

THIOXANTHONE ESTER DERIVATIVES: EFFICIENT TRIPLET SENSITIZERS FOR PHOTOPOLYMER APPLICATIONS

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Summary

Photochemical investigations and sensitivity measurements in sensitized reactions in solution and polymer matrices have been carried out with a number of new thioxanthone derivatives. These esters are efficient sensitizers having absorption maxima ranging from 333 to 416 nm and triplet energies ranging from 230 to 270 kJ mol⁻¹. Use of the thioxanthone esters is especially valid in photopolymer applications, as tested in the [2 + 2]-cycloaddition of homopolymers with pendent dimethylmaleimide groups and in the radical-initiated polymerization of acrylic monomers in the presence of donors.

1. Introduction

Imaging with polymers for lithography, photoresist and UV curing applications can be accomplished in a number of ways using a variety of photochemical reactions [1, 2]. The negative working systems are based on photo-cross-linkable polymers and photopolymerizable monomers. In order to improve the intrinsic and the spectral sensitivities of technical photopolymerization systems, optical sensitization is applied. Efficient sensitizers for this purpose are chosen to meet the following criteria.

(1) They must be excited by the technical irradiation equipment used. This means tuning of the spectral properties appropriate to the characteristics of the lamps.

(2) They should be capable of exciting the reactant molecules (energy transfer) as well as of accepting electrons from donor molecules (photo-reduction). This implies efficient and fast intersystem crossing of the absorbed energy to the triplet state. Long-living triplets are advantageous to facilitate the energy of the electron transfer.

(3) They need good solubility and compatibility in the matrix.

Thioxanthone derivatives are well known as triplet sensitizers for polymer photo-cross-linking systems [3 - 5] and as initiators for UV curing of coatings [6, 7], when used in conjunction with activators (donors).

The aim of this work is to introduce new thioxanthone derivatives which are highly soluble and possess a wide variety of light absorption characteristics.

2. Experimental details

2.1. Thioxanthone ester derivatives

Details relating to the preparation of the thioxanthone esters (*cf.* Table 1) have been given by Fischer and coworkers in previous publications [8].

2.2. Photochemical investigations

The measurements of quantum yields for the singlet \rightarrow triplet crossing process in solution were performed according to the method described by Lamola and Hammond [9]. The compound to be tested (see below, Fig. 4) is used as a sensitizer for a *cis-trans* isomerization and/or a [2+2]-cycloaddition reaction.

The determination of the quantum yields was carried out by illuminating degassed tetrahydrofuran (THF) solutions (3 ml) containing sensitizer (0.05 M) and olefin (0.05 M) with monochromatic light. The wavelength of the light source was adjusted according to the absorption properties of the sensitizer; photon fluxes were determined with a ferrioxalate actinometer ($48 - 112 \mu\text{einstein s}^{-1}$). The olefin reaction mixtures were analysed by gas column chromatography.

The triplet energies of the sensitizers were determined from the phosphorescence spectra recorded in glassy 2-methyltetrahydrofuran solutions (at 77 K).

2.3. Measurement of photographic sensitivity

2.3.1. Cross-linking of a polymer with pendent dimethylmaleimide groups

The polymer was prepared according to the method described in ref. 5 by esterification of poly(vinyl alcohol) (molecular weight $M_w \approx 13\,000$) with 3-(dimethylmaleimidyl)-propionic acid chloride.

The sensitivity of this photopolymer in the presence of various thioxanthone ester derivatives (*cf.* Table 3) was determined according to the method described by Finter *et al.* [4], using a 21-step continuous-tone photographic step tablet with optical density increments of 0.15. A 10 wt.% solution of the polymer plus 0.353×10^{-3} mol sensitizer (g solid polymer) $^{-1}$ in 1-ethoxy-2-acetoxyethane was coated onto a copper-clad epoxy fibreglass board yielding a dry coating thickness of 5 μm . The drying was carried out for 30 min at 90 °C. The coating was exposed through a 21-step tablet (Stouffer Sensitivity Guide) using a 5000 W high pressure mercury lamp (Sylvania MO 33). The light intensity was measured with an Oriel 8427-3 Radiant Powermeter, calibrated by actinometry. After exposure the coating was developed in 1,1,1-trichloroethane and the resulting relief image was

etched in an FeCl_3 solution. The irradiation energy required to reach a number 7 step was determined for each photopolymer-sensitizer composition.

2.3.2. Photoinitiator sensitivity measurements

Photoinitiation with thioxanthone ester derivatives and various activators was studied in a dry film formulation by using the following monomer-polymer binder composition. A solution of 14 g Scripset (styrene-maleic anhydride copolymer, $M_w \approx 10\,000$, Monsanto Corp.), 15 g trimethylolpropane triacrylate, various amounts of thioxanthone esters and activators (cf. Tables 4 and 5) in 71 g dimethylformamide was coated onto an aluminium sheet yielding a dry coating thickness of about $2\ \mu\text{m}$ (drying for 2 min at $100\ ^\circ\text{C}$). An overcoat, composed of a solution of 30 g Mowiol 4-88 (poly(vinyl alcohol), Hoechst Corp.), 1.5 g Brij 35^R (poly(oxyethylene lauryl ether), Atlas Powder Corp.) in 263.5 g pure water was then applied as an oxygen-protective layer, yielding a film thickness of about $0.5\ \mu\text{m}$ (drying for 5 min at $100\ ^\circ\text{C}$). The photopolymer coating was exposed through a 21-step tablet using a 5000 W high pressure mercury lamp (type and calibration as described above). After exposure, the coating was developed in a solution of 15 g sodium metasilicate nonahydrate, 0.3 g strontium hydroxide octahydrate, 3 g polyglycol 6000 (Fluka Corp.) and 0.5 g laevulinic acid in 1 l pure water, yielding a relief image. The irradiation energy required to reach a number 7 step was determined for each photopolymer composition.

3. Results and discussion

3.1. Absorption spectra

As shown in Fig. 1 and Table 1, the thioxanthone esters have absorption maxima ranging from 330 nm to 420 nm (in CH_2Cl_2). The extinction coefficients vary between 4300 and 7750 ($\times 0.1\ \text{m}^2\ \text{mol}^{-1}$). The absorption spectra depend on the chemical constitution of the different thioxanthone esters.

On the basis of the results obtained by Kaul [10], who investigated the indigoid chromophore, we assume that the carbonyl group acts as an electron acceptor group and the sulphur atom as a donor. The conjugation between the donor and the acceptor group through their connecting $-\text{C}=\text{C}-$ double bond is therefore responsible for the longest wavelength absorption. The polarized structure of type 1a (Fig. 2) is important.

When this donor-acceptor interaction is disturbed, *i.e.* diminished or enhanced by substituents in the 2 and 3 or 6 and 7 positions, the changes in the absorption characteristics of the thioxanthone esters (shown in Fig. 3) are in accordance with our expectations.

The action of the auxiliary donors or acceptors will lead to a bathochromic or hypsochromic shift of the absorption maximum of the longest wavelength absorption.

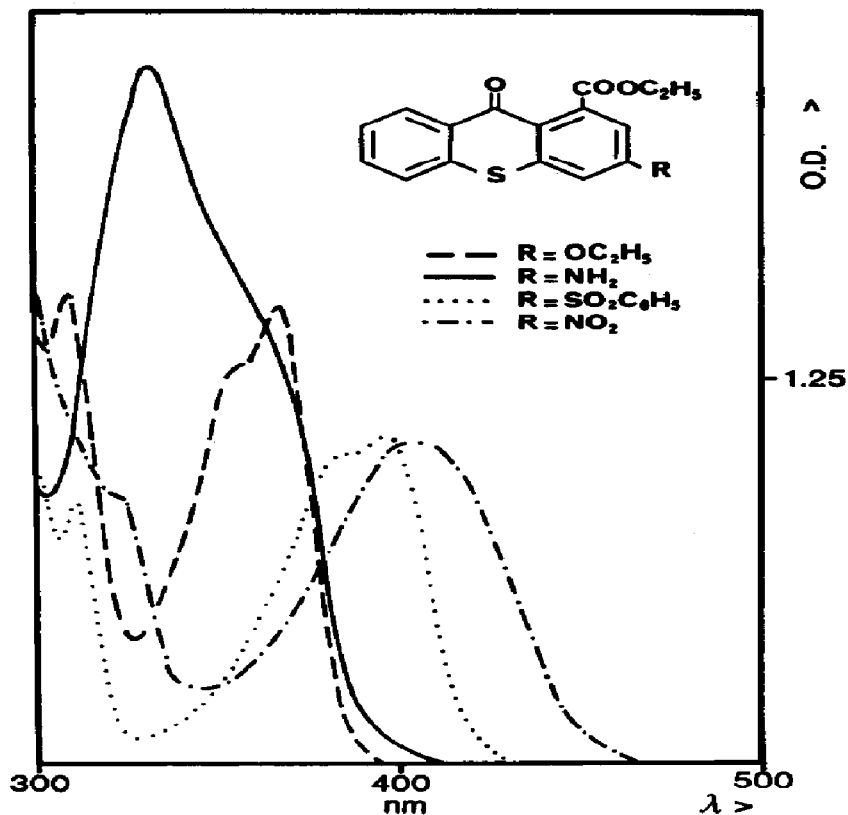


Fig. 1. Absorption spectra of thioxanthone ester derivatives in CH_2Cl_2 .

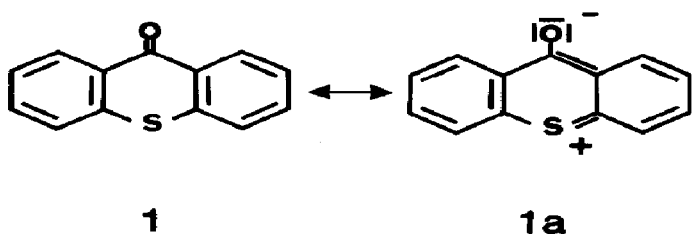


Fig. 2. Polarized thioxanthone group.

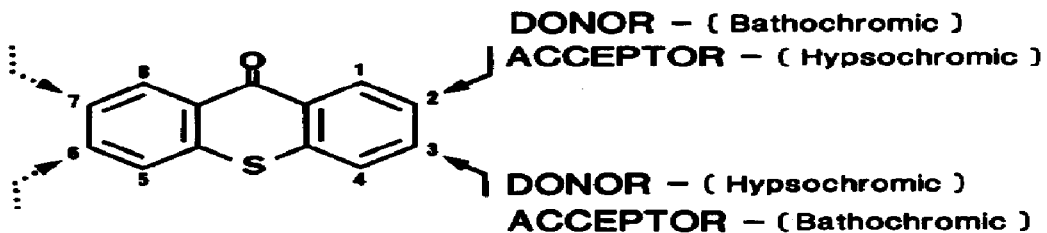
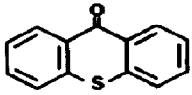
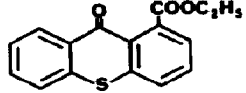
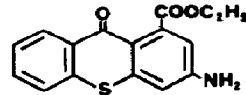
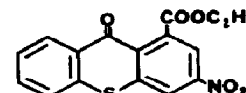
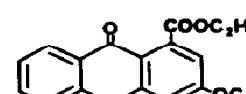
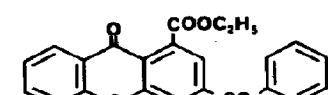
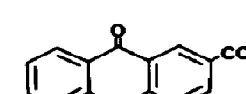
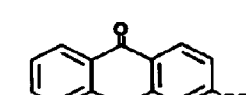
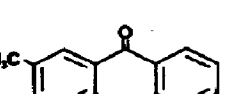
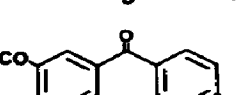
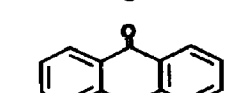


Fig. 3. Changes in absorption characteristics of the thioxanthone esters.

TABLE 1

Absorption data (CH_2Cl_2), triplet energies and intersystem crossing (ISC) quantum yields of thioxanthone ester derivatives for the *cis*-*trans* isomerization of 2-methylstyrene (Rct(1)), the *cis*-*trans* isomerization of 1-methylstilbene (Rct(2)) and the cyclodimerization of *N*-ethylidimethylmaleimide (Rct(3))

	Φ_{ISC}			E_{T} (kJ mol^{-1})	τ (ms)	λ_{max} (nm)	ϵ ($\times 0.1 \text{ m}^2 \text{ mol}^{-1}$)
	Rct(1)	Rct(2)	Rct(3)				
	92	98	103	265	95	376	6200
	103	—	100	265	85	383	6450
	104	—	—	255	95	333	11000
	7	36	18	230	85	407	4300
	99	—	—	270	65	368	6100
	91	89	105	250	90	398	5550
	81	97	111	265	85	377	5750
	104	—	106	245	200	397	6050
	103	—	102	245	120	403	6050
	66	82	29	230	220	416	6350
	103	—	105	260	105	386	7750

3.2. Photochemical investigations

The quantum yields Φ_{ISC} of the intersystem crossing efficiency of the different thioxanthone esters have been determined by reacting suitable acceptor molecules in high concentrations with the excited molecules according to the method described by Lamola and Hammond in ref. 9. Figure 4 shows the acceptor molecules involved and their reaction products. By reacting sensitizers which have relatively low triplet energies with the acceptors, besides the cis-trans isomerization of 2-methylstyrene ($E_T = 250 \text{ kJ mol}^{-1}$) the cis-trans isomerization of 1-methylstilbene ($E_T = 209 \text{ kJ mol}^{-1}$) was also used. In a further experiment the cyclodimerization of *N*-ethyl-dimethylmaleimide ($E_T = 217 \text{ kJ mol}^{-1}$) was followed quantitatively. Excitation of the sensitizer was carried out with monochromatic light. The values given in Table 1 show that the intersystem crossing efficiency of almost all the thioxanthone esters investigated is practically 100%.

The quantum yields for the isomerization reactions and especially for the cyclodimerization of the dimethylmaleimide derivative are low only for ethyl 7-methoxythioxanthone-3-carboxylate and for ethyl 3-nitrothioxanthone-1-carboxylate. The triplet lifetimes of all the sensitizers are between 65 and 220 ms.

These experimental investigations in solution show that thioxanthone esters should be efficient triplet sensitizers for a number of reactions.

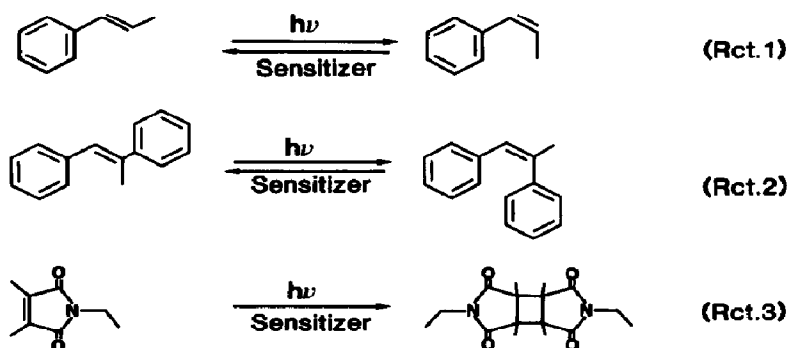


Fig. 4. Acceptor molecules and their reaction products.

3.3. Sensitivity of photopolymers with pendent dimethylmaleimide groups in relation to thioxanthone ester sensitizers

Polymers with pendent dimethylmaleimide groups insolubilize upon exposure to UV light, as shown in Fig. 5.

Dimethylmaleimide groups show UV absorption in the short UV region. For practical purposes these polymers must therefore be sensitized to absorb light in the near UV and visible region. Earlier studies carried out with different types of triplet sensitizers proved that thioxanthone gives good results [3]. However, there were problems due to the incompatibility of thioxanthone as well as its poor solubility in the homopolymers. With the

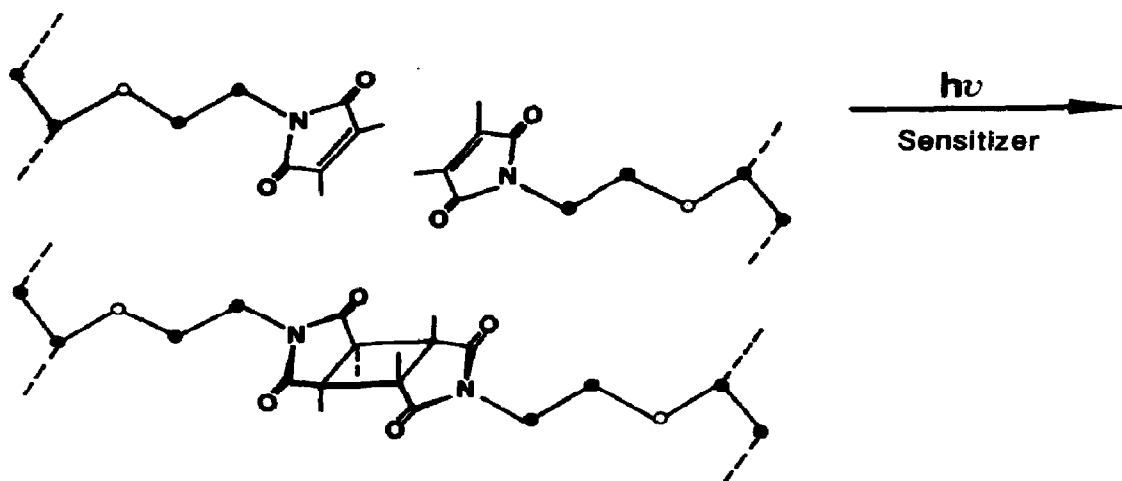


Fig. 5. Action of UV light on polymers with pendent dimethylmaleimide groups.

TABLE 2

Solubility of some thioxanthone ester derivatives in acrylic acid ethyl ester (20 °C)

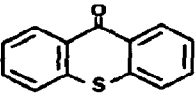
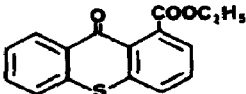
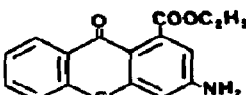
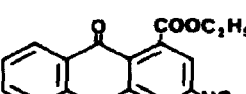
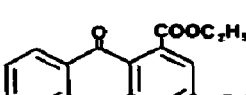
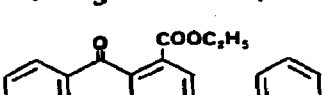
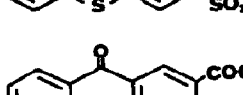
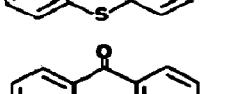
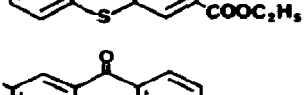
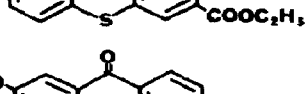
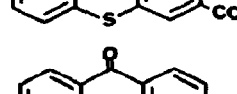
Thioxanthone ester	Solubility (W/V%)
	0.703
	1.773
	2.46
	0.822
	2.337

thioxanthone esters, however, no solubility problems have been observed (see Table 2).

Table 3 contains the results on the sensitivity of a polymer with pendent dimethylmaleimide groups and with different thioxanthone esters as

TABLE 3

Photosensitivity of a dimethylmaleimide polymer with different thioxanthone ester derivatives as the triplet sensitizer (0.353×10^{-3} mol sensitizer (g polymer) $^{-1}$)

	λ_{\max}^a (nm)	ϵ ($\times 0.1 \text{ m}^2 \text{ mol}^{-1}$)	Sensitivity (mJ cm^{-2})
	376	6200	22
	383	6450	11
	383	11000	55
	407	4300	55
	368	6100	22
	398	5550	11
	377	5750	22
	397	6050	22
	403	6050	22
	416	6350	34
	386	7750	11

^a Absorption data (CH_2Cl_2).

triplet sensitizers. The amount of sensitizer in all the experiments was $0.353 \text{ mol (kg polymer)}^{-1}$, a value which has been found to be optimal for a film thickness of $3 - 5 \mu\text{m}$ [5]. We measured the irradiation energy required to reach a number 7 step after the development (Stouffer 21 Step Sensitivity Guide, contact printing, mercury high pressure lamp, for details see Section 2). The sensitivity of the different photopolymers is given in millijoules per square centimetre.

The lowest sensitivity was found for photopolymers with ethyl 3-aminothioxanthone-1-carboxylate and ethyl 3-nitrothioxanthone-1-carboxylate with 55 mJ cm^{-2} . This means that the exposure time has to be doubled to obtain a sensitivity similar to that reached with a photopolymer with thioxanthone as the sensitizer (22.4 mJ cm^{-2}). Under the given experimental conditions, photopolymers with ethyl thioxanthone-1-carboxylate, ethyl 3-phenylsulphonylthioxanthone-1-carboxylate and ethyl thioxanthone-4-carboxylate show the highest sensitivity (11.2 mJ cm^{-2}). These photopolymer systems need only half the exposure time to show a sensitivity similar to that established with thioxanthone as the sensitizer.

Our investigation in solid photopolymer matrices in general show the same behaviour as that found in the liquid systems for the dimerization reaction of *N*-ethyl dimethylmaleimide (Table 1, reaction 3) and confirm that thioxanthone esters are valuable triplet sensitizers for such photopolymers.

3.4. Efficiency of thioxanthone esters and different activators in photopolymerization systems

The photoinitiated polymerization of olefinic monomers is an established field of industrial development for protective coatings or imaging systems. A mechanistic scheme of the photoinduced generation of radicals with the sensitizer-donor (activator) system is shown in Fig. 6.

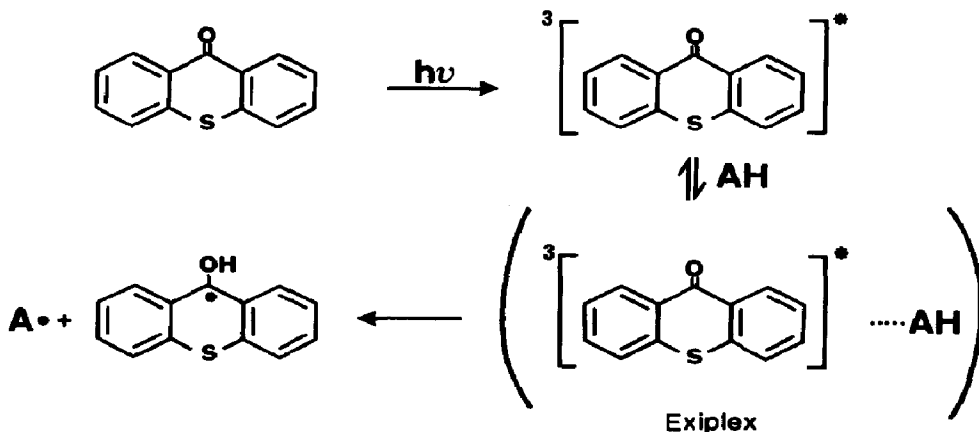


Fig. 6. Mechanistic scheme of the photoinduced generation of radicals with the sensitizer-donor system.

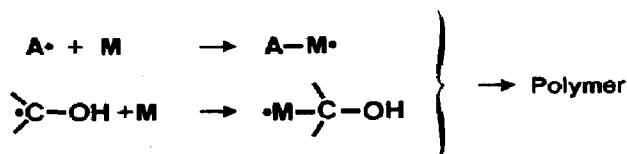


Fig. 7. Reaction of the radical A^\bullet with the monomer M .

The initiating efficiency of the sensitizer-donor system depends not only on the quantum yield of initiator triplet formation but also essentially on the reactivity of the initiator triplet towards the donor and the capability of the radicals generated of reacting with monomers M according to Fig. 7 [11 - 13].

Laser flash photolysis investigations by Schnabel [14] with thioxanthone-amine systems have shown that the radical generated on the donor is mainly responsible for initiating the polymerization of the olefinic monomers.

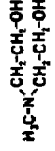
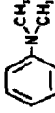




Our photoinitiation studies with the thioxanthone esters and different activators were carried out using a dry film format with a styrene-maleic anhydride copolymer as binder and trimethylolpropane triacrylate as monomer (film thickness, about $2 \mu\text{m}$). To avoid oxygen inhibition, an overcoat composed of poly(vinyl alcohol) was applied (film thickness, about $0.5 \mu\text{m}$). The irradiation energy required to reach a number 7 step after irradiation and development (Stouffer 21 Step Sensitivity Guide, contact printing, mercury high pressure lamp, for details see Section 2) was measured. Prior to the experiments with the novel thioxanthone esters the optimal sensitizer-activator concentration was evaluated.

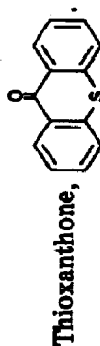
Table 4 contains the values for the photosensitivity in millijoules per square centimetre of the photopolymerization with different activators and thioxanthone as the sensitizer (molar ratio, 1:1) in relation to the concentration of the sensitizer-activator combination. The values found show that generally a concentration of 13.8×10^{-2} mol of each reagent per kilogram of polymer will give the optimal sensitivity. Therefore, experiments with different thioxanthone ester-activator initiation systems were carried out at this concentration.

Table 5 summarizes the results of the photoinitiation experiments with the various sensitizer-activator combinations. Generally, the reactivity increases in the order dimethylaniline < *N*-methyldiethanolamine < *N*-phenylglycine < *p*-methoxyphenylacetic acid < *p*-(*N*-dimethylamino)-phenylacetic acid ethyl ester. All thioxanthone esters show very high initiation activity in combination with *p*-(*N*-dimethylamino)-phenylacetic acid ethyl ester ranging from 1.5 to 8 mJ cm^{-2} , with the exception of ethyl 3-aminothioxanthone-1-carboxylate and ethyl 3-nitrothioxanthone-1-carboxylate whose activities were 31 mJ cm^{-2} and 124 mJ cm^{-2} respectively. These results correspond to the photochemical behaviour of the thioxanthone esters in the other experiments.

TABLE 4

Photosensitivity of a photopolymer system (styrene-maleic anhydride copolymer as binder and trimethylolpropane triacrylate) with different activators in relation to the thioxanthone-activator concentration (molar ratio, 1:1)

Initiator and donor concentration ($\times 10^{-2}$ mol kg $^{-1}$)	Photosensitivity (mj cm $^{-2}$)					
27.6						
13.8	110	146	53	6	8	8
6.9		212	38	13	8	6
3.45		292	53	23	16	16
		584	212	45	45	32



	110	110	106	11	8
	44	44	7	4	2
	31	44	23	3	3
	110	78	38	31	3
	110	78	94	6	4

The ethyl *p*(*N*-dimethylamino)phenylacetate in combination with the thioxanthone esters is very efficient whereas with tertiary amines, which should be equally good donors, the activations are comparatively slow. Also surprising are the high efficiencies of the *p*-methoxyphenylacetic acid in combination with these thioxanthone esters.

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