polymer reports

Reactivity of substituted S-phenyl thiobenzoates as photoinitiators of radical polymerization

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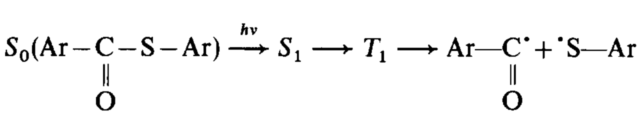
The reactivity in the excited state of new radical photoinitiators, S-phenyl thiobenzoates, was investigated. Laser flash photolysis experiments on various substituted compounds allowed both thiyl and benzoyl radicals to be observed. These two radicals arose from the α-cleavage of the C–S bond in the first excited triplet state. The ability to initiate radical polymerization was followed by dilatometry. From the results, it is found that the S-phenyl thiobenzoate photoinitiators can be even more reactive than benzoin ethers because of their better u.v. light absorption.

(Keywords: S-phenyl thiobenzoates; photoinitiators; radical polymerization)

INTRODUCTION

Many reactive cleavable photoinitiators have been synthesized, which belong to well known families of ketones[1–6]. Benzyl ketals, hydroxy alkyl acetophenones, dialkoxy acetophenones and amino ketones work according to an α cleavage process of the C–C bond under light exposure[7]. Photofragmentation of different chemical bonds has been explored and used for the development of new photoinitiator structures: N–O cleavage in benzoyl oxime esters[4], C–P cleavage in benzoyl phosphine oxides[4], C–S cleavage in aryl aryl sulphides[8] and sulphonyl ketones[9], C–O cleavage in oxysulphonyl ketones[10]. Recently, new α cleavable S-phenyl thiobenzoates have been introduced[11]. In an earlier paper[12], the photochemistry of these compounds was shown to proceed according to a C–S cleavage in the triplet state T_1 after light excitation of the $S_0 \rightarrow S_1$ transition:



$$S_0(\mathrm{Ar}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{S}-\mathrm{Ar}) \xrightarrow{h\nu} S_1 \longrightarrow T_1 \longrightarrow \mathrm{Ar}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}^{\bullet}+{}^{\bullet}\mathrm{S}-\mathrm{Ar}$$

In the present paper, both the reactivity in the excited states and the ability to initiate a radical polymerization are investigated and discussed in terms of the processes involved in various substituted compounds.

EXPERIMENTAL

Steady-state photopolymerization

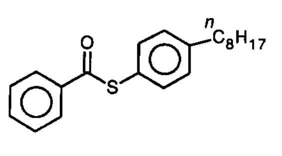
Solution polymerization reactions (methyl methacrylate, MMA, 7 M in toluene) have been carried out under monochromatic light ($\lambda = 366$ nm) from a 125 W medium pressure mercury lamp. The percentage conversion is followed by dilatometry.

Time resolved laser spectroscopy

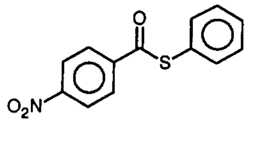
The experimental arrangement is described in detail elsewhere[13]. A Nd/YAG laser was used as the light excitation source (pulse duration ~3 ns). The time resolution of the analysing device was < 10 ns.

Samples

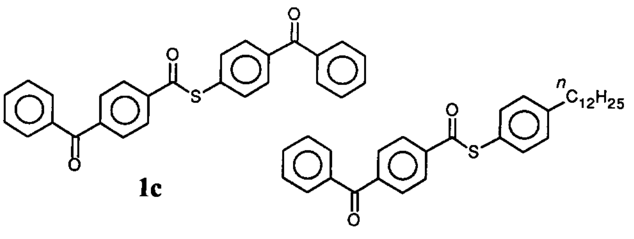
The following compounds were used[11]:



1a



1b



1c

1d

The ground state absorption spectra of compounds **1b**–**1d** and **2** are shown in *Figure 1*.

RESULTS AND DISCUSSION

Compounds **1a** and **1d** can be classified according to their structures. The initiators **1a** and **1b** are quite similar to compound **2** which has already been studied in an earlier paper[12]. Differences occur in the different substituents introduced on the phenyl side: and an alkyl chain for **1a** and a nitro group for **1b**. In the same way, the

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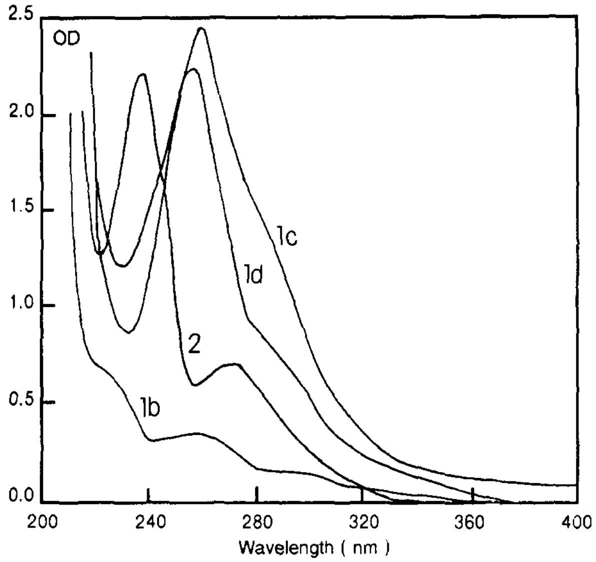


Figure 1 U.v. absorption spectra of **1b**–**1d** and **2** in deaerated toluene

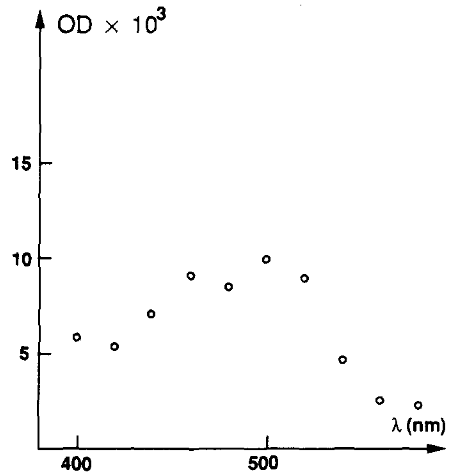
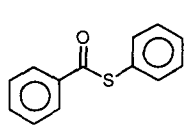


Figure 2 Overall transient absorption spectrum of **1a** in deaerated toluene

common structure of **1c** and **1d** is the compound **3**, whose excited triplet state has been studied previously[12].



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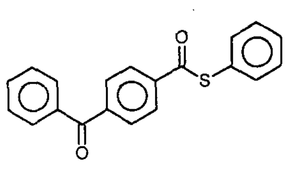

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In the present paper, the effect of different substituents upon the lifetime and deactivation of the first excited triplet state of the S-phenyl thiobenzoate photoinitiators **1a**–**1d** is considered.

Excited state processes

Compounds 1a and 1b. The laser excitation of **1a** at $\lambda = 355$ nm in deaerated toluene solution reveals the presence of a long-lived transient $R^\bullet$ absorbing around 480 nm. The absorption spectrum in *Figure 2* is quite similar to the one observed in the case of laser excitation of compound **2**[12]. The only difference arises from the maximum of the transient absorption at 500 nm. The observed spectrum can be the result of both benzoyl and arylthiyl radical absorption. It has been shown[14] that the thiyl radical ($C_6H_5S^\bullet$) presents an absorption band around 500 nm. The intensity of this band depends on the nature of the *para* substituent, the transient absorption bands at 490–525 nm produced by flash decomposition of *para*-disubstituted diaryl disulphides were attributed to the corresponding *para*-substituted benzenethiyl radicals[15,16].

Quenching by methylnaphthalene (MeN) results in the well-known triplet–triplet absorption ($\lambda = 420$ nm) and a decrease in the initial optical density (OD) of $R^\bullet$ due to the quenching of the triplet state by MeN. The usual Stern–Volmer plot:

$$\frac{1}{\mathrm{OD\,(MeN)}} \propto 1 + \frac{1}{k_T\tau_T^0}[\mathrm{MeN}]^{-1} \qquad (1)$$

cannot be accurately used in that case because the measured OD is the result of two components, both a decrease of OD ($R^\bullet$) and an increase of OD (^{3}MeN).

The quenching by an acrylic monomer such as MMA leads to a decrease of $[R^\bullet]$ as a consequence of the triplet state T_1 quenching reaction by the monomer:

$$\begin{tikzcd}
T_1 \arrow[r, "k_\alpha"] \arrow[dr, "k_q"', "\mathrm{MMA}"] & R^\bullet \\
 & \text{deactivation}
\end{tikzcd}$$

A Stern–Volmer plot (*Figure 3*)

$$\frac{1}{\mathrm{OD(R^\bullet)}} \propto 1 + k_q\tau_T^0[\mathrm{MMA}] \qquad (2)$$

[where OD($R^\bullet$) is the initial optical density of $R^\bullet$ immediately after the laser pulse] yields a value of $k_q\tau_T^0 = 1.8\,\mathrm{M}^{-1}$, comparable to the value obtained[12] in the case of compound **2**. However, neither k_q nor τ_T^0 can be evaluated. In this way, it can be concluded that alkyl substitution on the thiyl moiety of compound **1a** has little effect on the reactivity of this kind of photoinitiator in the presence of monomer.

In compound **1b** a NO_2 substituent has been introduced at the *para* position of the benzoyl moiety and the same experiments as above have been considered. The quenching by MeN yields $k_T\tau_T^0 = 11.5\,\mathrm{M}^{-1}$ (*Figure 4*) and a triplet state lifetime of 2.3 ns. Quenching by MMA according to equation (1) leads to $k_q\tau_T^0 = 2.14\,\mathrm{M}^{-1}$. The k_q value is equal to $9.3 \times 10^8\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (*Figure 5*).

In conclusion, **1a** and **1b** show the same characteristics as compound **2**. No significant effects due to the alkyl or nitro substituent at the *para* position on the thiyl side are observed.

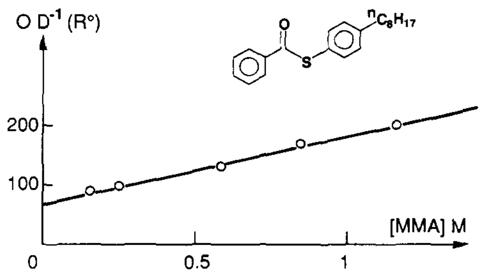


Figure 3 Quenching by MMA according to equation (2) for **1a**

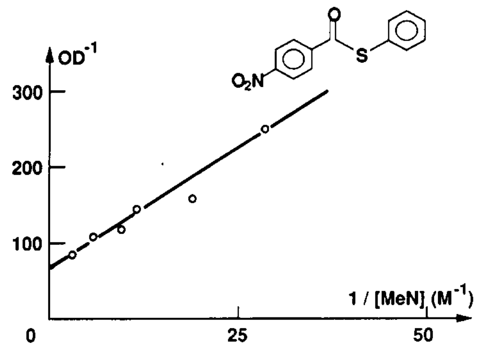


Figure 4 Stern–Volmer plot with MeN according to equation (1) for **1b**

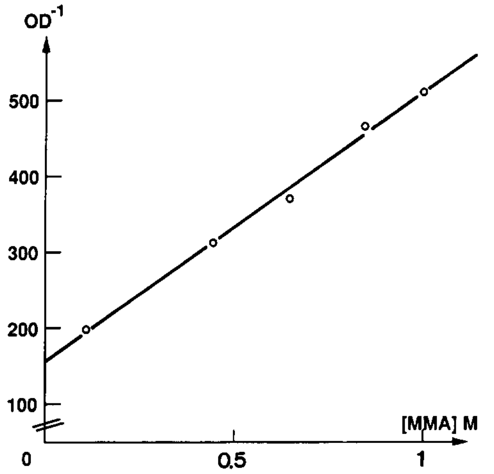


Figure 5 Quenching by MMA according to equation (2) for **1b**

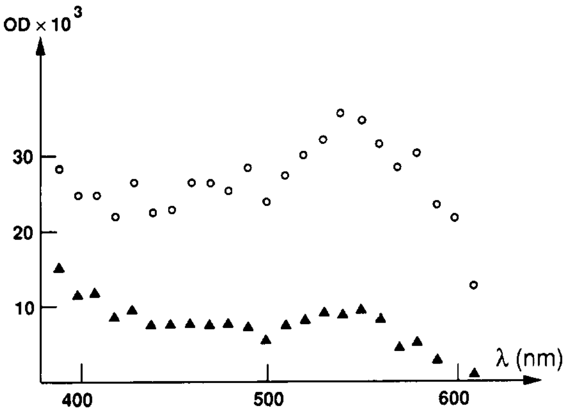
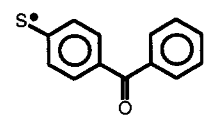


Figure 6 Transient absorption spectra of the triplet state (○, $t = 0\ \mu s$) and the radical (▲, $t = 11\ \mu s$) of **1c**

Compounds 1c and 1d. The behaviour of **1c** on laser excitation is similar to that of compound **3**. This excitation leads to the generation of two transients, clearly seen on the absorption spectra taken at two different times (*Figure 6*). The short-lived species is quenched by oxygen and MeN; thus, it is ascribed to the triplet state. The long-lived transient R$^\bullet$ decays according to second-order kinetics. As demonstrated earlier[12], the fast component in the decay curve is attributed to triplet relaxation. The transient spectra in *Figure 6* at time $t = 0\ \mu s$ and $t = 11\ \mu s$ are ascribed to triplet–triplet and R$^\bullet$ absorption, respectively. The maximum at $\lambda = 540$ nm could probably correspond to the radical



considering that most of the absorption maxima of thiyl radicals have appeared[15–17] between 490 nm and 525 nm. The observed shift of the maximum in **1c** is attributed to the nature of the *para* substituent (C_6H_5CO). Such a shift has been observed for the *p*-aminophenylthiyl radical where the maximum absorption was detected[15,18] around 550 nm.

The quenching by MMA monomer, leads to a decrease of the triplet state lifetime according to:

$$1/\tau = 1/\tau_T^0 + k_q[\mathrm{MMA}] \qquad (3)$$

A plot according to equation (3) is reported in *Figure 7*. The triplet lifetime $\tau_T^0 = 0.57\ \mu s$ and $k_q = 2.3 \times 10^6\ M^{-1}\ s^{-1}$.

The laser excitation of **1d** in deaerated toluene again yields two transient species. The absorption spectra in *Figure 8* are ascribed to the triplet–triplet absorption ($t = 0\ \mu s$) and to the R$^\bullet$ absorption ($t = 5\ \mu s$), respectively. There is a slight difference between the two spectra: the maximum at $\lambda = 480$ nm is more pronounced at $t = 0\ \mu s$ than at $t = 5\ \mu s$. The absorption spectra of **1a** and **1d** ($t = 5\ \mu s$) are quite similar, suggesting that the maximum

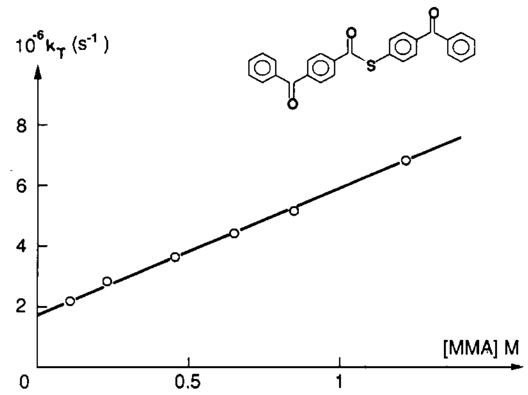


Figure 7 Quenching by MMA according to equation (3)

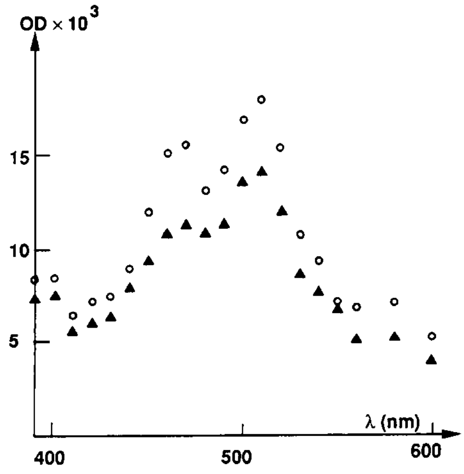


Figure 8 Transient absorption spectra of the triplet state (○, $t = 0\ \mu s$) and the radical (▲, $t = 5\ \mu s$) of **1d**

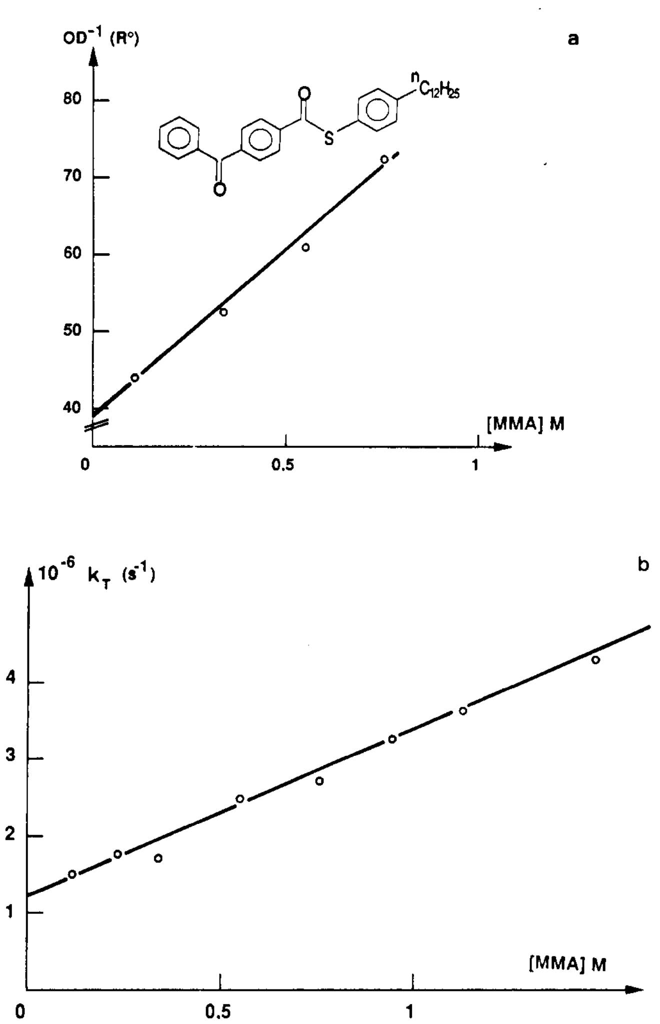
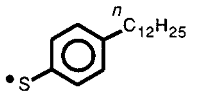


Figure 9 (a) Quenching of the radical of **1d** according to equation (4); (b) quenching of the triplet state by MMA according to equation (3)

at $\lambda = 510$ nm arises from the absorption of the alkyl-substituted thiyl radical:



Addition of MMA to a solution of **1d** in toluene results in a shortening of the triplet state lifetime according to equation (3) and a decrease in [R$^\bullet$]:

$$\frac{1}{\mathrm{OD(R^\bullet)}} \propto 1 + k_q \tau_T^0 [\mathrm{MMA}] \tag{4}$$

The results are treated in *Figure 9* by using equations (3) and (4), respectively. Fair agreement is found and a triplet state lifetime ($\tau_T^0 = 0.7\ \mu$s) and a bimolecular quenching rate constant ($k_q = 2.0 \times 10^6$ M^{-1} s^{-1}) are thus calculated.

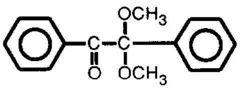
The four compounds **1a**–**1d** work through α cleavage. The yield of radical production (ϕ_α) in a typical photopolymerization reaction ([MMA] = 7 M) can be calculated according to equation (5):

$$\phi_\alpha = \frac{k_\alpha}{k_\alpha + k_q[\mathrm{MMA}]} = \frac{1}{1 + k_q \tau_T^0 [\mathrm{MMA}]} \tag{5}$$

where k_α is the α cleavage rate constant, an upper limit for this value being $1/\tau_T^0$. All the ϕ_α values are similar (~0.1). Considering the values of ϕ_α (*Table 1*), compounds **1c** and **1d** might be more efficient photoinitiators than **1a** and **1b**.

Photopolymerization experiments

Typical percentage conversion *versus* time curves for the photopolymerization of MMA (7 M in toluene), initiated by compounds **1b**–**1d** **2**, **3** and the well-known dimethoxyphenyl acetophenone **4** are displayed in *Figure 10*.



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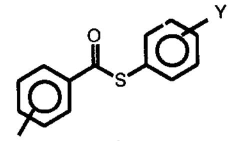
The relative rate of polymerization and relative yield of initiation (the reference is compound **4**) are listed in *Table 2*. From these results, it is apparent that S-phenyl thiobenzoates are efficient photoinitiators of acrylate

Table 1 Triplet state lifetimes (τ_T^0) in deaerated toluene solution, rate constant of quenching by MMA (k_q) and yield of radical production through α cleavage (ϕ_α) for compounds **1a**–**1d**^{a}



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	X	Y	τ_T^0 (ns)	$10^6 k_q$ (M^{-1} s^{-1})	$100\phi_\alpha$
a	H	4-nC$_8$H$_{17}$	^{a}	^{a}	7.5
b	4-NO$_2$	H	2.3	93	6.2
c	4-PhCO	4-PhCO	570	2.3	9.8
d	4-PhCO	4-nC$_{12}$H$_{12}$	700	2.0	9.5

^{a}[MMA] = 7 M. For **1**, $k_q \tau_T^0 = 1.8$ M^{-1}; for **2**, $\tau_T^0 \approx 5$ ns, $k_q \approx 4 \times 10^8$ M^{-1} s^{-1}

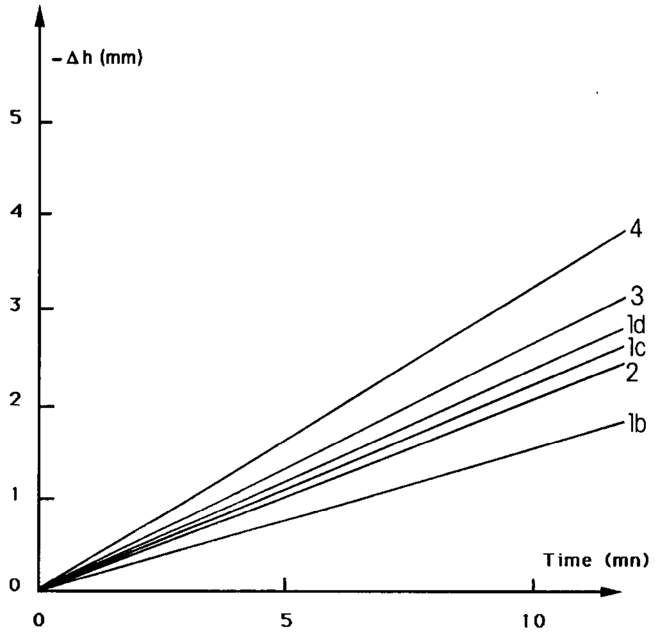

Figure 10 Evolution of the percentage conversion of MMA (7 M in toluene) as a function of time, followed by dilatometry

Table 2 Relative rate of polymerization (r_p, ratio between the rate of polymerization of the various photoinitiators and **4**), relative yield of initiation (ϕ_i) and yield of cleavage (ϕ_α)^a

	$100r_p$	ϕ_i	$100\phi_\alpha$
1b	47	22	6.2
1c	68	46	9.8
1d	73	53	9.5
2	63	39	6.6
3	82	67	15
4	100	100	100

$^a\phi_i=100r_p^2$ (for **4**, $\phi_i=100$ and $r_p=1$). [MMA]=7M in toluene. Optical density of the photoinitiator=0.1 at $\lambda=366$nm

polymerization, although their yields in radical production remain low, compared to benzoin ethers or **4**. Recently, thiyl radicals have been considered as poor initiating species[8] and active scavengers for the growing macromolecular chains[12]. Moreover, because of their u.v. absorption, S-phenyl thiobenzoates, when used at a fixed concentration, present a better light absorption than **4**, which even results in a higher percentage conversion (compared to **4** and related benzoin ethers) of the monomer under polychromatic light[11].

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