Low Extractable Photoinitiators Based on Thiol Functionalized Benzophenones and Thioxanthones

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Abstract: Previously described non or low extractable photoinitiators based upon monomer-photoinitiators including maleimides, vinyl acrylates, vinyl cinnamate, divinyl esters, and thiols are compared. These monomer-photoinitiators participate in the free-radical polymerization of acrylates that they initiate, and in the process are bleached and incorporated into the final network. All have noted drawbacks to their use including toxicity, efficiency and cost. Recently, in our lab other photoinitiators based upon thioxanthone and benzophenone derivatives with thiol functional groups attached to the para position of the phenyl rings via sulfides have also been synthesized and evaluated. These latter types of photoinitiators are as efficient as typical thioxanthone and benzophenone photoinitiators in the presence of amine cosynergists, but having reactive thiols they also are incorporated into the acrylate network via chemical attachment.

Introduction

There has been considerable interest for the last four decades in developing photoinitiators that are efficient, have high extinction coefficients with absorbance bands that correspond to output lines from medium pressure lamps, and can be synthesized from readily available starting materials. The design, performance and basic chemistry of photoinitiators have been described in detail.[1-8] There are two types of photoinitiators which have found widespread commercial use: cleavage and abstraction. The cleavage type photoinitiators, exemplified by trisubstituted acetophenones, in general are more efficient while the abstraction type photoinitiators are usually less expensive. Benzophenone and thioxanthone abstract type initiators and their substituted analogues have long been used as staple photoinitiators with co-initiator amines. The electron transfer/proton transfer sequential processes result in the transfer of hydrogen from a tertiary amine to produce a radical at the alpha carbon (next to the nitrogen) and a relatively stable semi-pinacol radical upon transfer of the hydrogen to the oxygen carbonyl. The radical on the tertiary amine initiates polymerization while the semi-pinacol radical is stable and only serves as a chain terminator. In order to enhance the extinction coefficients of benzophenone and thioxanthone type photoinitiators, sulfide linkages have been attached to the phenyl rings.[7,8] The resultant sulfides are extremely efficient, have high extinction coefficients and the absorbances are red-extended compared to their unsubstituted analogs.

While traditional photoinitiators provide excellent performance in a wide array of applications ranging from formulations for floor tiles to coatings on optical fibers and compact disks, there are still some limitations that exist. Paramount among these limitations in certain critical applications involving

food packaging and electronics are the susceptibility of photoinitiators that are not consumed in the photoinitiation process to remain in the cured coating and migrate to interfaces where they can diffuse into and contaminate the substrate. There have been numerous attempts to resolve the issue related to migration of unused fugitive photoinitiator involving two main strategies: attach reactive monomer groups such as acrylates to the photoinitiator in order to incorporate into the network during the curing process, or make macrophotoinitiators.[6] One way to overcome the reputed lower efficiencies of traditional macrophotoinitiators is to design macromolecular initiators with multiple initiating sites via linking groups.[6]

Over the past decade we have focused attention on monomers that are themselves both photoinitiators and reactive monomers. Hence, these monomer photoinitiators are completely consumed during the polymerization process and in fact bleach by the photocuring process that they initiate due to loss of the chromophore responsible for the light absorption upon being incorporated into the network. These reactive systems can in favorable cases result in very rapid polymerization processes that proceed to relatively high conversions.

Herein, we first provide a review of monomer photoinitiators used in our lab over the past decade as a preview for a complete description of the synthesis and characterization of new types of sulfide substituted thioxanthones and benzophenones with thiol end groups. These photoinitiators are very efficient in initiating acrylate polymerization and afford the opportunity for the initiator to be incorporated into the cured network by a very efficient free-radical process.

Experimental

Materials

Materials for synthesis of various monomer photoinitiators and reactive acrylates were obtained from Aldrich Chemical Company, Cytec, or Sartomer. Their synthesis and characterization has been described in numerous references.[9-18]

Characterization

Photo-DSC measurement techniques have been described.[10-18] 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 filled with dry air. The photopolymerizations were conducted in a cell prepared by sandwiching the samples between two sodium chloride salt plates with a thickness of approximately 20 μm. Other experimental parameters for the RTIR measurements as well as procedures used for various physical and mechanical testing procedures used in our lab have been reported elsewhere in detail.[10-18] A Fusion D-bulb source and belt system were used for curing large film samples.

Results and Discussion

Maleimides

Figure 1 shows the general structure of a typical maleimide monomer-photoinitiator that has been reported to initiate polymerization of acrylates.[9-10] It functions as a photoinitiator via a hydrogen transfer process when used in the presence of hydrogen donors such as alcohols, ethers or amines co-initiators. It also readily copolymerizes with acrylates in a free-radical chain reaction and hence bleaches and is bound into the final network. Unfortunately, it has two major disadvantages. First and

foremost, maleimides can be extremely toxic with the exact level of toxicity depending upon the nature of R''. However, even in very favorable cases such as when R''is aromatic, there are still significant questions as to its safe use. Second, the synthesis of maleimides on an industrial scale is expensive and hence it cannot compete effectively with other types of photoinitiators.
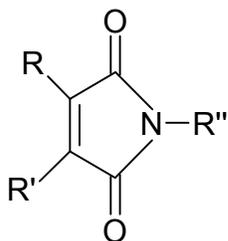

Figure 1. General structure of maleimide.

Vinyl Acrylate, Vinyl Crotonate and Vinyl Cinnamates

A variety of conjugated enes incorporating an electron rich vinyl ester ene and an electron poor ene of an α,β-unsaturated carbonyl were evaluated as photonitiators.[11-13] Figure 2 shows the structure of vinyl acrylate, vinyl crotonate and vinyl cinnamate. These unique monomer-photoinitiators require no co-initiator as they undergo an efficient α-cleavage reaction between the carbonyl carbon and the oxygen as shown in Figure 1 to produce two radicals that are extremely efficient in initiating acrylate polymerization. Due to significant conjugation between the acrylate (or cinnamate) and vinyl ester enes on both systems, the absorption spectra of vinyl acrylate, vinyl crotonate and vinyl cinnamate are red shifted and the extinction coefficients are comparable to the saturated analogs.

Vinyl Acrylate (VA)   **Vinyl Crotonate (VC)**   **Vinyl Cinnamate (VCinn)**
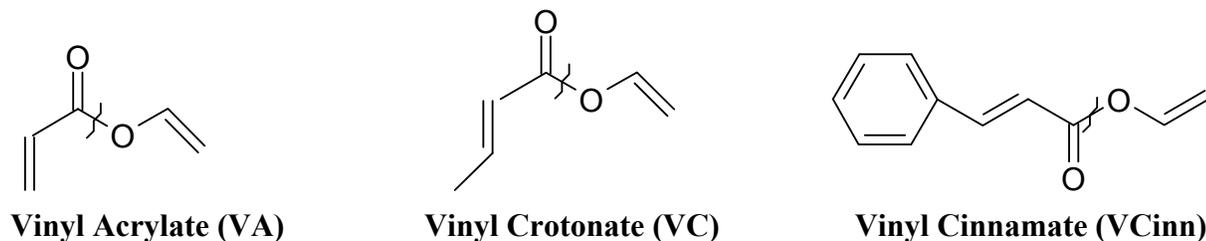
Figure 2. Structures of vinyl acrylate, vinyl crotonate and vinyl cinnamate.

Figure 3 shows a real-time infrared plot of percent conversion versus irradiation time for photopolymerization of 1,6-hexanedioldiacrylate using all three of the vinyl esters in Figure 3 as photoinitiators as well as α,α-dimethoxyphenyl acetophenone for comparison. Note that while initially the rates are fairly competitive for the systems using vinyl acrylate, vinyl crotonate and vinyl cinnamate, conversion is not high due to incorporation of each of the monomer-photoinitiators into the acrylate network thereby reducing their concentration as the polymerization progresses.
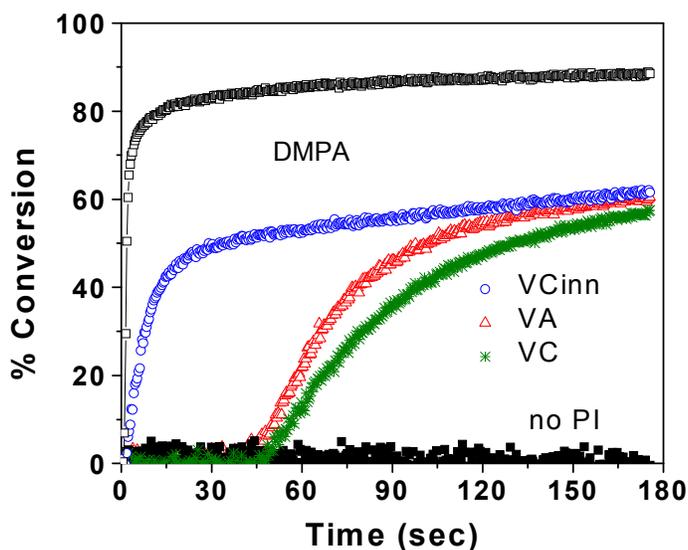
Figure 3. RTIR of HDDA photopolymerization using VA, VC, VCinn and DMPA photoinitiators.

Divinyl Fumarate and Ethyl Vinyl Fumarate

Two additional vinyl ester type monomer photoinitiators[14-16] are shown in Figure 4. They are characterized by extensive conjugation with corresponding red-shifted absorption spectra at wavelengths greater than 300 nm and efficient α-cleavage between the carbonyl carbons and the oxygen on the vinyl ester. These systems have two reactive double bonds for participating in acrylate polymerization and have been shown to be effective as non-extractable monomer photoinitiators. They are more efficient than the three photoinitiators in Figure 3 (due to space, the actual results are not presented in this manuscript). Their performance is the subject of another presentation at this conference.
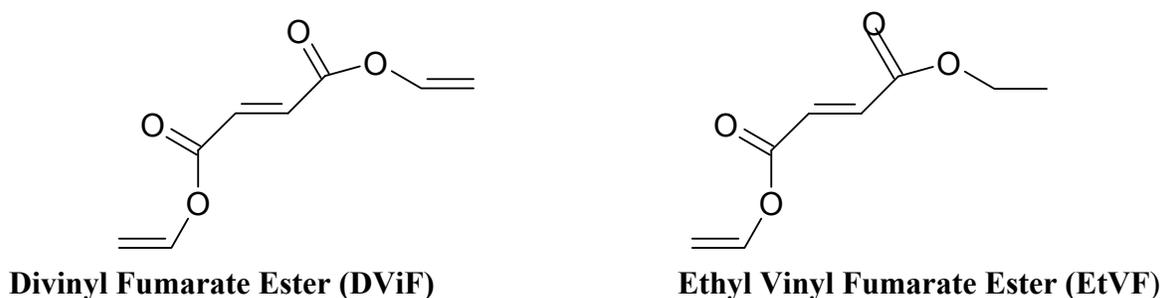

Divinyl Fumarate Ester (DViF)   **Ethyl Vinyl Fumarate Ester (EtVF)**

Figure 4. Structure of typical divinyl fumarate ester and vinyl ethyl fumarate.
Thiols

When thiols are added to acrylates they can be very effective photoinitiators via a cleavage of the sulfur-hydrogen bond to give thiyl and hydrogen radicals capable of initiating the free-radical polymerization of acrylates per equation 1 below.[17, 18]

$$RSH \quad \rightarrow \quad RS^{\bullet} + H^{\bullet} \quad\quad\quad\quad \text{Equation 1}$$

As shown in the photo-DSC exotherm in Figure 5, they are especially effective in initiating acrylate polymerization in air since thiols readily scavenge oxygen and thus render the polymerizing matrix oxygen free. And they copolymerize with the acrylates to give matrix films with significantly enhanced mechanical and physical properties: plus as the end of the photocuring process for systems with ~ between about 5 and ~15% thiol, the conversion of all functional groups is essentially 100% thus leaving little extractable species in the network. While not a efficient as high concentrations of a cleavage type photointitiator such as DMPA, thiols are still quite effective as photoinitiators/monomer components in many applications.
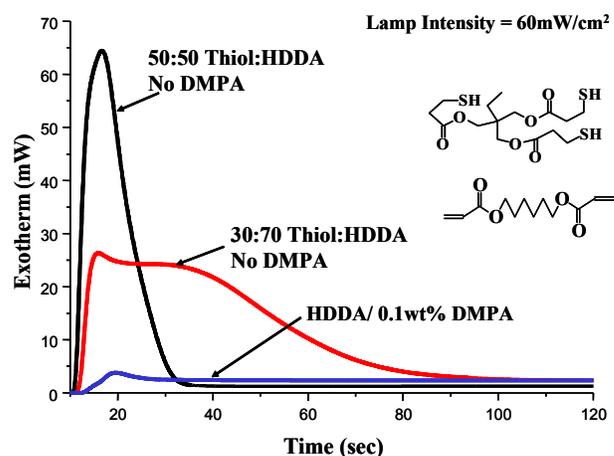

Figure 5. Photo-DSC of HDDA polymerization in air using a trithiol as the photoinitiator.

Benzophenones/Thioxanthones with Thiols

Figure 6 shows the structures of one thioxanthone and two benzophenone derivatives synthesized in our lab via typical reactions of 1,6-hexane dithiol with the corresponding chlorinated benzophenone or thioxanthone. These photoinitiators not only have higher absorbances than their benzophenone or isopropylthioxanthone counterparts due to the sulfide substitution at the para position in the phenyl ring, but they also have thiol groups which can react with the acrylate either via an amine catalyzed Michael addition prior to polymerization, or by a free-radical chain process during the acrylate free-radical polymerization process.
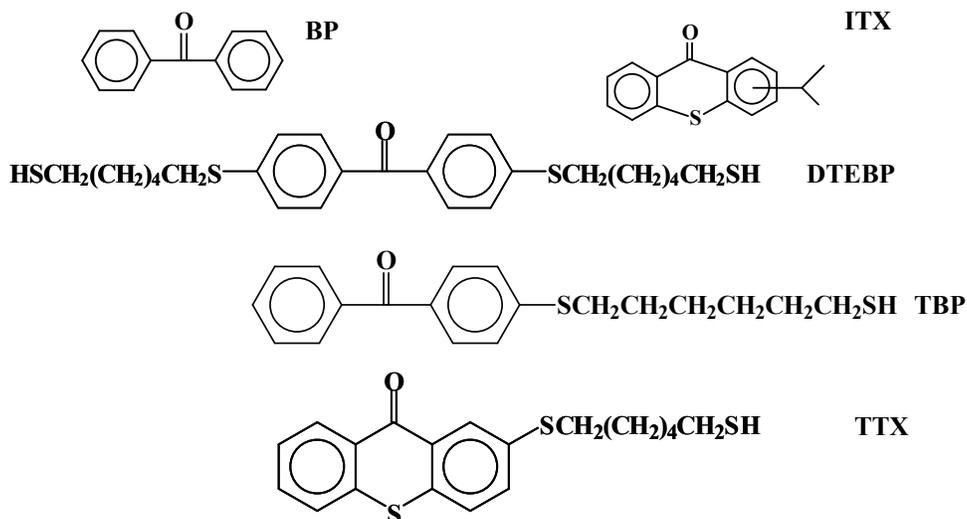
Figure 6. Structures and acronyms of benzophenone, thioxanthone and thiol functionalized benzophenones and thioxanthone derivatives.

Table 1 shows the acrylate components in a photocurable formulation that was used to evaluate the relative efficiency of BP, ITX, TBP, and DTEBP. Table 2 shows the exact composition of each acrylate formulation used and the extinction coefficients of each initiator along with the number of passes under a Fusion line equipped with a medium pressure mercury D bulb required to obtain a tack free film.

Table 1. Acrylate mixture used to prepare photocurable formulations.

Component	Description	Amount (%)
CD 501	Trimethylolpropane Polyoxypropylene Triacrylate	35
Ebecryl 8301	Acrylated Urethane	25
Ebecryl 1290	Acrylated Urethane	40

In Table 2, the photoinitiators were incorporated into the formulation on an equal weight basis, and in Table 3 the photoinitiators were incorporated on an equal absorbance at 365 nm basis. In both cases, it is obvious that the acrylate cured with DTEBP and TBP as photoinitiators cure to a tack free state approximately as efficiently as when BP or ITX is used. The systems with DTEBP and TBP have the added advantage that the photoinitiator is incorporated into the network via a free-radical chain-transfer process. Addition performance parameters related to evaluation of physical properties obtained using these and related photoinitiators will be given in the presentation. A scenario will be described for using

co-synergists which are also locked into the final matrix thereby creating a complete benzophenone/co-synergist or thioxanthone/co-synergist photoinitiator package where both components are chemically bonded to the final cured matix.

Table 2. Formulations with equal weight of photoinitiator for curing using Fusion D-bulb lamp system.

Formulations	Amounts (g)	ε_{365} (L/mol.cm)	Passes to Tack-Free Surface
BP MDEA ACRYLATES	0.01071 0.10165 4.89110	71	3
ITX MDEA ACRYLATES	0.01032 0.10165 4.90235	877	3
DTEBP MDEA ACRYLATES	0.01033 0.09910 4.90502	7879	3
TBP MDEA ACRYLATES	0.01092 0.10145 4.89444	378	3

Table 3. Formulations with photoinitiator concentration adjusted to provide equal absorbance at 365 nm for curing using Fusion D-bulb lamp system.

Formulations	Amounts (g)	ε_{365} (L/mol.cm)	Passes to Tack-Free Surface
BP MDEA ACRYLATES	0.15040 0.10563 4.75516	71	1-2
ITX MDEA ACRYLATES	0.00189 0.10327 4.80010	7879	4
DTEBP MDEA ACRYLATES	0.03201 0.10056 4.75023	877	2
TBP MDEA ACRYLATES	0.05196 0.10098 4.75572	378	2

Conclusions

Several new photoinitiators based upon benzophenone and thioxanthone were synthesized and their efficiency in initiating the free-radical polymerization of an acrylate formulation was evaluated.

These sulfide photoinitiators have very high extinction coefficients (for example 7879 L/mol-cm compared to 877 L/mol-cm at 365 nm for the new thioxanthone derivative compared to isopropyl thioxanthone) and are extremely efficient (by up to a factor of two) compared to traditional benzophenone and thioxanthone photoinitiators in initiating polymerization to give tack free films. Additionally, since they have thiol end groups, they are incorporated into the final photocured network.

Acknowledgements

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