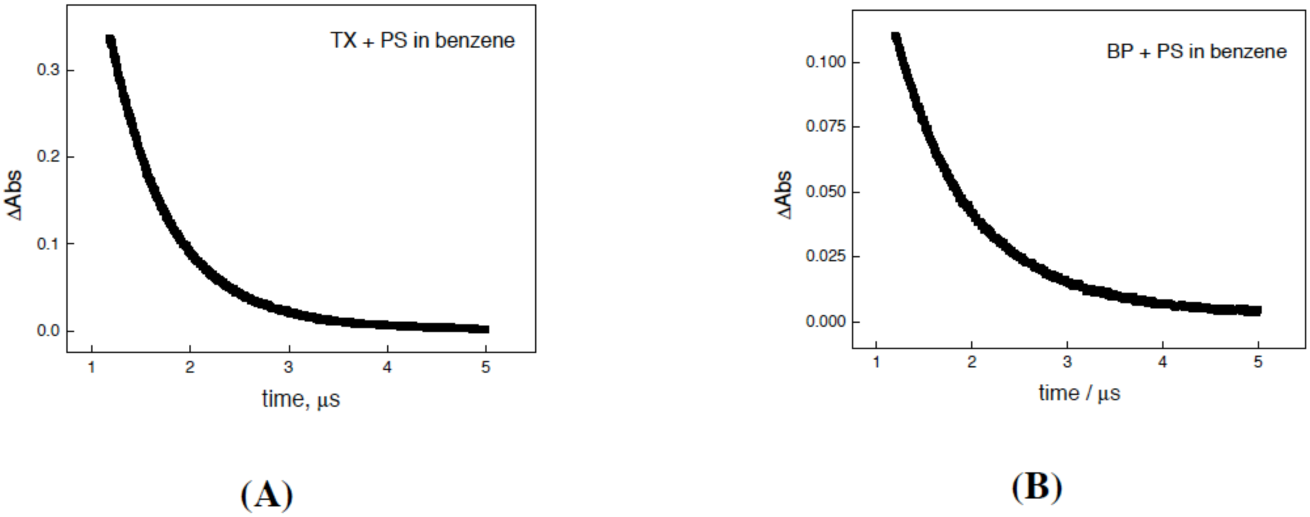

Figure 10: Decay of the transient absorption of TX at 650 nm (**A**) and of BP at 540 nm (**B**) in benzene solution of PS (20 g.L^{-1}).

Table 3: Lifetimes of Thioxanthone and Benzophenone in Different Systems

System	Sensitizer	Lifetime, μs
Benzene	Thioxanthone	6.4 [ref. 12]
	Benzophenone	6.9 [ref. 30]
Benzene + PS (20 g.L^{-1})	Thioxanthone	0.6
	Benzophenone	0.8
PS Powder	Thioxanthone	12
	Benzophenone	5

4. CONCLUSIONS

Benzophenone and thioxanthone have been proved to be efficient sensitizers for the photodegradation of polystyrene films. Both produce initiating species that lead to the same types of macroradicals and initiate a degradation chain reaction. Oxidized species are initially formed on the polymer chain, as was proved by the detection of hydroxyl, carbonyl and peroxy groups. Conjugated double bonds could also be detected when sensitizing with benzophenone. At the same time the molecular mass of the polymers decreases steadily.

Even after the complete depletion of thioxanthone, the polymer continued its degradation process, possibly due to the presence of thioxanthone photodegradation products, which absorb in the same region, as well as of species containing carbonyl and conjugated double bonds.

The apparent higher sensitizing effect found for thioxanthone when compared with benzophenone may be due to its higher absorptivity in the irradiating region.

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