

# Photochemistry and photopolymerization activities of novel phenylthiobenzophenone and diphenylthiophene photoinitiators

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The photoinduced polymerization activities of seven novel phenylthio substituted benzophenones have been determined and compared to that of benzophenone itself in different monomers and prepolymers using real time infra-red (RTi.r.) and pencil hardness methods. Four novel dibenzothiophene compounds have also been included in the investigation to examine the influence of bridging the sulfur atom between the benzophenone chromophore and phenyl groups *via* an alicyclic bridge. Absorption, fluorescence and phosphorescence analysis, as well as photoreduction/photolysis studies have been undertaken on the compounds and the data is inter-related to their photopolymerization activities. Fluorescence and phosphorescence analysis indicates a high rate of intersystem crossing to the triplet state. The latter is essentially a mixed excited  $n\pi/\pi\pi^*$  state in nature for the phenylthio derivatives as indicated by the phosphorescence lifetime data and quantum yields of emission. In comparison the dibenzothiophenes retained much of their  $n\pi^*$  character coupled with a rigid molecular structure giving rise to very high phosphorescence quantum yields. Compared with benzophenone all the phenylthio derivatives exhibit higher activity using commercial pencil hardness curing. Strong synergism is also observed with a tertiary amine compared to the activities of the dibenzothiophenes. This is also generally reflected in the RTi.r. data. The dibenzothiophenes exhibit lower activities than the phenylthio derivatives, but remained somewhat greater than that of benzophenone. The enhanced photoactivities of the phenylthio derivatives are associated with their higher extinction coefficients and longer wavelength absorptions in the near ultra-violet region above 300 nm. Steric effects in the case of the dibenzothiophenes are responsible for their poor synergism with tertiary amines. Their photoreduction quantum yields in the presence of an amine match exactly their photopolymerization effects determined by RTi.r. Microsecond flash photolysis showed weak ketyl radical formation in the region 500–600 nm due to hydrogen atom abstraction by the excited triplet state of the benzophenone chromophore in both structures. Significant transient absorption in region 300–400 nm is suggestive of side chain scission giving rise to additional aryl radical species. © 1997 Elsevier Science Ltd.

(Keywords: photochemistry; photoinitiators; photopolymerization)

## INTRODUCTION

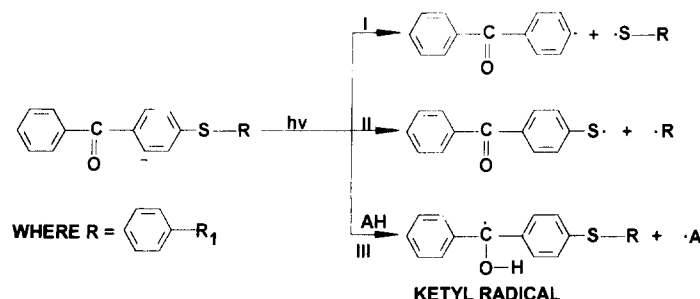
The present trend of producing tailor-made photoinitiators for specific applications has resulted in the prediction of relationships between molecular structure and properties<sup>1,2</sup>. The ever increasing market drive for better photoinitiators for coatings technology can be answered only by improving our knowledge concerning the mode of action of the photoinitiators under various conditions. In recent years there has been extensive interest aromatic ketone systems containing thio functionalities<sup>3–9</sup>. For example, the 4-methylthio derivative of benzophenone has increased photocuring activity over that of benzophenone which is associated with its red shifted absorption and lower triplet state activity toward the monomer in terms of their hydrogen atom abstracting ability<sup>8,9</sup>. Aside from the hydrogen atom abstraction reaction to form a ketyl radical

these types of compounds may also undergo photolysis reactions at the C–S bond as depicted in *Scheme 1*. These reactions are equally applicable to keto-sulfoxide derivatives<sup>3</sup> to produce alkyl and sulfoxide radicals. Direct scission at the aryl–S bond is also feasible to produce aryl and thio radicals<sup>3</sup>. Recently, we presented a study on the effect of different alkylthio groups on the photopolymerization activity of the benzophenone chromophore<sup>10</sup>. Increased absorption maxima and the formation of aryl and ketyl radicals were primarily responsible for their enhanced activities.

In view of the fact that structure and electron density appear to play a crucial role in influencing excited state activity for photocuring we have examined the photopolymerization/photocuring activities of eight novel 4-substituted phenylthiobenzophenones. Here the phenyl group is linked to the benzophenone chromophore *via* a freely rotating C–S bond. These structures are compared to the activities of a range of dibenzothiophenes where the

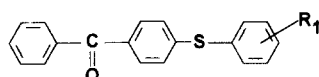
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RADICALS PRODUCED FROM PHOTOREACTIONS OF PHENYLTHIOBENZOPHENONES



STRUCTURES 1-8

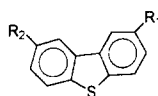
PHENYLTHIOBENZOPHENONES



Compound 1: Benzophenone Control	MPT: 49-51°C
Compound 2: R <sub>1</sub> =H 4-phenylthiobenzophenone	MPT: 73-74°C
Compound 3: R <sub>1</sub> =4-Me 4-(4-methylphenylthio)benzophenone	MPT: 73-83°C
Compound 4: R <sub>1</sub> =3-Me 4-(3-methylphenylthio)benzophenone	MPT: 37-39°C
Compound 5: R <sub>1</sub> =2-Me 4-(2-methylphenylthio)benzophenone	MPT: Liquid
Compound 6: R <sub>1</sub> =4-iPr 4-(4-isopropylphenylthio)benzophenone	MPT: 69-70°C
Compound 7: R <sub>1</sub> =4-MeO 4-(4-methoxyphenylthio)benzophenone	MPT: 89-90°C
Compound 8: R <sub>1</sub> =Cl 4-(4-chlorophenylthio)benzophenone	MPT: 130-131°C

STRUCTURES 9-12

DIBENZOTHIOPHENES



Structure 9: R <sub>1</sub> = PhCO R <sub>2</sub> =H	2-benzoyl dibenzothiophene	M.Pt: 156-157°C
Structure 10: R <sub>1</sub> = R <sub>2</sub> = COC <sub>6</sub> H <sub>5</sub>	2,8-dibenzoyl-dibenzothiophene	M.Pt: 158-159°C
Structure 11: R <sub>1</sub> = 3-MePhCO R <sub>2</sub> =H	2-(3-toluy)-dibenzothiophene	M.Pt: 83-86°C
Structure 12: R <sub>1</sub> = 4-MeOPhCO R <sub>2</sub> =H	2-benzoyl dibenzothiophene	M.Pt: 114-116°C

Scheme 1

phenyl ring is linked to the sulfur atom *via* an alicyclic ring. These activities are related to their photochemical and spectroscopic properties and the data compared with those of the commercial initiator, benzophenone, as a reference system.

EXPERIMENTAL

Materials

All the solvents, triethylamine, diethylethanolamine, methyl-diethanolamine, benzophenone and quinine sulfate used in this work were obtained from Aldrich Chemical Co. Ltd, UK, and were of analar, spectroscopic or HPLC grade quality. The phenylthiobenzophenones (2-8) and dibenzophenones (9-12) were supplied by the Great Lakes Fine Chemicals Ltd., Widnes, UK. The corresponding structures 1-8 and 9-12 are shown. All the compounds are chromatographically pure and have verified elemental C, H and S analysis.

Spectroscopic measurements

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-50B luminescence spectrometer. Fluorescence quantum yields were obtained by the relative method using quinine sulfate in 0.05 M sulfuric acid as a standard<sup>11</sup>. The quantum yield of quinine sulfate was assumed to be 0.55. Phosphorescence quantum yields were obtained in ethanol at 77 K in liquid nitrogen using the relative method with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol<sup>11</sup>. Clear glasses were obtained in absolute ethanol. All spectra were corrected using a Perkin-Elmer IBM compatible GEM package with an appropriate built-in correction factor for this purpose for the photoresponse of the photomultiplier and optics. Blank measurements were obtained on the solvents alone to correct for Raman scatter and subtracted from the original sample spectra. Phosphorescence lifetime measurements were obtained under the same condition (77 K) using benzophenone as a standard for lifetime comparison (6.0 ms). Under this condition the influence of oxygen diffusion will be insignificant. Measurements were obtained *via* the GEM software and electronically gating the emission signal decay taking into account the phosphorescence lifetime and delay/gate widths in the data acquisition.

Photoreduction quantum yields

Absolute quantum yields of photolysis ( $\phi_p$ ) of the initiators were determined in acetonitrile at 10<sup>-5</sup> M using an irradiation wavelength of 365 nm, selected from

a Philips high pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatted at 30°C and the solutions were nitrogen (< 5 ppm O<sub>2</sub>) saturated. The absorbed light intensity was measured using an International Light Model 700 radiometer previously calibrated by the Aberchrome 540 actinometer<sup>12,13</sup>. Because of product formation during the early stages of irradiation interfering with the quantum yield measurements only subsequent photolysis rates could be measured against light intensity for the range of phenylthiobenzophenones.

#### RTi.r.

The initiators were dissolved in a minimum quantity (2–3 cm<sup>3</sup> of tetrahydrofuran) followed by mixing with a prepolymer, Actilane 420 (Ethoxylated Bisphenol-A-dimethacrylate) (Akcros Chemicals, Eccles, Manchester, UK) (0.001 M). Traces of solvent were then removed by flushing with argon for 30 min followed by addition of 1% w/w of the co-initiator *p*-ethyl-4-(dimethylamino)benzoate (EDB) (Great Lakes, Widnes, UK).

The resin was then placed between pieces of low density polyethylene using a separator to give a film thickness of 50 μm. The polyethylene holder was then placed between two infrared salt plates and placed in the sample beam. Two polyethylene film samples were used as the reference. The decrease in absorbance at 1638 cm<sup>-1</sup> of the vinyl absorption band was then monitored using a Perkin-Elmer 842 dispersive infra-red spectrometer in real-time mode during irradiation using a fibre optic arrangement. The irradiation source used here was an ILC 302UV (Laser Lines Ltd, Beaumont Close, Banbury, Oxon, UK) (150 watt Xenon, 200 nm—i.r.) switchable between ultra-violet (u.v.) and visible light with a cut-off point at 400 nm. The u.v. energy up to 400 nm was measured at 150 mwatts cm<sup>-2</sup>. Plots of percentage conversion with time were obtained from which second plots of mol l<sup>-1</sup> versus time in s were obtained. From the initial slopes of the second plots *R<sub>p</sub>* values (mol l<sup>-1</sup> s<sup>-1</sup>) were obtained.

#### Commercial curing

The photoinitiators (2% w/w) and methyl-diethanolamine (3% w/w) were dissolved in a resin formulation made up of 55% Photomer 3148 (Epoxy acrylate oligomer), 20% tripropylene glycol diacrylate and 25% trimethylol propane triacrylate from Akcros chemicals Ltd, Manchester, UK. Cure speeds of the formulations were assessed using a single 80 W cm<sup>-1</sup> tube Minicure Unit (Jiga and Lamps Ltd, UK) coated at 12 μm thickness on glass slides and cured to give a pencil hardness of 2H. This is a simple test whereby the coating is cured such that it is able to be scored by a 2H grade pencil<sup>1,2</sup>. Cure rates were assessed by the belt speed for effective cure.

#### Microsecond flash photolysis

End-of-pulse transient absorption spectra on the microsecond time scale were obtained using a Hi-Tech kinetic flash photolysis apparatus equipped with two xenon-filled flash lamps (200 nm—i.r., 300 J) (operated at 10 kV) and a 150 W tungsten-halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope. Solutions (5 × 10<sup>-5</sup> M) were degassed using white spot nitrogen gas (< 5 ppm O<sub>2</sub>) and analysed in 10 cm pathlength quartz cells. Flash photolysis measurements were also carried out in the presence of triethylamine at 10<sup>-4</sup> M concentration.

## RESULTS AND DISCUSSION

### Photocuring and photopolymerization

The photopolymerization and photocuring data using RTi.r. and pencil hardness for the phenylthiobenzophenones and dibenzothiophenes are shown in *Tables 1* and *2* respectively. In the first instance for photocuring it is seen that all the substituted phenylthio derivatives exhibit a significantly higher activity than that of benzophenone itself. This trend is also reflected in the RTi.r. data from the *R<sub>p</sub>* values although under these conditions the unsubstituted phenylthio derivative exhibited the lowest activity of the phenylthio initiators. Under RTi.r. conditions the addition of a tertiary amine resulted in enhanced synergism except for the 4-isopropyl derivative. The dibenzothiophenes exhibit lower photocuring activities than the phenylthio derivatives and are only marginally more active than that of benzophenone (*Table 2*). Compound 11 exhibits the lowest photoactivity. The RTi.r. data also shows that synergism with a tertiary amine was not as effective with the dibenzothiophenes to the extent observed with the phenylthio derivatives.

### Spectroscopic properties

Absorption maxima and extinction coefficients (logarithmic) of all the phenylthio and dibenzothiophene derivatives examined here are compared by the data in *Tables 3* and *4*) respectively for a range of solvents. The absorption maximum for benzophenone is the main benzenoid ππ\* transition which undergoes a small red shift in solvents of increasing polarity. Substitution of phenylthio groups markedly red shifts the main absorption maximum above 300 nm due to increased electron donation *via* the sulfur atom. This would certainly account for their increased photoinitiation activity during photocuring. There is also a small red shift in their absorption maxima with increasing

**Table 1** Photopolymerization (RTi.r.) (in actilane 420) and photocuring (in epoxy acrylate) data with benzophenone and phenylthiobenzophenones as initiators

Compound	Photocuring <sup>a</sup> (m min <sup>-1</sup> )	Photopolymerization (RTi.r.) ( <i>R<sub>p</sub></i> mol dm <sup>-3</sup> s <sup>-1</sup> )	
		Without amine	With amine <sup>b</sup>
1	3.0	3.03	63.13
2	3.7	5.49	30.61
3	3.7	8.65	59.69
4	4.1	9.74	60.06
5	4.1	9.57	63.49
6	4.1	7.79	8.85
7	4.7	7.23	48.87
8	3.3	10.71	62.56

<sup>a</sup>2% w/w methyl-diethanolamine (data ± 0.2)

<sup>b</sup>1% w/w *p*-ethyl-dimethylaminobenzoate (EDB) (data ± 0.2)

**Table 2** Photopolymerization (RTi.r.) (in actilane 420) and photocuring (in epoxy acrylate) data with dibenzothiophenes as initiators

Compound	Photocuring <sup>a</sup> (m min <sup>-1</sup> )	Photopolymerization (RTi.r.) ( <i>R<sub>p</sub></i> mol dm <sup>-3</sup> s <sup>-1</sup> )	
		Without amine	With amine <sup>b</sup>
9	3.2	6.96	21.32
10	3.0	5.84	33.67
11	1.3	0.83	9.44
12	3.1	5.40	14.79

<sup>a</sup>2% w/w methyl-diethanolamine (data ± 0.2)

<sup>b</sup>1% w/w *p*-ethyl-dimethylaminobenzoate (EDB) (data ± 0.2)

**Table 3** Absorption properties of phenylthiobenzophenones in different solvent media

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
<b>1</b>	253	4.05	254	4.24	257	4.14	255	4.16
<b>2</b>	311	4.22	318	4.19	314	4.19	313	4.20
<b>3</b>	313	4.23	319	4.13	315	4.23	311	4.22
<b>4</b>	312	4.14	317	4.22	315	4.27	312	4.16
<b>5</b>	313	4.28	318	3.78	314	4.23	313	4.25
<b>6</b>	314	4.27	319	4.14	314	4.25	313	4.39
<b>7</b>	314	4.01	319	4.18	316	4.22	313	4.16
<b>8</b>	309	4.17	316	4.16	313	4.28	308	4.45

 $\epsilon$  is  $\pm 0.01$ **Table 4** Absorption properties of dibenzothiophenes in different solvent media

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
<b>9</b>	270/293	4.33/4.19	273/297	4.20/4.03	270/295	4.32/4.13	268/295	4.27/4.07
<b>10</b>	270/293	4.42/4.28	273/297	4.46/4.28	269/294	3.99/3.81	26/293	4.44/4.25
<b>11</b>	255/286/326	4.39/4.22/3.59	287/313/325	4.09/3.66/3.63	285/313/325	4.25/3.86/3.84	285/323	4.12/3.62
<b>12</b>	268/290	4.40/4.36	272/296	4.34/4.31	270/296	4.33/4.31	270/295	4.34/4.32

 $\epsilon$  is  $\pm 0.01$ **Table 5** Fluorescence properties of dibenzothiophenes in different solvents

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	$\lambda_{\max}$	$\phi_f$	$\lambda_{\max}$	$\phi_f$	$\lambda_{\max}$	$\phi_f$	$\lambda_{\max}$	$\phi_f$
<b>9</b>	343	0.0005	348	0.0005	346	0.0004	345	0.0022
<b>10</b>	344	0.0005	348	0.0008	345	0.0001	344	0.019
<b>11</b>	330/343	0.022	336/346	0.0016	347	0.0032	334/344	0.019
<b>12</b>	343/443	0.0025	346/462	0.0010	347/457	0.0007	340/455	0.0026

 $\phi_f \pm 0.0001$ 

solvent polarity indicative of the increased  $\pi$  character of the benzenoid system. The dibenzothiophenes exhibit smaller red shifts in their absorption maxima from that of benzophenone when compared with those for the phenylthio derivatives (Table 3). In this case two/three main absorption bands are observed whose wavelength maxima undergo minor blue and red shifts with increasing solvent polarity. This suggests a stable rigid molecular structure of possible mixed  $n\pi/\pi\pi^*$  character. This effect would account for their relatively lower activity than the phenylthio derivatives and minor activity over that of benzophenone.

Luminescence analysis of the phenylthiobenzophenone structures (2–8) indicated no significant fluorescence. As for benzophenone itself, this suggests that there is a high rate of intersystem crossing to the triplet state. Although phosphorescence was in fact, observed for all the compounds investigated their quantum yields were significantly less than that of benzophenone itself except that observed for structure 6. Weak fluorescence was observed from the dibenzothiophenes (Table 5). Quantum yields and emission wavelength maxima are not significantly influenced by solvent polarity and is again indicative of the presence of a rigid molecular lowest excited singlet mixed  $n\pi/\pi\pi^*$  state. The spectral features of the phosphorescence of the phenylthio derivatives are shown in Table 6 where it is noted that the emission wavelength maxima are red shifted from those of benzophenone, which is consistent with the

**Table 6** Phosphorescence properties of phenylthiobenzophenones in ethanol

Compound	Ethanol		
	$\lambda_{\max}$	$\phi_p^a$	$\tau$ (ms) <sup>b</sup>
<b>1</b>	414,443,474	0.74	6.0
<b>2</b>	444/471	0.12	57.1
<b>3</b>	443/470	0.14	68.9
<b>4</b>	444/470	0.15	22.7
<b>5</b>	439/469	0.49	77.7
<b>6</b>	443/469	0.80	81.4
<b>7</b>	443/470	0.28	62.7
<b>8</b>	442/468	0.24	99.0

<sup>a</sup>  $\pm 0.05$ <sup>b</sup>  $\pm 0.5$ 

electron donating effect of the phenylthio group. The emission spectra all retain some aromatic carbonyl symmetry while the emission lifetimes suggest partial mixing with some  $\pi\pi^*$  character possibly via a low lying mixed  $n\pi^*/\pi\pi^*$  state. Structure 6 exhibited a higher phosphorescence quantum yield than that of benzophenone itself. This could possibly be associated with enhanced molecular rigidity due to steric hindrance imparted by the isopropyl group. This effect could also account for weak exciplex formation with a tertiary amine and hence the much reduced synergistic activity by this structure on photopolymerization by RTi.r. (Table 1).

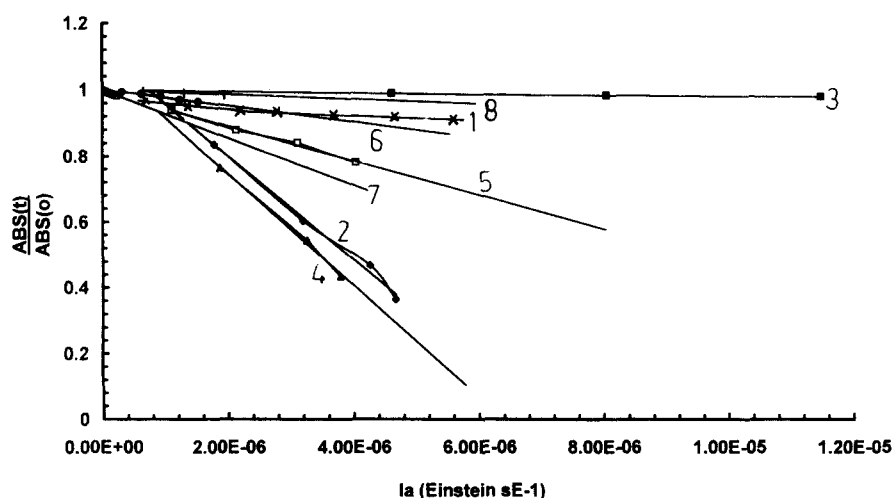


Figure 1 Photolysis of phenyl thiobenzophenones ( $10^{-5}$  M) at 365 nm in acetonitrile with diethylethanolamine ( $10^{-4}$  M)

Table 7 Phosphorescence properties of dibenzothiophenes in ethanol

Structure	$\lambda_{\max}$	$\phi_p^a$	$\tau$ (ms) <sup>b</sup>
9	421,450,484,521	0.65	11.3
10	422,450,482,520	0.86	12.5
11	424,449,481,520	0.23	15.8
12	417,446,478,516	0.97	10.0

<sup>a</sup>  $\pm 0.05$

<sup>b</sup>  $\pm 0.5$

Table 8 Photoreduction quantum yields at 365 nm for the dibenzothiophenes in acetonitrile ( $10^{-5}$  M) in the presence of diethylethanolamine ( $10^{-4}$  M)

Structures	$\phi_r$
9	0.210
10	0.380
11	0.017
12	0.120

The dibenzothiophenes appear to strongly retain their  $n\pi^*$  character. This is evidenced by the phosphorescence data shown in Table 7. The dibenzothiophenes exhibit short emission lifetimes and emission spectra with typical carbonyl symmetry. This is reflected in the observation of very high phosphorescence quantum yields with structure 12 exhibiting a most unusually high quantum yield of 0.97. These results are consistent with the presence of a very rigid molecular alicyclic structure where the molecular orbitals of the sulfur electrons are twisted out-of-plane of the benzoyl ring giving rise to much reduced conjugation and retention of the  $n\pi^*$  character of the lowest excited triplet state. This would account for reduced spectral shifts in absorption maxima and lower photopolymerization activities. Reduced activities in the presence of a tertiary amine would be consistent with the large molecular structure sterically hindering exciplex formation.

#### Photoreduction

Photolysis of some of the phenylthio initiators in acetonitrile in the presence of an amine, diethylethanolamine, gave product formation which interfered in the absorption measurements. However, during the later stages of irradiation photolysis rates could be measured and these are compared in Figure 1. It is interesting to note that a number of the compounds undergo rapid photolysis. Benzophenone itself exhibits a slow rate of photoreduction under these conditions except for compounds 3 and 8. These derivatives like the alkylthio derivatives can therefore, undergo direct photolysis via the excited singlet state to give phenylthio and aryl radicals<sup>3</sup>. Photoreduction quantum yields of the dibenzothiophenes are relatively high in acetonitrile/amine media (Table 8) and match exactly their photopolymerization activities as measured by RTi.r. in the presence of an amine cosynergist (Table 2). Direct intermolecular hydrogen atom abstraction by the lowest excited triplet

$n\pi^*$  state of the dibenzothiophene from the amine is the most likely process.

#### Micro-second flash photolysis

End-of-pulse transient absorption spectra for compounds 6 and 9 are shown in Figures 2 and 3 respectively as typical examples. All the phenylthio compounds displayed similar spectra of similar intensity in the region 300–700 nm. Essentially two main absorption bands were observed in the regions 300–400 and 500–700 nm. The latter is normally associated with the formation of the ketyl radical produced by the triplet state of the aromatic ketone abstracting a hydrogen atom from the environment (solvent). In the presence of triethylamine some radical anion may also be formed although its spectrum is difficult to distinguish with that of the ketyl radical and the kinetics of decay complex. In this case the amine appears to have little effect apart from a small enhancement in the shorter wavelength absorption for both derivatives<sup>14</sup>. The main feature of interest is the evident low intensity absorption at 550–600 nm for both compounds relative to those at shorter wavelengths 300–400 nm. The former peak is normally relatively higher in intensity for benzophenone<sup>14</sup>. The peak in the region 300–400 nm is also partially due to the ketyl radical but in this case is significantly higher in intensity especially in the presence of a tertiary amine. In the case of compound 6 the phenylthio group is known to photolyse to produce arylthio and aryl radicals. The shorter wavelength spectrum in Figure 2 has two absorption bands in the region 300–400 nm. The first lower intensity band is associated with the ketyl radical<sup>14</sup> while that at longer wavelengths with a maximum at 380 nm corresponds with the aryl benzophenone type radical<sup>3</sup> depicted in Scheme 1 (I). The formation of aryl type radicals is also evident in Figure 3 associated with side chain photolysis at the sulfur-ring. The longer wavelength shoulder is evident at 380 nm in the

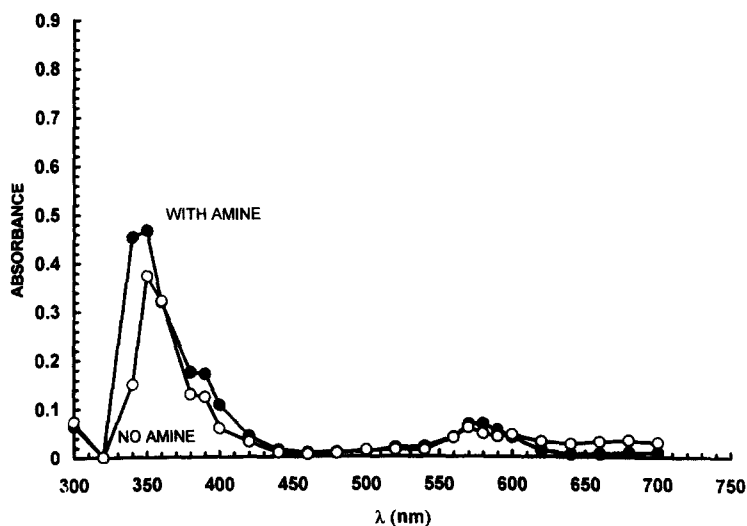


Figure 2 End-of-pulse transient absorption spectra of compound anaerobic 2-propanol ( $5 \times 10^{-5}$  M) in absence and presence triethylamine ( $10^{-4}$  M)

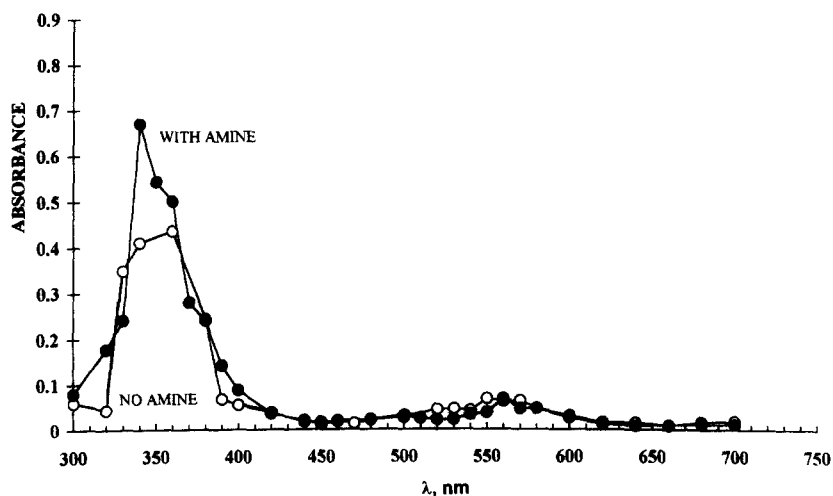


Figure 3 End-of-pulse transient absorption spectra of compound anaerobic 2-propanol ( $5 \times 10^{-5}$  M) in absence and presence triethylamine ( $10^{-4}$  M)

presence of the amine while the shorter wavelength peak is due to the ketyl radical.

## CONCLUSIONS

Using commercial pencil hardness curing all the phenylthio derivatives exhibit much higher activity than that of benzophenone. Strong synergism is also observed with a tertiary amine compared to the activities of the dibenzothiophenes. This is also generally reflected in the RTi.r. data. The dibenzothiophenes exhibit lower activities than the phenylthio derivatives but remained somewhat greater than that of benzophenone. The enhanced photoactivities of the phenylthio and dibenzothiophene derivatives are associated with their higher extinction coefficients and longer wavelength absorption maxima in the near u.v. region above 300 nm when irradiated under realistic polychromatic conditions. Steric effects restricting exciplex formation in the case of the dibenzothiophenes are responsible for their poor synergism with tertiary amines. The photoreduction quantum yields of dibenzothiophenes in the presence of an amine match exactly their photopolymerization effects determined by RTi.r. Fluorescence and phosphorescence analysis indicates a high rate of intersystem crossing to the triplet state for both sets of derivatives. The latter is essentially a mixed excited  $n\pi/\pi\pi^*$

state in nature for the phenylthio derivatives as indicated by the phosphorescence lifetime data and quantum yields of emission. In comparison the dibenzothiophenes retained much of their  $n\pi^*$  character coupled with a rigid molecular structure, giving rise to very high phosphorescence quantum yields. Microsecond flash photolysis showed weak ketyl radical formation in the region 500–600 nm due to hydrogen atom abstraction by the excited triplet state of the benzophenone chromophore in both structures. Significant transient absorption in region 300–400 nm is suggestive of side chain scissions giving rise to additional aryl radical species. These species are also likely contenders as initiators of free radical polymerization.

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