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Revisiting aromatic thiols effects on radical photopolymerization

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Abstract

Influence of thiols on kinetics of acrylate radical photopolymerization in the presence and absence of photoinitiators was studied. The kinetics was monitored by infrared absorption and photo-differential scanning calorimetry. It was found that aromatic thiols at concentrations, $<0.5\%$ (~ 0.05 M), can accelerate radical photopolymerization. Initiation of radical photopolymerization by some aromatic thiols in the absence of conventional photoinitiators was observed. As well as expected inhibition of photopolymerization at higher concentration of aromatic thiols due to chain transfer was detected. A ground state charge-transfer complex formation between thiols and benzoin based photoinitiators was detected.

Mechanism of thiols participation in photopolymerization involving reduction of oxygen inhibition and dissociation of charge-transfer complexes is discussed.
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Keywords: Radical photopolymerization; Aromatic thiols; Photoinitiation

1. Introduction

The term 'chain transfer' in radical polymerization refers to termination of one growing chain and initiation of another [1,2]

$$\mathrm{R:H} + \mathrm{P}_x^{\cdot} \rightarrow \mathrm{P}_x + \mathrm{R}^{\cdot} \quad \text{chain transfer}$$

$$\mathrm{R}^{\cdot} + \mathrm{M} \rightarrow \mathrm{P}_j^{\cdot}$$

$$\ldots$$

where $\mathrm{P}_x^{\cdot}$ is a growing polymer chain containing x monomeric units, M is monomer molecule and R:H is a hydrogen donating chain transfer agent. The chain transfer, obviously, leads to shorter chains and competes with the reactions of chain growth and termination

$$\mathrm{M} + \mathrm{P}_x^{\cdot} \rightarrow \mathrm{P}_{x+1}^{\cdot} \quad \text{chain growth}$$

$$\mathrm{P}_x^{\cdot} + \mathrm{M} \rightarrow \mathrm{P}_{x+2}^{\cdot}$$

$$\mathrm{P}_x^{\cdot} + \mathrm{P}_y^{\cdot} \rightarrow \mathrm{P}_{x+y}^{\cdot} \quad \text{chain termination}$$

$$\mathrm{P}_x^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{P}_x\mathrm{O}_2^{\cdot}$$

$$\ldots$$

When chain growth and transfer reactions have similar rate constants, the presence of chain-transfer agent does not affect overall rate of monomer conversion and polymerization. 'Under appropriate conditions, almost any molecule may act as a chain-transfer agent, including initiator, monomer, solvent, and dead polymer' [1,2]. Amines, alcohols and thiols are most efficient in chain transfer, because of easy cleavage of secondary alkyl hydrogen (in case of amine and alcohol) and cleavage of sulfhydryl hydrogen in thiol [3–5].

Thiols do not initiate radical polymerization during storage of the photopolymerizable composition. Oxygen inhibition of radical reactions involving thiols is lower than that of radical reactions without thiols. Thus, thio-compounds are chain-transfer agents of choice in many photopolymerizable coatings and adhesives [6]. Photoresists and photopolymers for printing and publishing often are based on thiol-olefin compositions, best known are thiol-ene systems [7].

Practical importance of thiols-containing compositions prompted numerous investigations of thiol influence on photopolymerization kinetics [8–18]. Thiol-containing compounds were shown to co-initiate and initiate radical polymerization in solutions [12,13,17]. The results of Yan and co-workers [12], Kuramote and co-workers were complimentary to those reported by DuPont scientists,

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who used aromatic thiols, 2-benzoxazolethiol and 2-benzothiazolethiol, as hydrogen transfer co-initiators in printing and proofing material and photoresists [19–21].

UV-curable surface coatings and adhesives are solvent-free. These compositions consist of initiators, oligomer and additives dissolved in a monomer or a mixture of monomers. Upon exposure to UV-light these compositions form almost completely crosslinked polymer networks. Polymerization of thiols-containing compositions was studied in solvent-free UV-curable adhesives [8,15]. Below we describe an extension of our earlier investigations [15] of the effects of aromatic thiols on kinetics of photopolymerization in solvent-free compositions.

2. Experimental

Solutions of initiator, aromatic thiol and, in some cases, di-functional urethane acrylate oligomer in monomers were used. Hexanediol diacrylate (HDDA) and isobornyl acrylate (IBOA) (Sartomer) were monomers (reactive diluents). 1-Hydroxycyclohexyl phenyl ketone and 2,2-dimethoxy-2-phenylacetophenone (Irgacure® 184 and Irgacure® 651 form Ciba) were used to photoinitiate photopolymerization, at concentrations of 0%, 1% or 3% by weight. Aromatic thiols, 2-benzoxazolethiol (BOT) and 2-benzothiazolethiol (BTT) (Aldrich) were used at concentration ranging from 0.01 to 5%. Urethane diacrylate oligomer (CN963B80, Sartomer) was used for viscosity modification and to form mechanically stable cured polymer films, ~70 μm thick.

Fourier transform infrared absorption (FTIR) monitoring of photopolymerization kinetics was conducted at acrylate double bond absorption maximum at 810 cm^{-1} using FTIR spectrophotometer (Nicolet). Liquid resin was deposited between two KF crystal windows in thin layer. The crystal ‘sandwich’ was placed in the optical path of analyzing light in FTIR spectrometer and exposed to UV light (intensity ~22 $\mathrm{mJ/cm}^2$) for various time intervals, while the IR absorption was recorded.

The mechanical properties of the cured films were tested using a conventional instrumentation (Instron Corp.). Differential scanning calorimetry (DSC) was conducted in nitrogen flow [15].

3. Results and discussion

Previously reported initiation and co-initiation by thiols were relatively inefficient [18–20]. Therefore, to detect a change in photoinitiation rate caused by an addition of aromatic thiols, photoinitiation had to be inefficient in the absence of thiol. At >3% of benzoin-type photoinitiator, polymerization photoinitiation in inert atmosphere is close to the limit of efficiency [22,23]. At concentration of 1% of benzoin-type initiator, conversion of acrylate double bond is slower. The effect of thiol was expected to be more noticeable in such composition. Indeed it was observed that addition of 0.1% of BOT accelerated photo-conversion of HDDA and IBOA acrylate double bond in the presence of 1% of Irgacure® 184 (Fig. 1).

An increase in reaction rate observed in the presence of BOT was reproduced in the presence of BTT as well. In the presence of alternative photoinitiator, Irgacure® 651 instead of Irgacure® 184, acrylate photo-induced disappearance was monitored at the same concentration of BOT and BTT. The results confirmed that thio-group effects are not associated with particular initiator used.

The rate of polymerization was evaluated by the degree of acrylate double bond conversion after certain period of UV-illumination. The acrylate group conversion was recorded in HDDA and IBOA systems as a function of BOT or BTT concentration (Fig. 2). Acceleration of acrylate double bond conversion was observed at low concentration of aromatic thiols, <0.5%. It is common to observe decrease in the rate of photo-induced conversion of the acrylate at higher concentration of chain-transfer agents, as was the case in the present work as well (Fig. 2).

An unexpected acceleration of acrylate photo-conversion in the presence of small amount of mercaptan was confirmed by photo-DSC measurements. Photo-DSC confirmed that there was a definite maximum in the dependence

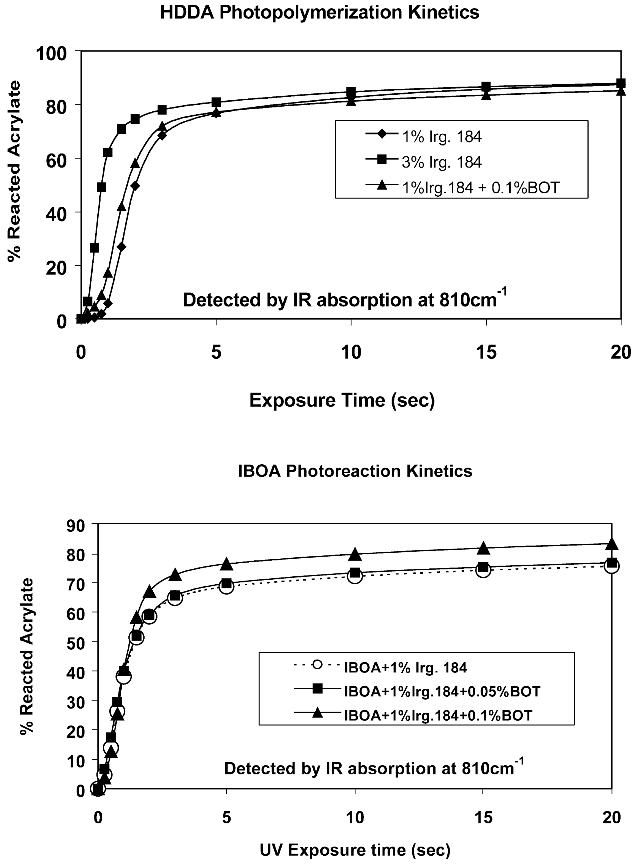

Fig. 1. Kinetics of photo-conversion of acrylate double bond in HDDA and IBOA solutions of Irgacure® 184 in the presence of 2-benzoxazolethiol.

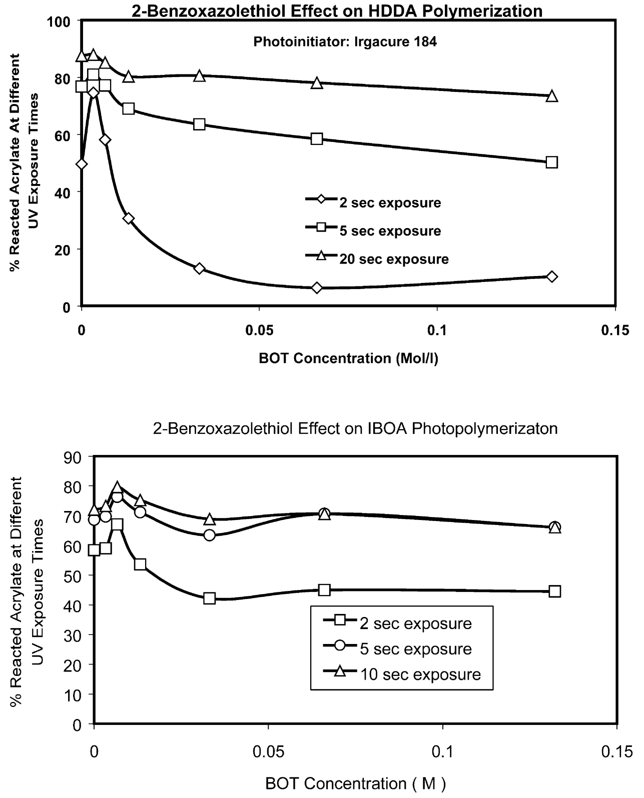

Fig. 2. Dependence of acrylate double bond photo-induced conversion in the presence of 1% of Irgacure® 184 on concentration of 2-benzoxazolethiol.

of photo-conversion enthalpy of solution of 1% Irgacure® 184 in HDDA on the concentration of added aromatic thiol. We detected that at 0.2–0.5% of BOT or BTT the heat emitted during photo-induced reactions of HDDA or IBOA was higher than that in the absence of thiols (Fig. 3).

Increased rate of acrylate group photo-conversion detected by FTIR or by photo-DSC does not necessarily signify an increased polymer yield or increased rate of photopolymerization. Indeed, acrylic monomer radicals may photo-react with thiol without yielding high molecular weight molecules. Mechanical properties of the cured acrylate composition and the glass transition temperature are better indicators of whether molecules of high molecular weight were formed. Polymerization of monomers, HDDA and IBOA, did not result in good enough films to allow differential measurements of the mechanical properties. The compositions containing urethane diacrylate oligomer (CN963B80), and Irgacure® 184 dissolved in HDDA and various concentrations of BOT were tested during and after photo-exposure. Again, as in the case of photoreactions of pure monomers, an increase in acrylate conversion yield and rate was observed at BOT concentration ≈0.1% (Fig. 4).

Since the film formed by photo-curing of compositions containing oligomer were mechanically stable, the tensile properties of these films were measured. It was found that tensile strength, modulus and, to a lesser extent, elongation of the cured polymer films exhibited a local maximum at ≈0.1% of BOT (Fig. 5). BTT addition effects were similar.

Decrease in cured films tensile strength, modulus, and increase in elongation at break indicated that molecular weight and degree of crosslinking of polymer is lower than that in the absence of chain-transfer agent. This is well known and widely utilized effect of all chain-transfer agents and thiols, in particular. At thiol concentration ≥5%, photo-curing of the compositions similar to ones described here did not result in films dry to the touch at room temperature [24].

It was expected that addition of chain-transfer agent to photopolymerizable composition would decrease mechanical strength and increase elongation of the formed polymer films. This follows from the reaction scheme presented above. However, strength and elongation increase when ≤0.2% of BOT was added, was surprising.

It was also observed that glass transition temperature of the photocured polymer films containing 0.1–0.2% BOT

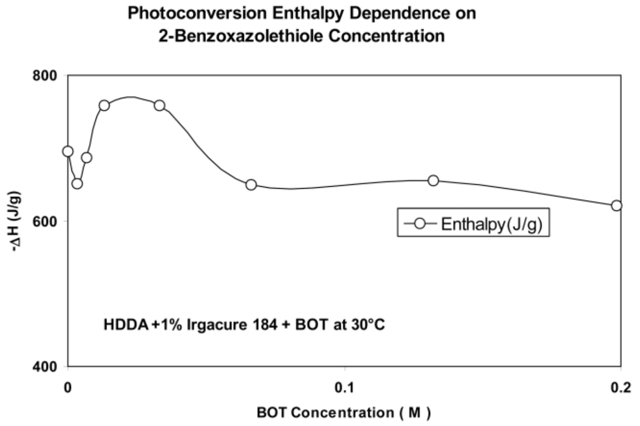

Fig. 3. Photo-DSC detected increase in acrylate photo-conversion rate at certain concentration of aromatic thiols [15].

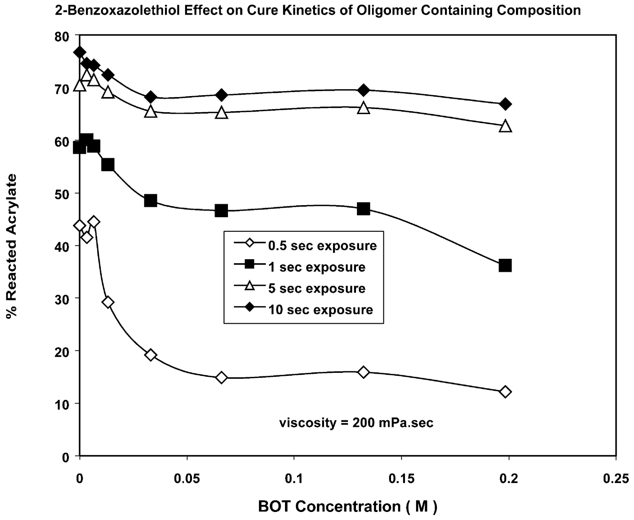

Fig. 4. Dependence of acrylate double bond photo-conversion kinetics on concentration of aromatic thiol in higher viscosity formulations.

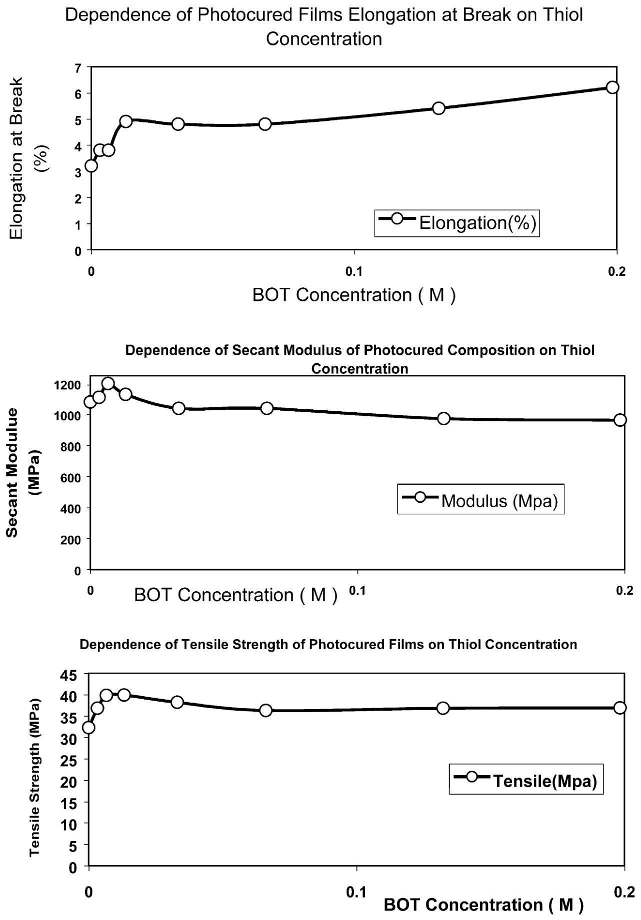

Fig. 5. Dependence of mechanical properties of photo-cured compositions (oligomer, HDDA, Irgacure® 184) on BOT concentration.

was higher than that of the films with lower or higher thiol concentration (Fig. 6). This also indicated higher degree of crosslinking at 0.1% of BOT.

What is a potential mechanism of an increase in the yield and rate of radical photopolymerization in the presence of thiol?

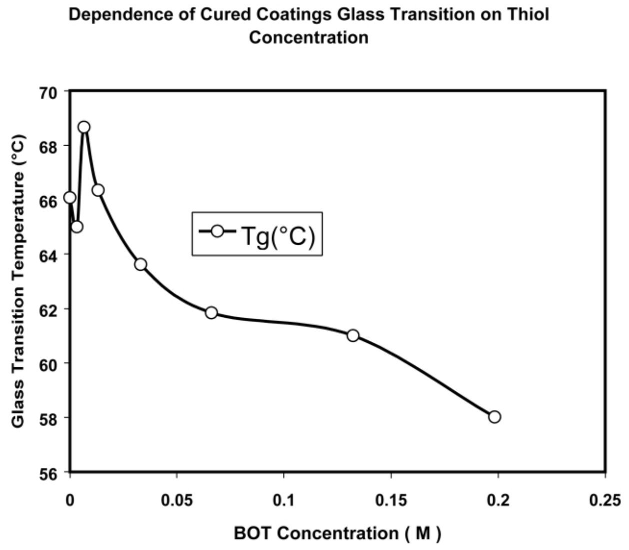

Fig. 6. Dependence of photo-cured films glass transition temperature on concentration of aromatic thiol, BOT.

Oxygen dissolved in the resin forms peroxide radicals that are not capable of continuing chain process. Khoros demonstrated in 1951 [25], that in solutions peroxy-radicals react with mercaptans forming a stable peroxide and thio-radical capable of initiating acrylate polymerization:

$$ROO^{\cdot} + HS\text{-}R_1 \rightarrow ROOH + SR_1^{\cdot}$$

Thus, it is possible that up to a certain concentration of thiols in photopolymerizable composition, the dominant effect is oxygen binding. When thiol concentration is higher than that which is necessary to ‘rejuvenate’ chains terminated by oxygen and negate the effects of oxygen dissolved in the photopolymerizing mixture, the chain-transfer and terminating effects of thiols become dominant. Therefore, at low concentration of thiols an increase of cure rate and polymer yield is observed, while at higher concentration of thiols we detected expected decrease in the rate and yield. Since earlier studies were conducted at thiols concentration exceeding 0.5%, the acceleration of photopolymerization was not detected previously in the photopolymerizing resins. Other factors may also contribute to photopolymerization rate increase at low thiols concentration.

It was observed in the past that thiols form charge-transfer complexes with various aromatic compounds [26]. It is also known that radical polymerization can be initiated by decomposition of charge transfer complexes [27,28]. In the past, it was postulated that aromatic thiols act as co-initiators for hexaarylbiimidazole through postulated charge-transfer mechanism [21]. No experimental confirmation was presented. We investigated possibility of charge transfer complexation between BOT, or BTT and photoinitiator.

Addition of absorption spectra of pure Irgacure® 184 and 2-benzoxazolethiol did not yield the red-shifted line observed in the spectrum of their mixture. Red-shifted absorption spectra are characteristic for charge-transfer complex formation [29]. We concluded that 2-benzoxazolethiol and Irgacure® 184 form a ground state charge transfer complex. Thus, it is conceivable, that photolysis of Irgacure® 184-thiol complex contributes to an increase in initiation efficiency. Such conclusion is consistent with the earlier data on 2-benzoxazolethiol effects (Fig. 7).

Aromatic thiols were used in the past for co-initiation with hexaarylbiimidazole initiator in holographic, printing and proofing photopolymers and in photoresists [19–21]. However, to the best of our knowledge, the co-initiation by thiols used in combination with benzoin-type photoinitiator such as Irgacure® 184 and Irgacure® 651, as described above, was not reported previously. Indeed, the effect was difficult to detect, since usually thiols were used at much higher concentrations.

Aromatic thiols, such as 2-benzoxazolethiol and 2-benzthiazolethiol, strongly absorb light in ultraviolet part

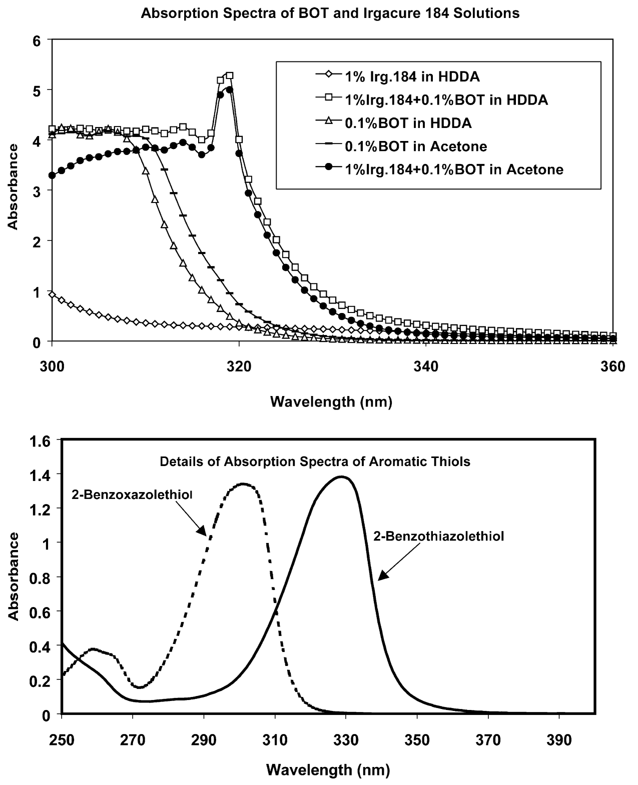

Fig. 7. Absorption spectra indicating formation of charge-transfer complex between benzoin-based initiator and 2-benzoxazolethiol.

of the spectrum at wavelengths ≤350 nm. Together with the ability of thio-group to dissociate producing H^{+} and $RS^{\cdot -}$ ion-radicals or $H^{\cdot}$ and $RS^{\cdot}$, this indicated that thiol molecules may be capable of initiating photopolymerization. Indeed, we observed that in the presence of BOT or BTT, the HDDA and IBOA photopolymerize without additional initiators (Fig. 8). 2-Benzothiazolethiol was a substantially more efficient photoinitiator than 2-benzoxazolethiol. To determine why BTT is more efficient as photoinitiation, the mechanism of photoinitiation by aromatic thiols must be studied further. It is remarkable that photoinitiation is inefficient at concentration >1% for BOT and >3% for BTT (Fig. 8).

Mechanism of observed photopolymerization rate increase in the presence of aromatic thiols can be better understood by monitoring radical processes directly by electron spin resonance or other direct methods. The presented data present the evidence of the effect and point the direction for new photocurable resins development.

4. Conclusion

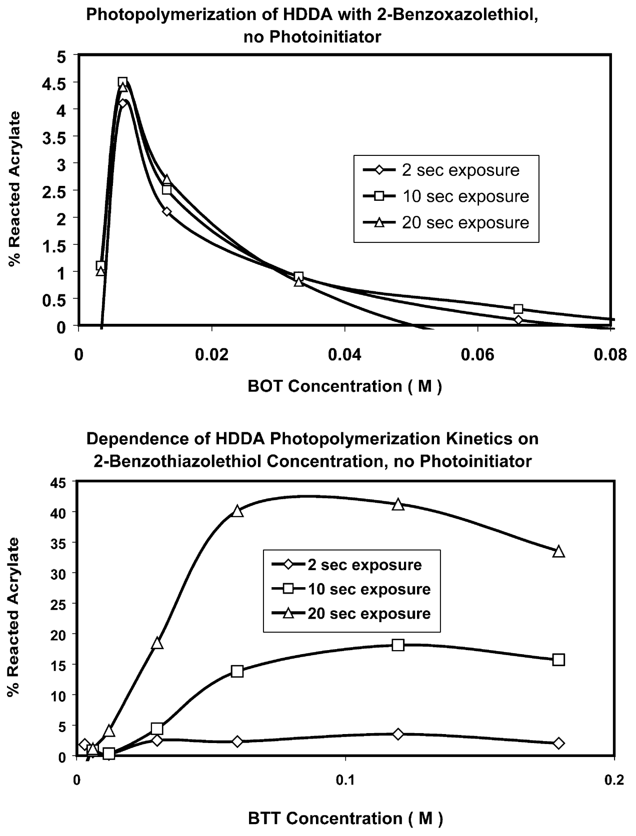

Fig. 8. Initiation of acrylate photo-conversion by aromatic thiols, BTT and BOT, no 'conventional' photoinitiator was present.

It was found that aromatic thiols, 2-benzoxazolethiol and 2-benzothiazolethiol, can be used as photopolymerization co-initiators and as inefficient initiator. Indication of possible mechanism of thiol influence on photopolymerisation kinetics were found, such as formation of charge transfer complexes, the results are inconclusive. Direct detection of radical or ion-radical species during photoexcitation of polymerizable composition is required for confirmation of charge-transfer and oxygen binding mechanism of initiation and co-initiation by aromatic thiols. Electron spin resonance in conjunction with pulsed laser or electron beam excitation can be used to follow radical reaction kinetics and charge-transfer initiation [30]. In the absence of mechanistic studies, the observed effects can be used to increase photoinitiation efficiency, and modification of mechanical properties of cured films and coatings.

Acknowledgements

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