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Non-extractable photoinitiators based on thiol-functionalized benzophenones and thioxanthones

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ABSTRACT

Non-extractable photoinitiators could be advantageous for use in biological, electronic, and food packaging applications. Therefore, thioxanthone and benzophenone derivatives were synthesized from 1,6-hexane dithiol and chlorinated benzophenone or thioxanthone. The efficiency of thiol-functionalized photoinitiators in combination with amine co-initiators was compared to benzophenone and isopropylthioxanthone with amine co-initiators, and the cleavage of photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one in acrylic resins. The reaction kinetics were analyzed using photo-differential scanning calorimetry and real-time FTIR. Coating physical properties were evaluated by pendulum and pencil hardness, steel–wool scratch and mandrel bend tests. The non-extractable photoinitiators had higher absorbance than their benzophenone or isopropylthioxanthone counterparts due to the sulfide substitution on the phenyl ring, and the free thiol groups reacted with the acrylate by either an amine catalyzed Michael addition or a free-radical chain process. The combination of thiol-functionalized photoinitiators with secondary amines provides an efficient photoinitiator system that is locked into the photopolymerized network and cannot be extracted with typical solvents.

1. Introduction

During the past 2-3 decades, photopolymerization has expanded rapidly due to a wide range of economic and ecological advantages. Accordingly, UV light sources and efficient monomers and photoinitiators have been developed [1]. Photoinitiators play an essential role in all successful photocurable formulations. There have been significant advances in development of efficient photoinitiators that can be synthesized from readily available starting materials and have high extinction coefficients with absorbance bands that correspond to output lines from medium-pressure lamps [2–11]. These photoinitiators provide excellent performance in a wide range of applications such as coating on floor tiles, optical fibers, photoresists, furniture, and compact disks. However, there are still limitations in using traditional photoinitiators for critical applications involving biological, electronics materials and food packaging [7,12]. Specifically, photoinitiators not consumed in the photoinitiation process remain in the cured coating and can migrate to interface surfaces where they can ultimately diffuse into and contaminate substrates. Before discussing options for overcoming photoinitiator migration, a brief overview of traditional photoinitiators will be presented.

There are two basic types of photoinitiators which have found widespread commercial use: cleavage and hydrogen abstraction [11]. For cleavage type photoinitiators, which are the most efficient, initiating radicals are produced by an intramolecular bond cleavage upon absorption of a photon of the light. On the other hand, hydrogen abstraction

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type photoinitiators which are generally less expensive generate initiating radicals via a biomolecular hydrogen transfer between the excited state photoinitiator and hydrogen donors such as alcohols, amines and thiols. The most effective system is a sequential electron transfer/proton transfer process involving hydrogen transfer from an amine to produce a radical at the alpha carbon and a comparatively stable semi-pinacol radical upon transfer of the hydrogen to the oxygen carbonyl. The radical on the amine initiates polymerization while the semi-pinacol radical is stable and only serves as a chain terminator [13,14]. The biomolecular hydrogen transfer must compete with other side reactions such as oxygen quenching of the excited state photoinitiator. The efficiency of hydrogen abstraction type photoinitiators are strongly affected by the structure of the amine co-initiator [13,15]. For example, tertiary amines such as *N*-methyldiethanolamine (MDEA) are widely used as an efficient co-initiator which can react with oxygen [16], thus preventing oxygen inhibition of free-radical polymerization. Interestingly, secondary amines have been reported to add to methacrylates by an efficient Michael addition process which ultimately allows them to be efficiently incorporated into network systems, thus preventing any residual amine in the system from migrating to the surface of cured films [17]. In order to enhance the extinction coefficients of benzophenone and thioxanthone type photoinitiators, sulfide linkages have been attached to the phenyl rings [8,9]. The resultant sulfides are extremely efficient, have high extinction coefficients and red-extended absorption compared to their unmodified analogs. Recently, thiol modified initiators based on thioxanthones were synthesized and evaluated as one-component photoinitiator systems [15,16]. It is not necessary to add amine co-initiator, although adding amine increases the efficiency. In these cases, the thiols were substituents on the aromatic ring.

Despite of significant advances in traditional photoinitiating systems, their use in several applications such as food packaging and electronics is very limited due to requirements of low extractable materials in the final cured materials [7]. There have been several attempts to sort out these issues related to migration of photoinitiator using two main strategies: macrophotoinitiators or photoinitiators with reactive monomer groups such as acrylates attached in order to provide a reactive conduit for incorporation into the network during the curing process. Problems with traditional macrophotoinitiators include low efficiency, higher viscosity and reduced solubility compared to traditional photoinitiators. To overcome these issues, molecular weight adjustments and incorporation of multiple initiating sites into a single macromolecule have been investigated [7]. Small molecule photoinitiators with reactive functional groups are very effective in many cases. Monomers which are both photoinitiators and reactive monomers that are completely consumed during the polymerization process have also been evaluated [16–28]. For example, conjugated vinyl ester type monomer initiators [22] as well as maleimides [27] were found to be effective in initiating acrylate polymerization. Unfortunately when the vinyl ester or maleimides were incorporate into the network, they were no longer effective as initiators and hence high conversions could not be attained. Also maleimides have toxicity issues.

In this paper, we describe the synthesis of a new class of sulfide substituted thioxanthones and benzophenones with aliphatic thiol end groups. Characterization of these photoinitiators both in the presence and absence of co-initiator amines in acrylic resins shows to be very efficient in initiating acrylate polymerization. Most importantly the initiator still remains effective even after being incorporated into the network as it is forming. Hence, high conversions are attained and the initiators are chemically bound to the network and cannot be extracted.

2. Experimental

2.1. Materials

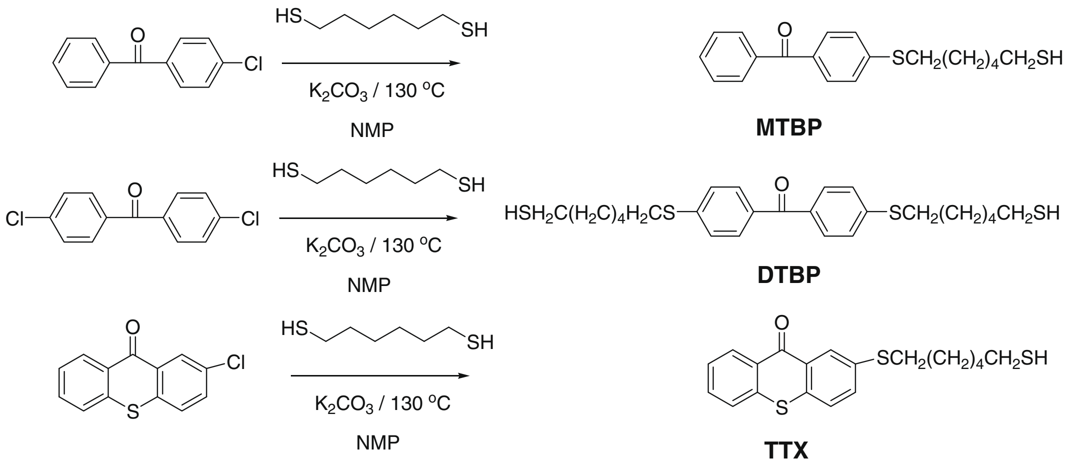
Methyl diethanol amine (MDEA), diethanol amine (DEtOHA), diethyl amine (DEA), hexylamine, 1,6-hexanedithiol, 4-chlorobenzophenone, and 1-methyl-2-pyrrolidone (NMP) were purchased from Aldrich Chemical Co. Ethoxylated (20) trimethylolpropane triacrylate (E-TMPTA), 1,6-hexanediol diacrylate (HDDA) and propoxylated (6) trimethylolpropane triacrylate (P-TMPTA) were obtained from Sartomer. Benzophenone and 2,2-dimethoxy-1,2-diphenylethan-1-one (DMPA) were obtained from Ciba Specialty Chemicals Corporation. Isopropylthioxanthone (ITX) was obtained from Albemarle Chemical Co. The hexafunctional aliphatic urethane acrylate and hexafunctional aliphatic urethane acrylate oligomer were obtained from Cytec. All chemicals were used as received.

2.2. Synthesis of photoinitiators based on thiol-functionalized benzophenones and thioxanthones

The procedure for preparation of the aliphatic thiol based photoinitiators are shown in Scheme 1, and ^{1}H NMR spectra of each product is shown in Fig. 1. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 400 MHz NMR in $CDCl_3$ with tetramethysilane (TMS) as the internal reference. The extinction coefficient at 365 nm of each initiator was obtained by UV-absorption spectra in THF solution using a Varian Cary 500 spectrometer as shown in Table 1. The procedure for preparation of each product is described in detail.

2.2.1. Synthesis of MTBP

4-Chlorobenzophenone (3 g, 13.8 mM), and 1,6-hexanedithiol (12.5 g, 83.1 mM) were dissolved in 1-methyl-2-pyrrolidone (35 mL). The reaction mixture was stirred and heated at 130 °C in the presence of potassium carbonate under nitrogen for 5 h. Potassium carbonate worked as a base to trap the HCl which was generated during the reaction. The mixture was cooled down to room temperature and washed by hexane three times to remove excess 1,6-hexanedithiol. After concentration of the mixture, the residue was purified by column chromatography (SiO_2, eluent 40% ethyl acetate in hexane) to give MTBP (3.2 g, 70.3% yield) as a white wax: ^{1}H NMR ($CDCl_3$) δ 7.80–7.25 (m, 9H), 3.00 (t, 2H), 2.67 (t, 2H), 1.80–1.60 (m, 4H),



Scheme 1. Synthesis of non-extractable photoinitiators based on thiol-functionalized benzophenones and thioxanthones.

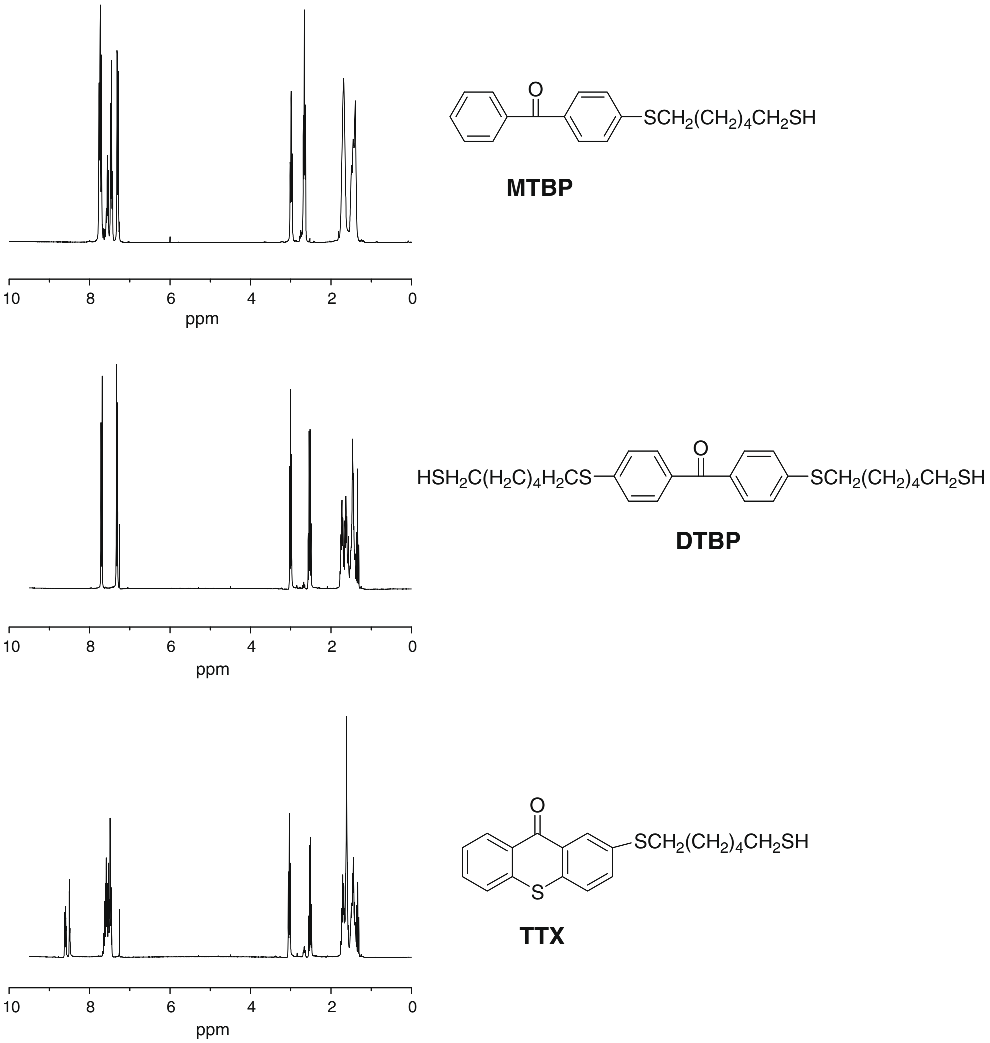


Fig. 1. ^{1}H NMR spectrum of non-extractable photoinitiators.

Table 1
Molar extinction coefficients of photoinitiators in THF.

Initiator	$\varepsilon_{365\ nm}$ (L/mol cm)
BP	71
MTBP	414
DTBP	877
TTX	2541
ITX	4650
DMPA	136

1.55–1.25 (m, 5H) ^{13}C NMR (CDCl$_3$) δ 196.2, 144.2, 137.8, 133.8, 132.2, 130.8, 129.4, 128.1, 126.0, 38.8, 31.9, 29.2, 28.6, 28.5, 28.

2.2.2. Synthesis of DTBP

4,4′-Dichlorobenzophenone (1.60 g, 6.36 mM), and hexanedithiol (11.58 g, 77.0 mM) were dissolved in 1-methyl-2-pyrrolidone (35 mL). Potassium carbonate (3 g) was added and the reaction mixture was heated to 130 °C under nitrogen while stirring until no dichlorobenzophenone was detectable by thin layer chromatography, after which the reaction was continued for another 30 min. The mixture was allowed to cool down to room temperature and precipitated from methanol to give DTBP (1.8 g, 59%yield). ^{1}H NMR (CDCl$_3$) δ 7.71 (d, 4H), 7.33 (d, 4H), 3.01 (t, 4H), 2.65–2.47 (m, 4H), 1.80–1.25 (m, 14H) ^{13}C NMR (CDCl$_3$) δ 196.4, 143.9, 129.3, 127.2, 36.4, 32.5, 29.6, 29.2, 28.9, 18.8.

2.2.3. Synthesis of TTX

2-Chlorothioxanthen-9-one (2.30 g, 9.32 mM), and hexanedithiol (11.58 g, 77.0 mM) were dissolved in 1-methyl-2-pyrrolidone (35 mL). Potassium carbonate (3 g) was added and the reaction mixture was heated to 130 °C under nitrogen while stirring until no dichlorobenzophenone was detectable by thin layer chromatography after which the reaction was continued for another 30 min. The mixture was purified by chromatography (SiO$_2$, eluent 70% ethyl acetate in hexane) to give TTX (2.1 g, 63% yield) as a yellow powder, mp: 64–65 °C: ^{1}H NMR (CDCl$_3$) δ 8.59 (d, 1H), 8.51 (s, 1H), 7.72–7.48 (m, 5H), 3.06 (t, 2H), 2.51 (m, 2H), 1.78–1.22 (m, 9H).

2.3. Kinetics

2.3.1. Real-time infrared

Real-time infrared (RTIR) spectra were recorded on a modified Bruker 88 spectrometer. UV light from an Oriel lamp system equipped with a 200-W high-pressure mercury–xenon bulb was channeled through an electric shutter and fiber optic cable in the sample chamber. Photopolymerizations were conducted in a cell prepared by sandwiching the samples between two sodium chloride plates at a thickness of approximately 20 μm. The light intensity (listed on each Figure) was measured with an IL-1400 calibrated radiometer from International Light and adjusted using neutral density filters and a 365 nm band pass filter. The characteristic infrared absorbance band used to monitor the disappearance of the acrylate was 812 cm^{-1}.

2.3.2. Photo-DSC

E-TMPTA was mixed with each photoinitiator (BP, ITX, DMPA, and MTBP) and co-initiator, MDEA (2 wt%) in the sonicator for 10 min. The mixture (~2 mg) was applied to an aluminum sample pan and then placed in the photo-DSC at 20 °C under the nitrogen or air purge. Photo-Differential Scanning Calorimetry (Photo-DSC) was performed on a Parkin-Elmer DSC-7 modified with quartz windows in the sample head cover and a shuttered 450 W medium-pressure mercury lamp. A 365 nm band pass filter was used and the light intensity was controlled by using neutral density filters.

2.4. Characterization

The acrylic films were prepared by using a 120 μm draw down bar on glass and steel plates, and exposed to the output of a Fusion high intensity lamp system with conveyer belt. The lamp system was equipped with a D-bulb (400-W/input) and had a line speed of 12.2 m/min and irradiance of ~3.0 W/cm^2. Persoz pendulum hardness was measured based on ASTMD-4366 using a BYK-Gardner pendulum hardness tester with a square frame pendulum. Pencil hardness, steel–wool resistance, and Mandrel bend testing were carried out based on ASTM methods. For the tack free test, the films were exposed at a line speed of 36.7 m/min.

2.5. Coating additive extraction test

Coating films for this study consist of E-TMPTA in the presence of 0.62 wt% of initiators and 2 wt% amines. The films were prepared by using a 120 μm draw down bar on glass, followed by exposure to the output of a Fusion high intensity lamp system with conveyer belt at a line speed of 12.2 m/min. The lamp system (D-bulb) had an irradiance of 3.0 W/cm^2. After 10 times running under the lamp, the films were cut in 2 × 3 cm samples sites and dipped into 10 g of methylenechloride for 7 days. Methylene chloride was an excellent solvent for all initiators and amines. Ten grams of the extractives were concentrated for ~0.5 g and analyzed using an Agilent 6890N GC equipped with a Fused Silica Capillary Column, SUPELCO-WAX 10 (30 m × 0.53 mm × 0.5 μm). A half microliter of extract solution was injected. The injection temperature was 250 °C. After maintaining the GC for 5 min at 50 °C, the temperature was increased 10 °C per minute from 50 to 250 °C and held at 250 °C for 10 min. Retention times of MDEA, DEtOHA, benzophenone, MTBP, and ITX were 17.4, 18.4, 21.3, 24.2, and 33.2 min, respectively. A calibration curve was made for each initiator (BP, MTBP, and ITX) and co-initiator (MDEA and DEtOHA) to correlate to the amount of each species extracted from polymeric samples. Samples were prepared by mixing each species in methylene chloride at five different concentrations and tested under the conditions previously mentioned for unknowns.

Calibration curves were prepared by plotting the area under the curve as a function of concentration. Then quantitative analysis was performed by comparing unknown samples to the calibration curve.

3. Results and discussion

All photoinitiator components and acronyms, including amine co-initiators and reactive acrylate monomers, used in this investigation are shown in Chart 1. The sulfide-based benzophenone and thioxanthone photoinitiators have both sulfide linkages at the para positions of the phenyl rings and reactive thiol end groups that render the photoinitiator capable of reacting with acrylate groups by thiol–ene reactions, either free-radically or via a catalyzed Michael addition reaction.

3.1. Molar extinction coefficients of thiol modified photoinitiators

The three basic thiol photoinitiators were synthesized by a simple reaction of an alkene dithiol with 2-chlorothioxanthen-9-on or 4-chlorobenzophenone as shown in Scheme 1. Relatively high yields were obtained using moderate conditions, and the products were characterized by an alkyl–aromatic sulfide linkage as well as a aliphatic thiol group. The sulfide linkage resulted in high molar extinction coefficients for the resulting benzophenone and thioxanthone derivatives, while the thiols provided a

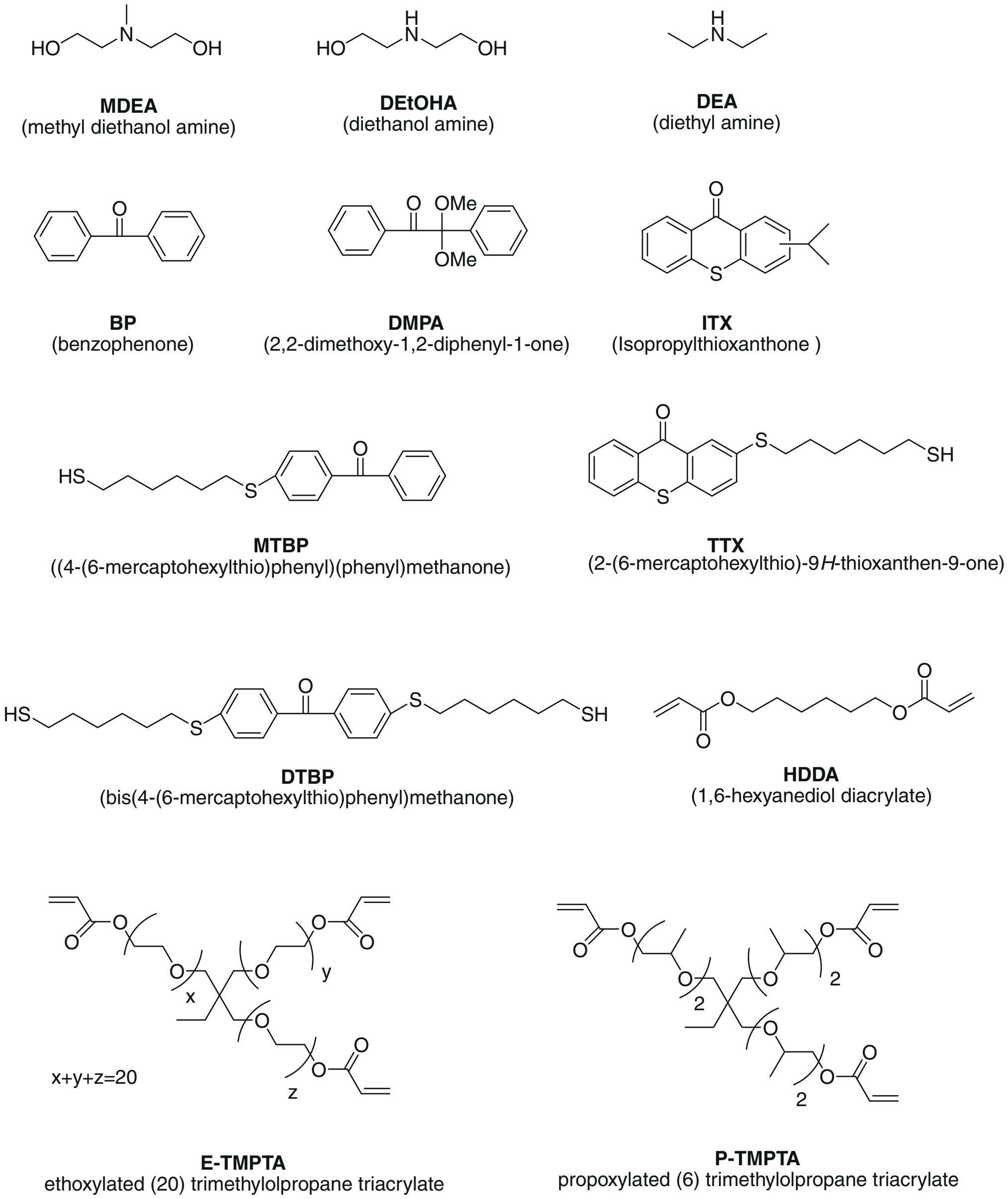


Chart 1. Chemical structures of compounds used.

conduit for incorporation into the final network. The sulfide linkages resulted in a red-shift in the absorption spectrum (Fig. 2) in agreement with literature reports [17,29]. The extinction coefficients of the sulfide modified photoinitiators at 365 nm are given in Table 1. The extinction coefficients of MTBP and DTBP at 365 nm, 417 and 877 L/mol cm, were much higher than that of benzophenone (71 L/mol cm) due to the sulfide groups at the para position of the phenyl ring. The extinction coefficient of TTX, 2541 L/mol cm, was less than that of ITX at 365 nm since the para sulphide substituent extends the absorption as shown in Fig. 2. The absorption spectra of TTX is obviously red-shifted compared to ITX because of the sulfide linkage at the para position. As previously reported, the red-shift in the absorption spectrum and increase in molar extinction coefficients are significant since lower photoinitiator concentrations can be employed, making them ideal for used pigmented systems which require initiators high extinction coefficients in the visible region.

3.2. Kinetics of thiol modified photoinitiators

In order to evaluate the basic efficiency of each photoinitiator, the UV absorbances in a typical triacrylate were all adjusted according to the extinction coefficients in Table 1 to have identical values at 365 nm. Each sample was then exposed by the isolated 365 nm line of a high-pressure mercury lamp. For comparison, real-time FTIR kinetics profiles of photopolymerization propoxylated (6) trimethylolpropane triacrylate (P-TMPTA) containing thiol-functionalized photoinitiator and traditional photoinitiators with identical absorbance at 365 nm are shown in Fig. 3. The thiol-functionalized photoinitiator MTBP with MDEA as a co-initiator resulted in a faster and more efficient polymerization than for benzophenone with MDEA and approximately the same efficiency as ITX with MDEA. The cleavage type initiator dimethoxyphenyl acetophenone (DMPA) produced the fastest polymerization reaction under the conditions employed in the absence of external oxygen, i.e., the samples were prepared by sandwiching between two sodium chloride plates.

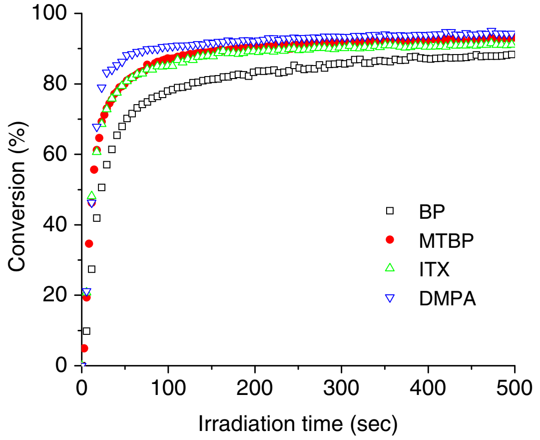


Fig. 3. Real-time FTIR kinetic profiles for the photopolymerization of P-TMPTA containing different photoinitiators with equal absorbance (0.02) at 365 nm. Light intensity: 6 mW/cm^2 at 365 nm. Initiators: (1) 1.74 wt% of DMPA, (2) 0.62 wt% of MTBP and 2 wt% of MDEA, (3) 0.043 wt% of ITX and 2 wt% of MDEA, and (4) 2 wt% of BP and 2 wt% of MDEA.

While the results in Fig. 3 are useful for describing the basic photoinitiator efficiency in situations when air is not presence, most photopolymerization reactions are actually conducted in air where oxygen is present. Since oxygen retards the free-radical polymerizations of acrylates by reacting with the carbon radical chain ends, the efficiency of photoinitiators should be evaluated in the presence of oxygen. Accordingly, photo-DSC results in Fig. 4 show comparisons of exotherm curves for photopolymerization of P-TMPTA using different photoinitiators with DMEA as the co-initiator under nitrogen and air with three light intensities at 365 nm. In nitrogen, the efficiency of each initiator in the photo-DSC showed the same basic trend as seen from the real-time FTIR conversion versus time plots (Fig. 3). However in air, photopolymerization of all components was much slower than in nitrogen due to oxygen inhibition. Notably, the efficiency of the DMPA cleavage photoinitiator decreased much more than the other systems. This phenomenon was especially prominent at lower light intensities as shown in Fig. 4C and D. In other

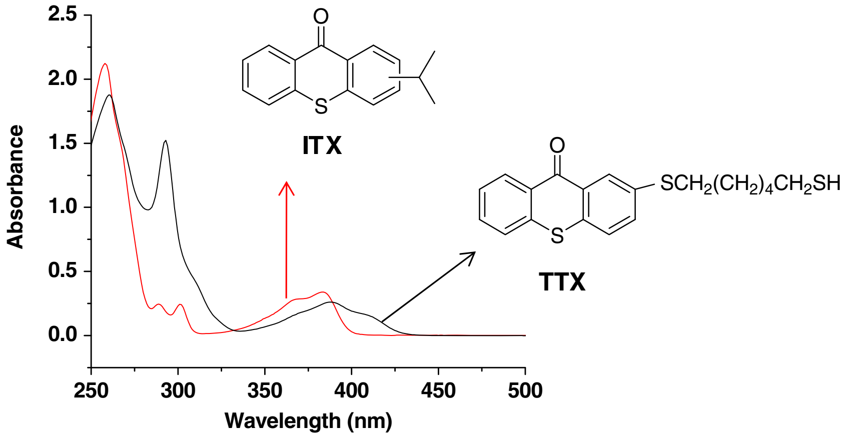


Fig. 2. Absorption spectra of thioxanthone derivatives ITX and TTX at 5.8 × 10^{-5} M in THF.

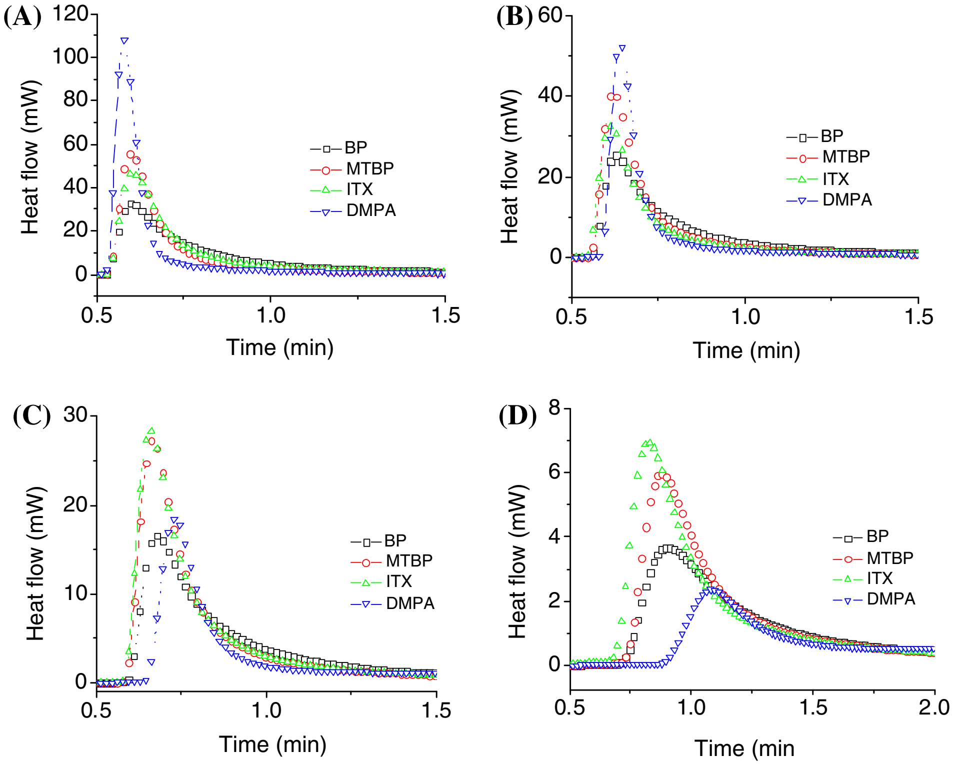


Fig. 4. Photopolymerization exotherms for P-TMPTA recorded on a photo-DSC with various photoinitiators with 2 wt% of DMEA. Irradiation conditions at 365 nm: (A) 1.43 mW/cm^2 under nitrogen, (B) 1.43 mW/cm^2 in air, (C) 0.45 mW/cm^2 in air, and (D) 0.14 mW/cm^2 in air. Photoinitiators used: BP (2 wt%), DMPA (1.74 wt%), MTBP (0.67 wt%), and ITX (0.043 wt%). The absorbance at 365 nm was adjusted to be 0.02 for all photoinitiators.

words, the lower the light intensity, the more sensitive the system to oxygen inhibition becomes. Under low light intensity, the hydrogen abstraction type initiators with amine systems were more efficient than the cleavage type initiator since the amine co-initiators can react with oxygen rendering the acrylate photopolymerization less sensitive to oxygen inhibition [17].

3.3. Thiol modified initiator without amine

MTBP was also evaluated in 1,6-hexanediol diacrylate (HDDA) without the MDEA tertiary amine added as shown in Fig. 5. Photo-DSC profile showed that the HDDA polymerization exotherm with MTBP was much faster than that with benzophenone without amine since MTBP has abstractable hydrogen on the thiol end group, i.e., the MTBP excited triplet state abstracts a hydrogen from the thiol, and the resultant thiol radical initiates the polymerization. Although MTBP without amine system was much less efficient than with MDEA, this result indicates that the MTBP can serve as a one-component system which, despite its lower efficiency, might be quite useful for some applications.

3.4. Non-extractable amines

There is little question that for hydrogen donor type initiators, selection of the amine proton donor structure is important in defining the efficiency of the initiation process. Tertiary amines, such as MDEA are well known as efficient co-initiators. Secondary amines, such as DEA and DEtOHA also have reactive hydrogens and could serve as efficient co-initiators, although due to their secondary structure they are much less efficient than tertiary amines. It is well known that primary and secondary amines undergo a very efficient Michael addition to electron poor

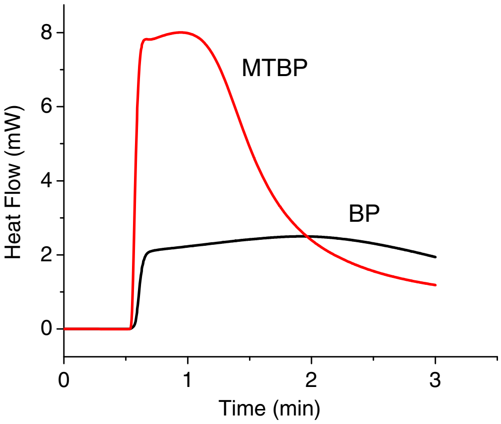
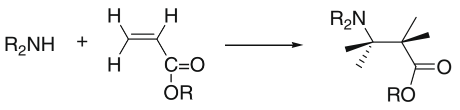


Fig. 5. Photopolymerization exotherms recorded on a photo-DSC of HDDA initiated with BP (2 wt%) and MTBP (0.67 wt%) without amine co-initiator. Irradiation conditions: 1.43 mW/cm^2 at 365 nm under nitrogen.



Scheme 2. Michael addition of secondary amine to acrylate double bond.

enes such as acrylates as shown in Scheme 2 [30]. This would afford the synthesis of a tertiary amine attached to reactive acrylate groups if a multiacrylate, such as a triacrylate, was used as the electron poor substrate for reaction with a secondary amine. To investigate the affect of amine co-initiator structure, three different types of amines with BP and MTBP were evaluated as photoinitiator systems for photopolymerization of a typical triacrylate (E-TMPTA) using photo-DSC to monitor the reaction (Fig. 6). To provide a base line for evaluating the efficiency of each photoinitiator, the photo-DSC exotherms of E-TMPTA, a typical triacrylate, were obtained using the tertiary amine MDEA and two representative dialkyl amines, DEA and DEtOHA. Since DEA and DEtOHA can undergo Michael addition to acrylate functional groups, they were added to E-TMPTA for several time periods ranging from 0 to 48 h prior to initiating photopolymerization by excitation of BP and MTBP. In both cases, for BP in Fig. 6A and MTBP in Fig. 6B, the rate was greatest for the system with MDEA, presumably the result of enhanced mobility of MDEA which was not bonded chemically to the acrylate, as was the case for DEA and DEtOHA which reacts with the acrylate groups on E-TMPTA. Also, the rates were higher for the MTBP based systems for a given amine since the para sulfide substitution is known to enhance the initiation efficiency as previously described in Section 1 [17,29]. The important result in Fig. 6 is that reasonable polymerization rates are obtained, even if enough time is allowed for the Michael addition to take place. In other words, the secondary amines, which will be shown be non-extractable from the final cured films are still effective as co-initiators.

3.5. Coating physical properties and tack free time

Coating physical properties and tack free times for all photocured films were evaluated using a typical photocurable acrylic formulation: P-TMPTA/Acrylate Urethane1 (Ebecryl 8301) /Acrylate Urethane2 (Ebecryl 1290) = 35/25/40. For evaluation of tack free times, films were exposed to the output of a Fusion lamp system at a line speed of 36.7 m/min. For assessment of coating physical properties, the film was exposed at a line speed of 12.2 m/min for 10 passes to ensure that the film was fully cured. The tack free test results are shown in Table 2. In Table 2A, the photoinitiators were incorporated into the formulation

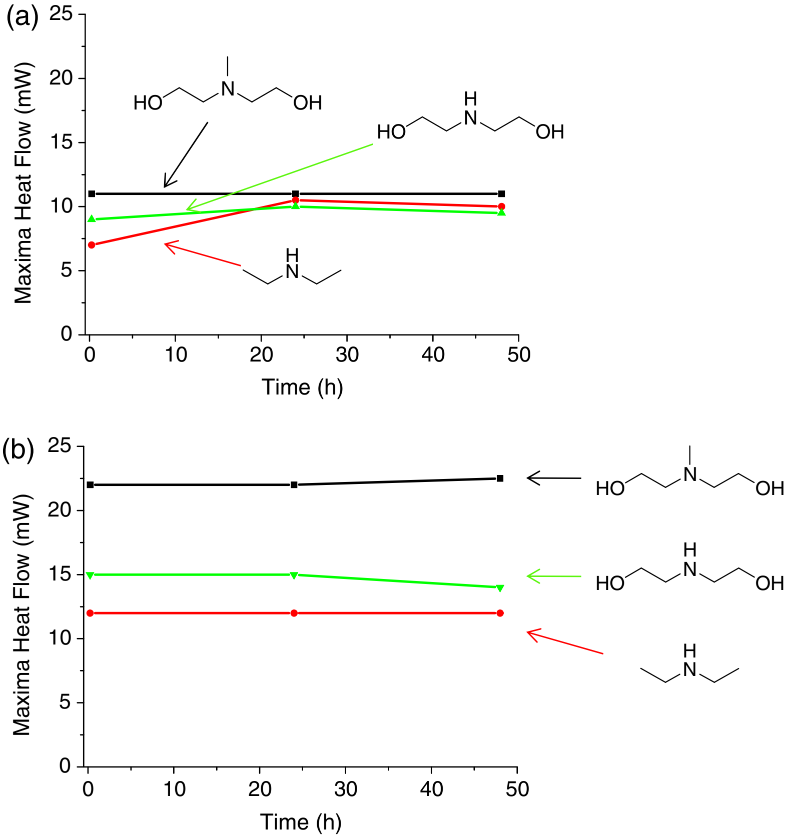


Fig. 6. Plots for photopolymerization DSC exotherm maximum versus time after mixing of E-TMPTA with an initiator in the presence of various amines (2.0 wt%). Irradiation: 1.43 mW/cm^2 at 365 nm under nitrogen. Initiator: (a) 2.0 wt% of BP and (b) 0.62 wt% of MTBP.

Table 2A
Number of passes to obtain tack free acrylic film containing different photoinitiators of equal weight (0.62 wt%).

Entry	Photoiniator		Number of passes to tack free
	Initiators (wt%)	Amines (wt%)	
1	DMPA 0.62	[a]	15
2	BP 0.62	MDEA 2	3
3	MTBP 0.62	MDEA 2	3

[a] No amines were added.

on an equal weight basis, and in Table 2B they were used on an equal absorbance basis at 365 nm. In both cases, the number of passes under the curing lamp to obtain a tack free film surface with MTBP was much smaller than that of DMPA, and approximately the same as BP. This significant difference between cleavage type initiators (DMPA) and hydrogen abstraction type initiators (MTBP and BP) with amine clearly shows that the acrylic polymerization is less sensitive to oxygen inhibition in the presence of amine, in accordance with literature reports [17]. Physical properties of the photocured acrylic formulation with different initiator were evaluated on an equal weight basis (Table 3) and on an equal absorbance basis at 365 nm. In both cases, the samples cured with MTBP exhibited approximately the same physical properties achieved using the conventional initiator systems (BP and DMPA).

3.6. Coating additive extraction test

In order to confirm that the thiol based photoinitiator MTBP and secondary amines were attached to the photocured acrylate network, solvent extraction of the films (Table 4) was performed as described in Section 2. Samples 1–6 were prepared using the tertiary amine and secondary amines with each photoinitiator, waiting 15 h after mixing to making sure that both the Michael addition reactions between the secondary amines, as well as MTBP, were complete prior to initiating the polymerization by exposure to light. Traditional photoinitiators, BP and ITX were extracted from each of the cured films in the range of 4–6.5 ppm (Samples 1–4). The thiol based photoinitiator, MTBP, was incorporated into the network via either the free-radical polymerization or amine catalyzed thio-Michael addition and not extracted from the films. In all cases where the tertiary amine, MDEA, was used, it was extracted from films in the range of 116–141 ppm. Finally, the secondary amine DEtOH that was prereacted with the acrylate via Michael addition could not be extracted from the cured films. Hence, the combination of thiol-functionalized photoinitiator with secondary amines provides an efficient photoinitiator system that cannot be extracted from the photocured acrylate network.

Table 2B
Number of passes to tack free acrylic film containing different photoinitiators with equal absorbance (0.2) at 365 nm.

Entry	Photoinitiator		Number of passes to tack free
	Initiator (wt%)	Amine (wt%)	
1	DMPA 1.74	[a]	8
2	BP 2	MDEA 2	2
3	MTBP 0.62	MDEA 2	3

[a] No amines were added.

Table 3
Mechanical properties of acrylic films cured with various photoinitiators at 0.62 wt%.

Mechanical property	DMPA	BP[a]	MTBP[a]
Pencil hardness	7H	5H	6H
Persoz damping	312s	262s	280s
Steel–wool	10/10	10/10	10/10
Crack resistance	4.5	4.5	4.5
% Elongation mandrel bend	3.5%	3.5%	3.5%

[a] BP and MTBP with 2 wt% of MDEA.

Table 4
Coating additive extraction test of acrylic films consisting of E-TMPTA/photoinitiator/amine = 100/0.62/2.0 (wt%).

Sample	Photoinitiator	Co-initiator	Extracted amount	
			Photoinitiator (ppm)	Co-initiator (ppm)
1	BP	MDEA	4.1	141
2	BP	DEtOHA	6.5	<0.01
3	ITX	MDEA	6.5	116
4	ITX	DEtOHA	4.0	<0.01
5	MTBP	MDEA	<0.01	137
6	MTBP	DEtOH	<0.01	<0.01

4. Conclusions

Thiol-functionalized photoinitiators based on thioxanthone and benzophenone were synthesized. The reaction kinetics and physical properties of a traditional acrylate system initiated with both the thiol modified and unmodified derivatives were compared to determine their photoinitiation efficiency. The photoinitiators had high extinction coefficients due to the sulfide substitution on the phenyl ring, and were more efficient than traditional benzophenone and thioxanthone photoinitiators for initiation of free-radical polymerization. The results of an extraction analysis confirmed that thiol groups reacted with the acrylate by either an amine catalyzed Michael addition or by free-radical polymerization. Hence, combination of thiol-functionalized photoinitiators with secondary amines provided an efficient photoinitiator system which was locked into the photocured networks. This system is useful for many applications where it is essential to reduce and/or eliminate migration of small molecule components from photocured network films.

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