



Invited Review Paper / Çağrılı Derleme Makalesi
RADICALIC PHOTOINITIATORS IN UV-CURING

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Geliş/Received: 02.05.2006

ABSTRACT

Photopolymerization science has become an increasing interesting subject because of its widespread applications . In the development of this technology, photoinitiator systems play a very important role. Absorption of light radiation of the appropriate wavelenght by a photoinitiator lead to the formation of primary radical species able to convert a multifunctional monomer into a crosslinked network. The performance of the photoinitiation system is related to high absorptivity, high efficiency in terms of both quantum yield for radical formation and high reactivity towards the monomer, low odor and toxicity and good storage stability. Photoinitiated radical polymerization may be in itiated by both cleavage (type I) and H-abstracting (type II) initiators. In this survey, Type I and type II initiator systems were investigated and additionally recently developed one-component thioxanthone based photoinitiators were reported.

Keywords: Photoinitiator, UV-curing, photoinitiated polymerization.

UV İLE SERTLEŞMEDE KULLANILAN RADİKALİK FOTOBASLATICILAR

ÖZET

Fotopolimerizasyon bilimi , uygulama alanlarındaki artış nedeniyle gittikçe artan bir öneme sahip olmaktadır. Bu teknolojinin gelişiminde fotobaşlatıcı çok önemli bir role sahiptir. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan primer radikaller çok fonksiyonlu akrilatları çapraz bağlı yapılara dönüştürürler. Fotobaşlatıcı sistemin etkinliği , absorpsiyon özelliğine , radikal oluşumu ve radikalın monomere katılımının etkinliğine, kokusuz ve zehirsiz and iyi depolanma özelliğine sahip olması ile ilgilidir. Fotobaşlatılmış radikal polimerizasyonu bölünebilen (I.tip) ve H- alan (II.tip) başlatıcılardan her ikisi ile başlatılabilir. Bu incelemede, I.Tip ve II. Tip fotobaşlatıcı sistemleri ele alınmıştır ve ilave olarak son zamanlarda geliştirilen tek bileşenli tiyokzanton bazlı fotobaşlatıcılarda rapor edilmiştir.

Anahtar Sözcükler: Fotobaşlatıcı, UV ile sertleştirme, fotobaşlatılmış polimerizasyon.

1. INTRODUCTION

The photoinitiated free radical polymerization reactions are used widely on a commercial scale for a number of different applications such as curing of coatings on various materials, adhesives, printing inks and photorezists [1-5]. The growth of radiation curing industry is dependent on continued innovation to support this technology. A wide range of free radical photoinitiating systems, fullfilling requirements for industrial application, e.g. wavelength selectivity, solubility e.t.c. are now available . A large portion of today's relevant research concerns photoinitiators , i.e. introduction of new initiators or improving the solubility of available initiators[1-4]. Photoinitiated radical polymerization may be initiated by both cleavage (Type I) and H-

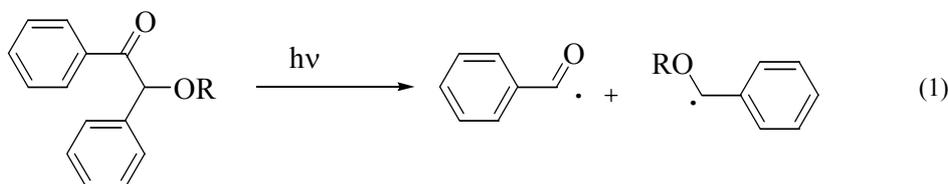
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abstraction type (Type II) initiators. Because of their vital role in photopolymerization, photoinitiators are the subject of particularly extensive research. In contrast to thermally initiated polymerizations, photopolymerization can be performed at room temperature. This is a striking advantage for both classical polymerization of monofunctional monomers and modern curing applications. As far as curing of coatings or surfaces is concerned it has to be noted, that thermal initiation is often not practical, especially if large areas or fine structures are to be cured or if the curing formulation is, like for dental fillings, placed in a surrounding that should rather not be heated. Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as pointed out above without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sun light. These features make photopolymerization an ecologically friendly and economical technology, that has high potential for further development.

Aromatic Carbonyl Compounds

1.1. Benzoin Derivatives

Benzoin and its derivatives are the most widely used photoinitiators for radical polymerization of vinyl monomers. As depicted in (1), they undergo α -cleavage to produce benzoyl and α -substituted benzyl radicals upon photolysis.



The importance of these photoinitiators derives from the following: they possess high absorptions in the far UV region ($\lambda_{\text{max}} = 300\text{-}400$ nm, $\epsilon_{\text{max}} \geq 100\text{-}200$ l mol⁻¹ cm⁻¹), high quantum efficiencies for radical generation and a relatively short-lived triplet state [6].

Regarding the photochemistry of benzoin derivatives, starting from excited triplet states populated after intersystem crossing, Norrish Type I bond scission is the main chemical reaction occurring under various experimental conditions [7-11]. In the consequence of this bond cleavage, benzoyl and ether radicals are formed. In the absence of monomer, hydrogen abstraction takes place leading to benzaldehyde, benzil and pinacol derivatives [7-9]. The reactivity of benzoyl and benzyl ether radicals were found to be almost the same provided the concentration of radicals is low and that of monomer high. On the other hand, if the concentration of radicals is high and that of monomer low, benzoyl radicals are more reactive towards monomer molecules present than the ether radicals [10, 12].

Regarding practical applications it has to be mentioned that benzoin derivatives are only storable for limited time at ambient temperature, i.e., they slowly but steadily decompose thermally during storage.

1.2. Benzilketals

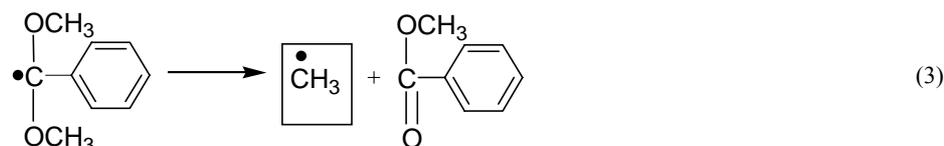
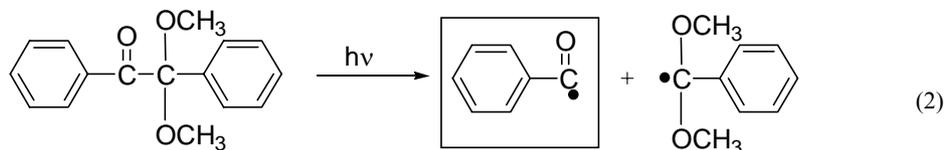
Benzilketals are another important class of photoinitiators developed for free radical vinyl polymerization. Benzilketals exhibit higher thermal stability than benzoin compounds due to the absence of thermally labile benzylic hydrogen. The most prominent member of this class is the commercially used DMPA. This initiator shows indeed an excellent efficiency in photopolymerizations and is at the same time easy to synthesize. Other benzilketals are also suitable initiators but do not reach the price performance ratio of DMPA.

Table 1. Benzilketals for Photopolymerization

2,2-dimethoxy-2-phenylacetophenone (DMPA) [13, 14-16]	2,2-diethoxy-2-phenylacetophenone	benzilglycolketal (BGK) [13,17]

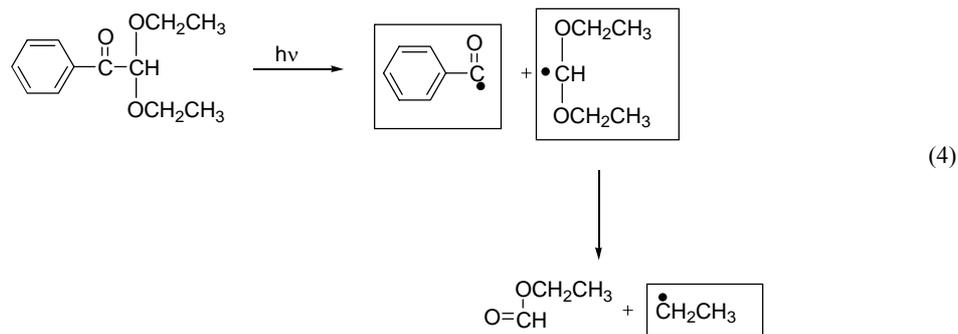
Like benzoin ethers, benzilketals undergo α -cleavage whereby a benzoyl radical and a dialkoxybenzyl radical is formed. While the benzoyl radicals are, as explained earlier, vigorously reacting with olefinic bonds of vinyl monomers, dialkoxybenzyl radicals were found to be of low reactivity. Actually, one of seven dialkoxy benzyl radicals formed is found to be incorporated into the polymer chain during the photopolymerization of methylmethacrylate initiated by DMPA [18]. However, to what extent this portion of dialkoxy benzyl groups is caused by termination rather than initiation remains unclear.

Dimethoxybenzyl radicals undergo a fragmentation yielding methyl radicals [42-44], which act as additional initiating species in radical vinyl polymerization [14,19-22].



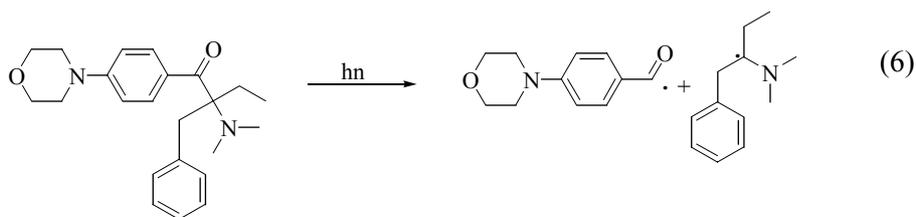
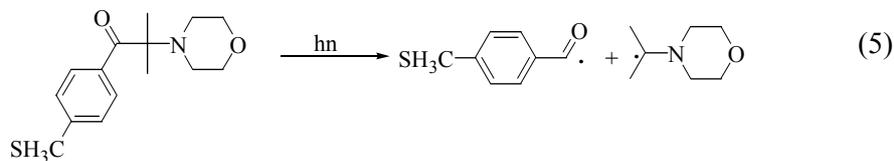
1.3. Acetophenones

α -Substituted acetophenones are another important class of photoinitiators used in various applications of free radical polymerizations [19, 23-25]. These initiators exhibit excellent initiator properties especially in micellar solutions [26]. The most prominent example of this class of photoinitiators is the commercially available α , α -diethoxyacetophenone (DEAP); furthermore 1-benzoylcyclohexanol and 2-hydroxy-2-methyl-1-phenylpropanone are initiators with good properties. Besides high efficiency additional advantage of acetophenones include high storage stability and little tendency towards yellowing. Regarding photochemistry, both Norrish Type I and Norrish Type II bond ruptures were evidenced [22]. However, only the α -cleavage (Norrish Type I) gives initiating radicals: benzoyl radicals directly formed upon the light induced α -cleavage and ethyl radicals, generated in a subsequent thermal fragmentation reaction.



1.4. α -Aminoalkylphenones

α -Aminoalkylphenones have recently been developed for the use in pigmented photopolymerizations.

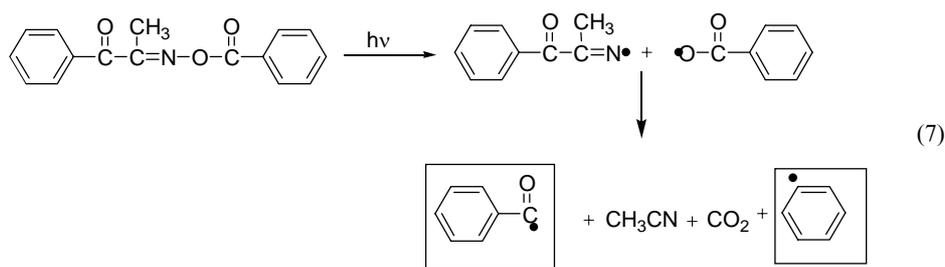


These compounds possess better absorption characteristics than many other aromatic ketone photoinitiators and are, therefore, quite amenable to practical applications where irradiation at longer wavelengths is desired. There is no doubt that α -aminoalkylphenones undergo α -cleavage to yield initiating benzoyl radicals and other carbon centered radicals [27-28]. By means of thioxanthone as triplet sensitizer the sensitivity of the initiating formulation can be extended to the near UV or even visible region of the spectrum [29-31]. Recently, ammonium group containing benzoin ethers have turned out to be efficient, water-soluble photoinitiators in the polymerization of trimethylolpropane triacrylate [32].

1.5. O-acyl- α -oximino Ketones

O-acyl- α -oximino ketones are known to undergo cleavage with high quantum efficiency [34] and have been used as photoinitiators for acrylates and unsaturated polyesters [34-36]. Besides benzoyl radicals, phenyl radicals are produced in a secondary reaction. Both radical types are reactive in initiation. The most prominent example of these initiators is O-benzoyl- α -oximino-1-phenylpropane-1-one, the reaction of which is illustrated in (7).

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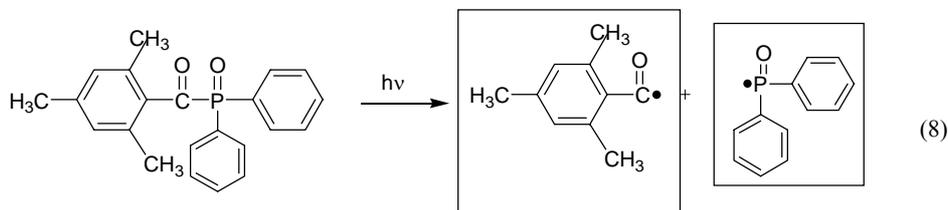
Although these compounds absorb more strongly in the near UV than most of the other aromatic photoinitiators, their use as photoinitiators is limited, since they are thermally not very stable. The relatively weak N-O bond dissociates both photochemically and thermally at moderate temperatures.

1.6. Acylphosphine Oxide and its Derivatives

Acylphosphine oxides and acylphosphonates with different structures have been used as photoinitiators for free-radical initiated photopolymerization .

Long wavelength absorption characteristics make these compounds particularly useful for the polymerization of TiO₂ pigmented formulations containing acrylate or styrene type monomers and of glass fiber reinforced polyester laminates with reduced transparency [37-43]. These initiators are thermally stable up to 180°C and no polymerization takes place when the fully formulated systems are stored in dark. Moreover, very little yellowing occurs in coatings cured with acylphosphine oxides. With respect to the storage of curing formulations and the curing itself it has to be taken into account that acylphosphine oxides may react with water, alcohols or amines, what leads to the cleavage of the C-P bond [43]. By introducing bulky groups in *ortho*-position of the benzoyl group the solvolysis is significantly slowed down. Furthermore, these substituents seem also to be able to increase the proneness to α -scission .

Extensive investigations on the photochemistry of acylphosphine oxides revealed that they do undergo α -cleavage with fairly high quantum yields [44]. Furthermore it was found that the phosphonyl radicals formed are highly reactive towards vinyl monomers.

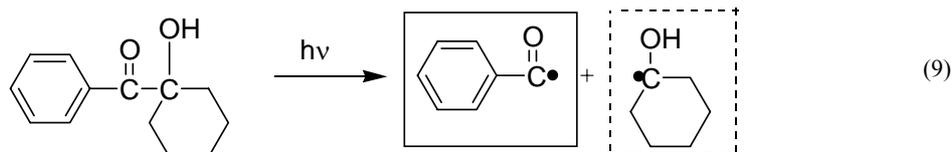


Notably, dialkoxyphosphonyl radicals are highly reactive towards monomers. For carbon centered benzoyl radicals significantly lower rate constants are detected. The excellent reaction efficiency of phosphonyl radicals is attributed to the high electron density at the phosphorous atom and the pyramidal structure of the radicals providing more favorable steric conditions for the unpaired radical site to react with monomers.

1.7. α -Hydroxy Alkylphenones

α -Hydroxy alkylphenone is another photoinitiator containing benzoyl groups that has found practical application in many vinyl polymerizations [45-47]. This initiator has both a high light sensitivity and good thermal stability. Furthermore, coatings prepared using α -hydroxy alkylphenone do show only very little yellowing, what makes these compounds particularly suitable for clear coatings [15]. Another striking advantage is that α,α' -dialkyl hydroxyphenones are liquid at room temperature and are of relatively low polarity. Therefore, they are easy to dissolve in non-polar curing formulations [48-52].

However, for 1-hydroxycyclohexylphenylketone (see (9)) initiated polymerization of methyl 2-*tert*-butyl acrylate it has been shown by analysis of photolysis products that hydroxyalkyl radicals add to the double bond of the monomer [53].



2. TYPE II PHOTOINITIATORS

Aromatic ketone / coinitiator system

Photolysis of aromatic ketones, such as benzophenone, in the presence of hydrogen donors, such as alcohols, amines or thiols, leads to the formation of a radical stemming from the carbonyl compound (ketyl type radical in the case of benzophenone) and another radical derived from the hydrogen donor. Provided vinyl monomer is present the latter may initiate a chain polymerization. The radicals stemming from the carbonyl compound are usually not reactive towards vinyl monomers due to bulkiness and/or the delocalization of the unpaired electron.

Apart from benzophenones, thioxanthone, anthraquinones, ketocoumarins and some 1,2 diketones are used in conjunction with coinitiators for initiating vinyl polymerizations. Since the initiation is based on a bimolecular reaction, type II photoinitiators initiate generally slower than type I photoinitiators. These systems are, therefore, more sensitive to the quenching of excited triplet states, which are the reactive precursors of light induced chemical changes for carbonyl compounds. In view of applications, the selection of the coinitiator is undoubtedly of great importance. Mostly, amines are used because of their high efficiency and the relatively low price. Excited carbonyl triplet states are usually by two to three orders of magnitude more reactive towards tertiary amines than towards alcohols or ethers.

2.1. Benzophenones

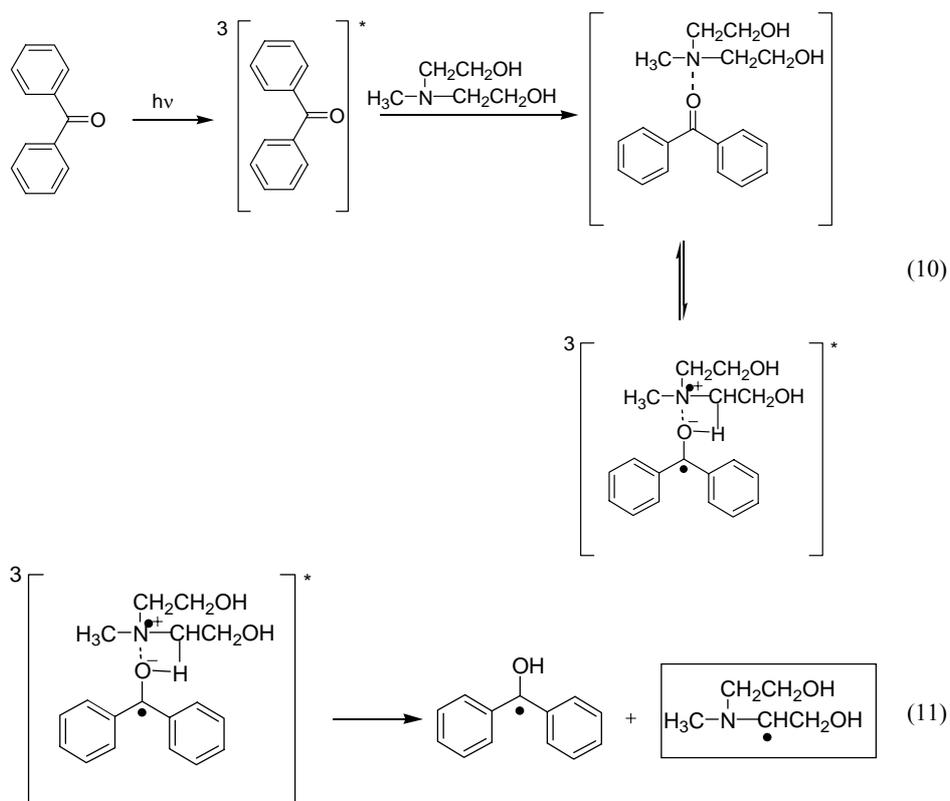
Hydrogen abstraction by the excited triplet manifold of benzophenone, which is populated with quantum yields close to unity, from tertiary amines (N-methyl diethanolamine) is depicted in (10) and (11) [54]. The carbon centered radical stemming from the amine is able to initiate free radical polymerizations of suitable monomers. α -Aminoalkylradicals are especially suitable for the polymerization of acrylates [55] and are less efficient in styrene polymerization, what is explainable in terms of triplet quenching by styrene. The ketyl radicals add due to resonance stabilization and for steric reasons only scarcely to olefinic double bonds but instead undergo recombination and disproportionation reactions, as shown in (12). Furthermore, they may act as chain terminators in the polymerization leading to ketyl moieties incorporated into polymer chains and relatively short chains [56].

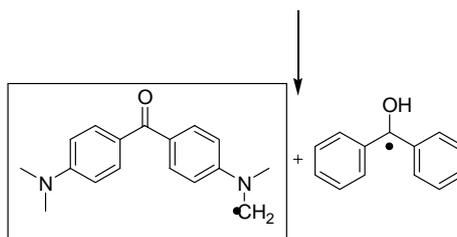
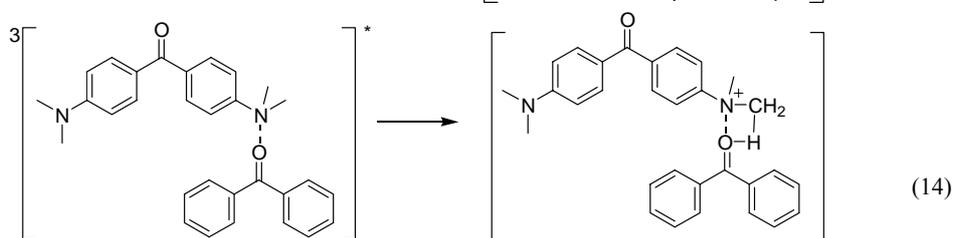
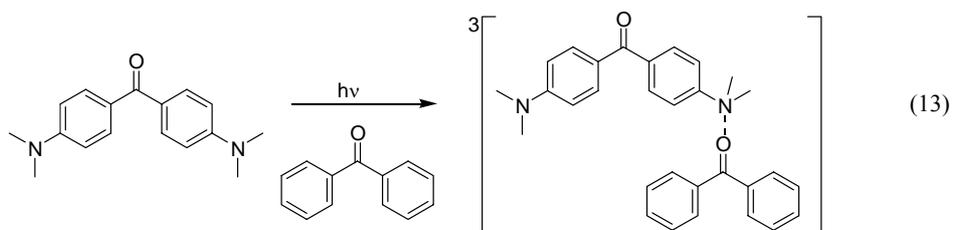
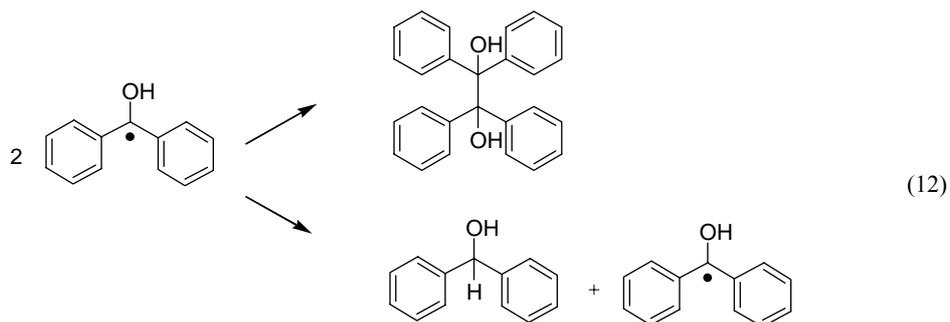
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In order to avoid chain termination by ketyl radicals, additives such as onium salts [57-59] or certain bromocompounds [60] have turned out to be useful. These additives react with the ketyl radicals thus suppressing chain termination. In the case of onium salts, phenyl radicals, which initiate polymerizations instead of terminating growing chains are produced by the interaction of ketyl radicals with salt entities. Thus, the overall effect of these additives is an enhancement in polymerization rate.

2.2. Michler's Ketone

Michler's ketone, 4,4'-bis(dimethylamino)benzophenone, is another efficient hydrogen abstraction type photoinitiator that possesses both chromophoric aromatic ketone and tertiary amine groups in its structure. It absorbs much stronger light of 365 nm than does benzophenone. Michler's ketone may undergo photoinduced hydrogen abstraction from ground state molecules, but with a relatively low efficiency [61]. However, in most cases it is used in conjunction with benzophenone and serves as a hydrogen donor. The mechanism involves electron transfer in the exciplex formed and subsequent hydrogen abstraction (13-14) [62].





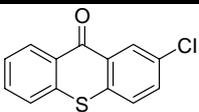
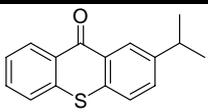
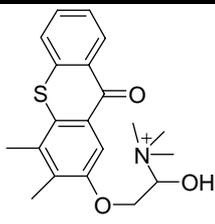
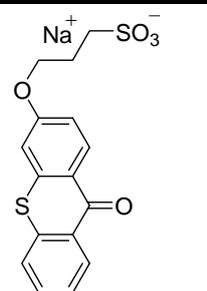
Noteworthy, the combination of Michler's ketone and benzophenone gives a synergistic effect: this system is more efficient in forming initiating radicals than are the two components in conjunction with amines. A disadvantage of Michler's ketone is the yellow color, coatings cured with this ketone possess. It prevents a utilization of the highly efficient benzophenone / Michler's ketone system in white pigmented formulations. Moreover, regarding Michler's ketone there is suspicion of carcinogenicity.

2.3. Thioxanthenes

Thioxanthenes in conjunction with tertiary amines are efficient photoinitiators [63] with absorption characteristics that compare favorably with benzophenones; absorption maxima are in the range between 380 to 420 nm ($\epsilon = 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) depending on the substitution pattern.

The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques [64-67]. It was found that in conjunction with tertiary amines reactions similar to that of benzophenone / amine systems take place.

Table 10. Thioxanthone Derivatives for Photoinitiation

			
[65]	[18]	[68-69]	

The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. Furthermore, ionic thioxanthone derivatives have been developed, which may be employed for water based curing formulations [68-69]. A great advantage is that thioxanthones are virtually colorless and do not cause yellowing in the final products.

As for other type II initiating systems, quenching by monomer has to be taken into account, provided monomers with low triplet energies are used. Thus, the bimolecular rate constants of the reaction of various thioxanthones with styrene are between 3 to $6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. For acrylonitrile, for example, values in the range between 4×10^5 and $4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ are found indicating very little quenching [44].

Interestingly, when N-ethoxy-2-methylpyridinium salt is added to the mixture consisting of monomer (methyl methacrylate) and thioxanthone, a significant enhancement of the polymerization rate is detected [70]. This effect has been attributed to a reaction of ketyl radicals stemming from thioxanthone with the pyridinium salt, what leads to the generation of initiating ethoxy radicals.

2.4. One component photoinitiators

In this chapter, it was reported here a new strategy for the photoinitiating systems. This novel one component systems based on the thioxanthone which is very well known Type II initiator, and it also contains initiating part which is attached to thioxanthone chromophore. We synthesized a thiol derivative of thioxanthone (TX-SH) at first and reported the use of it as a photoinitiator for free radical polymerization. A great advantage is that this photoinitiator does not require an additional co-initiator, its capability to act as an initiator for the polymerization of methylmethacrylate, styrene and multifunctional monomers were examined.

The mechanism is based on the intermolecular reaction of triplet, $^3\text{TX-SH}^*$, with the thiol moiety of ground state TX-SH. When TX-SH was irradiated in the presence of a monomer, it was found that it can serve as both a triplet photosensitizer and a hydrogen donor. The resulting thiyl radicals initiate the polymerization.

Intramolecular hydrogen abstraction was excluded by laser flash photolysis experiments. Flash photolysis (355 nm excitation) of a highly diluted solution of TX-SH affords a readily detectable transient absorption spectrum, which decayed in a first-order kinetic with a lifetime of $20 \mu\text{s}$ (Figure 1).

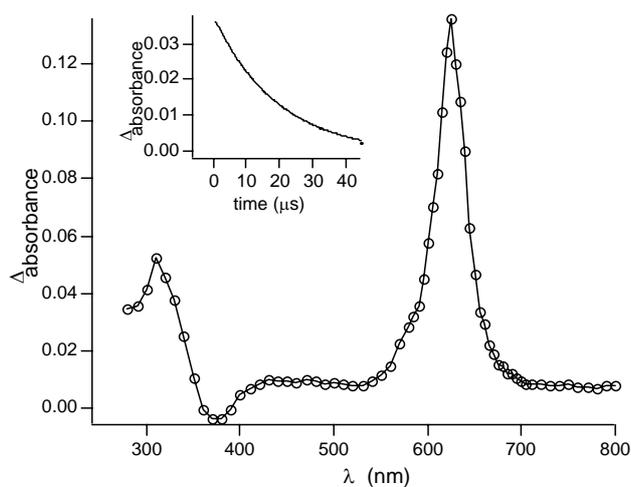
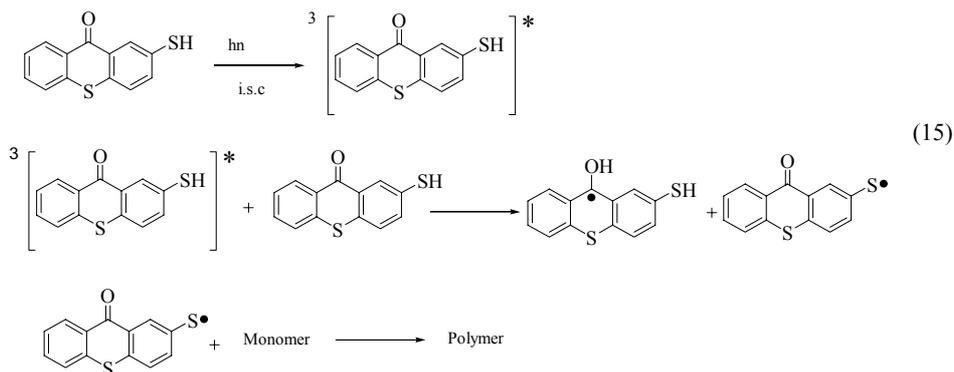


Figure 1. Transient optical absorption spectrum recorded 1-5 μs following laser excitation (355 nm, 5 ns) of 2-mercaptothioxanthone (TX-SH) (1×10^{-4} M) in argon-saturated acetonitrile solution at 23°C. Inset: Transient absorption kinetic observed at 625 nm.

Transient absorption and lifetime was similar to the triplet-triplet absorption of the parent TX[71-72]. Therefore, it was concluded that the transient absorption corresponds to the triplet-triplet absorption of TX-SH. If intramolecular hydrogen abstraction would dominate, then the transient decay kinetic should be significantly faster. This is consistent with an unfavorable interaction of the excited carbonyl group with the thiol moiety caused by the rigidity of the linked aromatic groups. Similar limitations were accounted for Michler's ketone[73-74] as a photoinitiator which also possesses both chromophoric and hydrogen donating sites. Phosphorescence spectra of TX covalently attached polymers provided further evidence for the initiation mechanism. Phosphorescence spectra in 2-methyltetrahydrofuran at 77 K of TX-SH and PMMA obtained from photopolymerization initiated by TX-SH were very similar. It was also found that the excitation spectra for the emission signal are in good agreement with the absorption spectra of TX-SH. The phosphorescence lifetimes at 77 K, were also very similar; 147 ms and 145 ms, respectively. Thus, various spectroscopic investigations revealed that thioxanthone groups are incorporated into the polymers.

Moreover, phosphorescence measurements were useful to gain information on the triplet configuration of TX-SH. Phosphorescence spectra of ketones with $n-\pi^*$ nature of the lowest triplet state are usually structured, due to the vibrational progression of the C=O vibration, and $\pi-\pi^*$ triplets are mostly unstructured[75-76]. In addition, the phosphorescence lifetime for $n-\pi^*$ triplets are significantly shorter (in the order of several milliseconds) compared to $\pi-\pi^*$ triplets (more than 100 ms)[71,75]. Thus, the broad structureless phosphorescence of TX-SH, together with the long phosphorescence lifetime in a matrix at 77 K, indicates a $\pi-\pi^*$ nature of the lowest triplet state. This was in agreement with the $\pi-\pi^*$ nature of the lowest triplet state of unsubstituted TX[77]. TX-SH is an efficient photoinitiator for free radical polymerization. This odorless new photoinitiator is very attractive, since it does not require an additional hydrogen donor and initiates the polymerization of both acrylate and styrene monomers in the presence and absence of air. In addition, TX-SH possesses excellent optical absorption properties in the near UV spectral region, ensuring efficient light absorption from most UV-curing tools[78].

The efficiency of the TX-SH in the photocuring of formulations containing multifunctional monomers was also studied. The disappearance of double bonds during the photocuring of the formulations was followed by Fourier transform real-time spectroscopy (RTIR) that has spread out widely in recent years. By monitoring changes in the characteristics monomer IR absorption bands it allows to follow fast polymerization process continuously. In Figure 3 kinetic profiles referring to the polymerization of the mixture epoxyacrylate and tripropyleneglycoldiacrylate under polychromatic light are shown. TX-SH and TX/MDEA served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1} corresponding to the frequency of the twisting vibration of the double bonds. The shape of the curves indicates the existence of two stages. A rapid first stage which is followed by a slow stage. It can be seen that at sufficiently high concentrations polymerization takes place more rapidly with TX-SH than that of the corresponding with TX/MDEA. Figure 4 depicts the response of the polymerization of trimethylolpropanetriacrylate to photoinitiation by TX-SH in the absence and presence of MDEA. A curve for the polymerization with TX/MDEA system is also provided for comparison. Again, slightly higher conversions is observed with TX-SH photoinitiator.

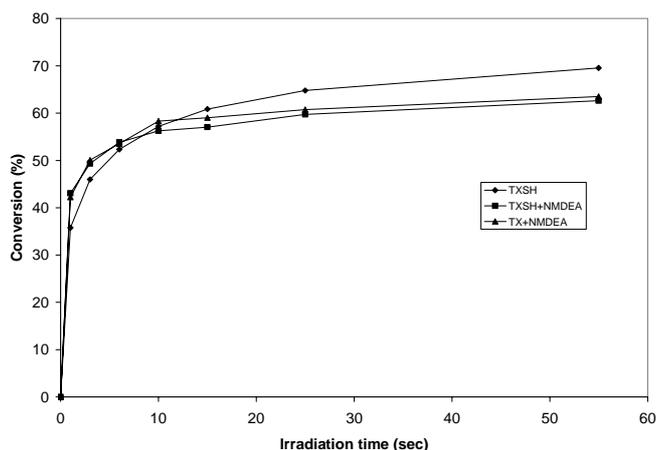
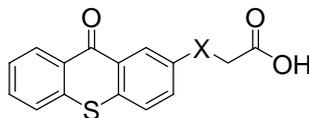


Figure 2. Kinetic profiles demonstrating the photopolymerization of trimethylol propanetriacrylate containing different photoinitiators with polychromatic light. Photoinitiator (1 %): (♦)TX-SH (■) TX-SH and NMDEA, and (▲) TX and NMDEA

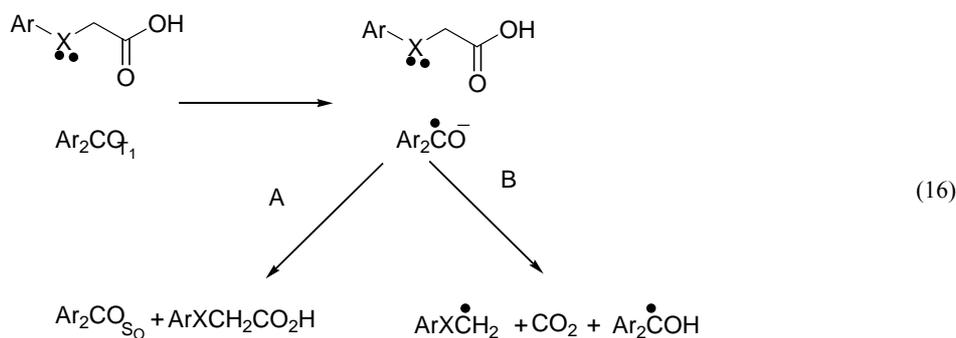
As part of our continuing interest in novel one component photoinitiating systems, we reported the synthesis, the use of and mechanism of acetic acid derivatives of thioxanthone of the

structures shown below as photoinitiators for free radical polymerization. The light absorbing and electron donating and, consequently, hydrogen donating sites are in the photoinitiator molecules[79].



X: O,S

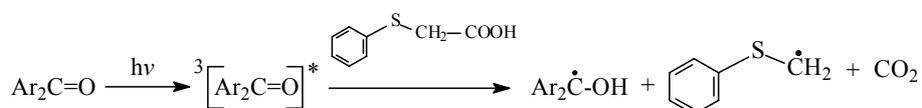
Early mechanistic studies on two component systems of this type suggested an aromatic carbonyl sensitized decarboxylation mechanism. According to Davidson and co-workers[80-81], excited aromatic carbonyl compounds such as benzophenone can undergo electron transfer with sulfur -or -oxygen-containing carboxylic acids to give carboxylate radicals. Subsequent decarboxylation of this radical produces an alkyl radical (16)



In our case, a mechanistic study concerning photoinitiated free radical polymerization by using thioxanthone thio-acetic acid (TX-S-CH₂-COOH) as one-component *Type II* photoinitiator was performed.

As stated in our previous article[79] and can be seen from Figure 3, TX-S-CH₂-COOH has an excellent optical absorption in the near UV ($\epsilon_{290} = 20490 \text{ mol}^{-1} \text{ L cm}^{-1}$ and $\epsilon_{384} = 3900 \text{ mol}^{-1} \text{ L cm}^{-1}$) which may find practical application in UV-curing of pigmented systems as free radical photoinitiator.

In view of the decarboxylation behavior¹³⁻¹⁶ of the sulfur containing carboxylic acids upon reaction with photoexcited aromatic carbonyl compounds as depicted below on the example of benzophenone (see Scheme 3), photolysis of TX-S-CH₂-COOH results in the formation of free radicals. The decarboxylation nature of the photoinitiation was demonstrated by concomitant evolution of carbon dioxide. In order to clarify the mechanistic details, we performed steady state and time-resolved fluorescence and laser flash photolysis measurements together with polymerization experiments.



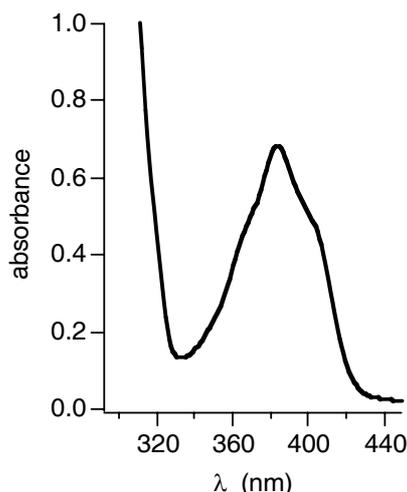


Figure 3. Optical absorption spectrum of TX-S-CH₂-COOH in 2-methyltetrahydrofuran.

Scheme 3

The quantum yield for fluorescence emission (ϕ_f) in 2-methyl tetrahydrofuran at 23 °C was found to be 0.06 which is similar to that of unsubstituted thioxanthone.

Steady-state and time-resolved excitation and emission spectra of TX-S-CH₂-COOH were also measured at 77 K in the same solvent. The two emission bands were found at 430 nm and 508 nm and are attributed to fluorescence and phosphorescence, respectively. Phosphorescence measurements were useful to gain information on the triplet configuration of TX-S-CH₂-COOH. In addition, the phosphorescence lifetime for $n-\pi^*$ triplets were significantly shorter (in the order of several milliseconds) compared to $\pi-\pi^*$ triplets (more than 100 ms) [73,82]. Thus, the broad structureless phosphorescence of TX-S-CH₂-COOH, together with the long phosphorescence lifetime, i.e. 127 ms in a matrix at 77 K, indicates a $\pi-\pi^*$ nature of the lowest triplet state. This was in agreement with the $\pi-\pi^*$ nature of the lowest triplet state of unsubstituted TX and also with TX-SH [78].

To investigate the triplet state of TX-S-CH₂-COOH further, laser flash photolysis was performed. Figure 4 shows the transient absorption spectra of a deoxygenated acetonitrile solution containing TX-S-CH₂-COOH recorded 10-30 ns and 300-400 ns after irradiation with laser pulses of 355 nm. The spectrum shows two peaks at 660 nm and 340 nm. The peak at 660 nm was assigned to the triplet-triplet absorption of TX-S-CH₂-COOH based on similarities with the triplet-triplet spectra of TX and TX-SH. Figure 5 (right) shows the decay kinetic of the transient absorption at 660 nm. The triplet-triplet absorption at 660 nm decayed in a first-order kinetic corresponding to a lifetime of 65 ns. In contrast, the transient absorption at 340 nm decayed orders of magnitudes slower (12 μ s) (Figure 5, left). Notably, both transients were quenched by oxygen with rate constants close to the diffusion limit ($k_{O_2}^{340\text{ nm}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{O_2}^{660\text{ nm}} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) suggesting a radical or triplet nature of the transients.

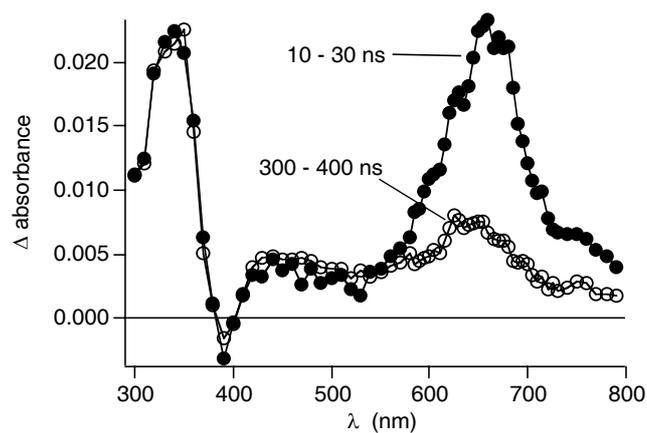


Figure 4. Transient optical absorption spectrum recorded 10 – 30 ns and 300 – 400 ns following laser excitation (355 nm, 5 ns) of TX-S-CH₂-COOH in argon saturated acetonitrile solution at 23 °C.

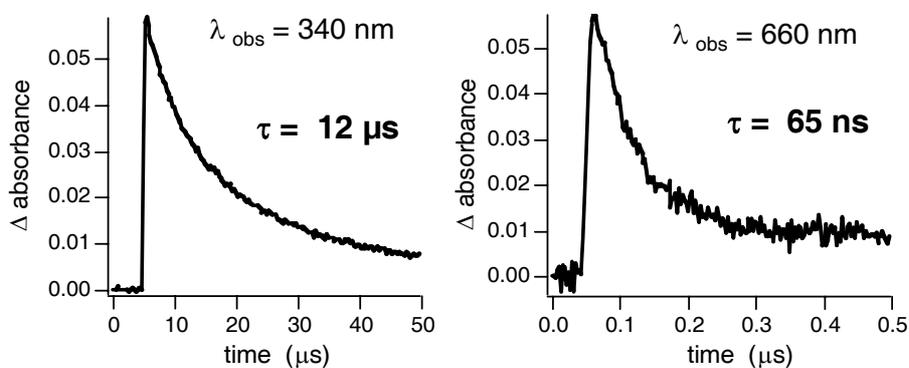


Figure 5. Transient absorption kinetics observed at 340 nm (left) and 660 nm (right) following laser excitation (355 nm, 5 ns) of TX-S-CH₂-COOH in argon saturated acetonitrile solution at 23 °C.

Typically, triplet states of TX derivatives, such as TX or TX-SH possess triplet lifetimes longer than 10 μs (TX-SH: $\tau_T = 21 \mu\text{s}$) [78]. In contrast, TX-S-CH₂-COOH showed a triplet lifetime of only 65 ns, which indicates the involvement of a fast intramolecular quenching process. We proposed that the fast intramolecular quenching process was a fragmentation reaction leading to carbon centered radicals (see below), which then can initiate the polymerization. Previously, we have shown that TX-S-CH₂-COOH is a good photoinitiator to initiate free radical polymerization of acrylates, indicating that TX-S-CH₂-COOH generates efficiently radicals[81]. To test, if triplet quenching occurs in an intramolecular process or intermolecular process, laser flash photolysis experiments were performed at two different concentrations of TX-S-CH₂-COOH, 2.5×10^{-5} M and 5×10^{-5} M. At both concentrations, an identical triplet lifetime (65 ns) was observed, showing that at these low photoinitiator concentrations no intermolecular reaction

occurs, where the triplet of TX-S-CH₂-COOH gets quenched by another molecule of TX-S-CH₂-COOH in the ground state. Furthermore, such a bimolecular quenching process is unlikely at these low concentrations of TX-S-CH₂-COOH (5×10^{-5} M), because of the short triplet lifetime (65 ns).

To investigate if bimolecular quenching can occur at higher concentrations, a model compound was used, thiophenoxyacetic acid (Ph-S-CH₂-COOH), as quencher of triplet states of TX-S-CH₂-COOH (analog reaction in Scheme 3). Laser flash photolysis experiments were performed with deoxygenated acetonitrile solutions of TX-S-CH₂-COOH (5×10^{-5} M) and different concentrations of Ph-S-CH₂-COOH ($0 - 2.5 \times 10^{-2}$ M). Pseudo-first order treatment of the decay kinetics of the TX-S-CH₂-COOH triplet states observed at 660 nm gave a quenching rate constant of $8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This shows that a bimolecular quenching process, where the triplet of TX-S-CH₂-COOH gets quenched by another molecule of TX-S-CH₂-COOH in the ground state, can only compete with the intramolecular quenching at concentrations in the order of several mM.

We also performed stationary polymerization experiments. The dependence of conversion of methyl methacrylate to polymer upon irradiating in DMF in air, on the concentration of the initiator, is shown in Figure 6. Initially, the rate of initiation is proportional to the absorbed light and consequently the amount of initiator. However, when the concentration of the initiator was above a certain level the intermolecular hydrogen abstraction may become a dominant process.

Therefore, the formation of free radicals capable of initiating polymerization, was determined by the competition of intra and intermolecular hydrogen abstraction processes. Indeed, the polymers obtained by using low initiator concentration ($[I] = 1 \times 10^{-3}$ M) do not exhibit the characteristic absorption band of the thioxanthone moiety.

On the contrary, the UV-vis spectra of the corresponding poly(methyl methacrylate) PMMA obtained by using a very high initiator concentration ($[I] = 5 \times 10^{-3}$ M) and purification by several precipitation presents an absorption band with a shoulder at 383 nm which is similar to the absorption spectrum of pure TX-S-CH₂-COOH.

The covalently attached TX-moiety to the polymer is more clearly shown by luminescence spectroscopy. Figure 7 shows fluorescence and phosphorescence spectra of the same solutions of the UV-vis measurements (As can be seen from Figure 7, fluorescence and phosphorescence spectra in 2-methyltetrahydrofuran at 296 and 77 K, respectively, of the initiator and the corresponding polymer are very similar. methyltetrahydrofuran solutions at room temperature (c,d) or frozen matrixes at 77 K (a,b) of the purified polymer (several precipitations) obtained by photopolymerization of methyl methacrylate initiated by TX-S-CH₂-COOH (5×10^{-3} M). For comparison, the luminescence spectra of pure TX-S-CH₂-COOH are also shown (solid lines).

The slight blue shift may be attributed to the slightly different structure of the polymer linked TX compared to the pure initiator. The excitation spectra for the emission signals (Figure 7, dashed lines) are in good agreement with the absorption spectrum of the precursor TX-S-CH₂-COOH (solid lines). In addition, the phosphorescence lifetimes at 77 K are also very similar; 127 and 123 ms, respectively.

Based on the study on the above spectroscopic and flash photolysis of TX-S-CH₂-COOH, and polymerization studies, we proposed the scheme (see Scheme 4) illustrating major processes that may occur during photoinitiated polymerization.

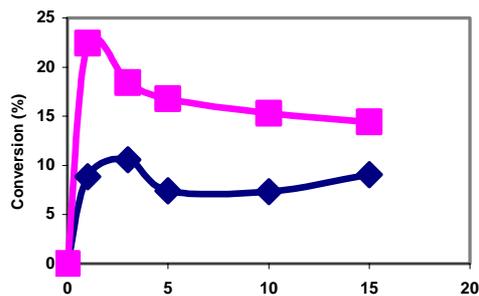


Figure 6. Photopolymerization of methyl methacrylate[4.68 mol.l^{-1}] by using TX-S- $\text{CH}_2\text{-COOH}$ in DMF for 10 min (◆) and 15 min (■).

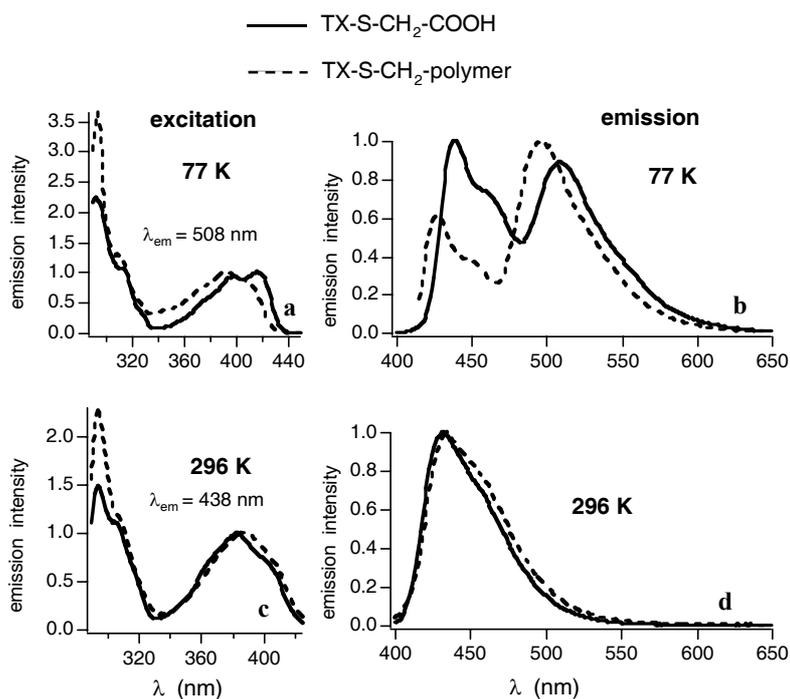
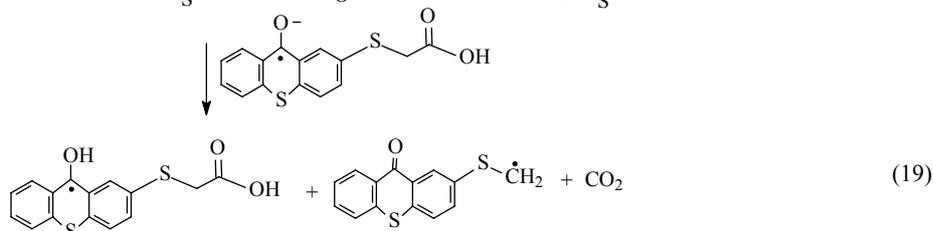
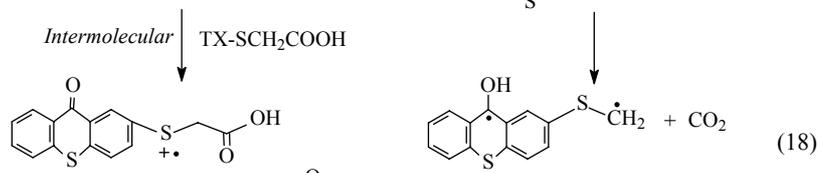
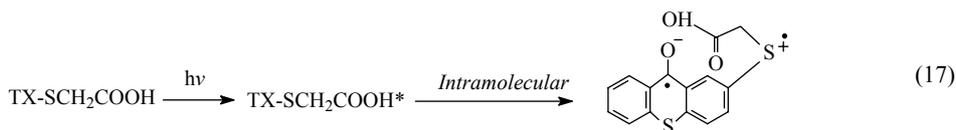


Figure 7. Dashed lines: luminescence excitation (left) and emission spectra (right) of 2-methyltetrahydrofuran solutions at room temperature (c,d) or frozen matrixes at 77 K (a,b) of the purified polymer (several precipitations) obtained by photopolymerization of methyl methacrylate initiated by TX-S- $\text{CH}_2\text{-COOH}$ ($5 \times 10^{-3} \text{ M}$). For comparison, the luminescence spectra of pure TX-S- $\text{CH}_2\text{-COOH}$ are also shown (solid lines).



Under low initiator concentrations, the dominant path of the reaction is intramolecular electron transfer followed by hydrogen abstraction and decarboxylation. At the concentrations above 5×10^{-3} M, however, the respective intermolecular reactions may be operative.

Formulations consisting of either TX-S-CH₂-COOH or TX-O-CH₂-COOH as photoinitiator in multifunctional monomers were studied by using of RT-FTIR method. In Figure 7 and 8 kinetic profiles referring to the polymerization of the mixture PEG-6, epoxyacrylate and tripropyleneglycoldiacrylate under polychromatic light are shown for different irradiation times. TX-S-CH₂-COOH or TX-O-CH₂-COOH served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 810 cm⁻¹ corresponding to the frequency of the twisting vibration of the double bonds

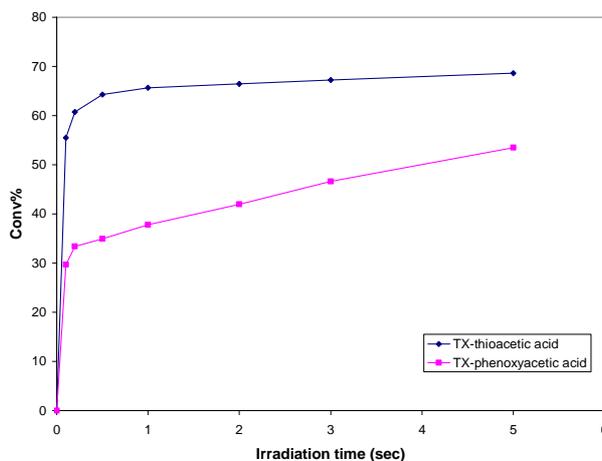


Figure 8. Kinetic profiles demonstrating the photopolymerization of PEG-6 and Photomer 3038 (Epoxyacrylate+25% Tripropyleneglycoldiacrylate) containing different photoinitiators with polychromatic light. Photoinitiator (1 %): (◆)TX-thioacetic acid (■) TX-phenoxyacetic acid

When we prolonged the irradiation time up to 120 sec (Figure 9) both formulation reached to nearly the same conversion percentage values. Conversion percentage values were slightly higher for TX-S-CH₂-COOH than TX-O-CH₂-COOH

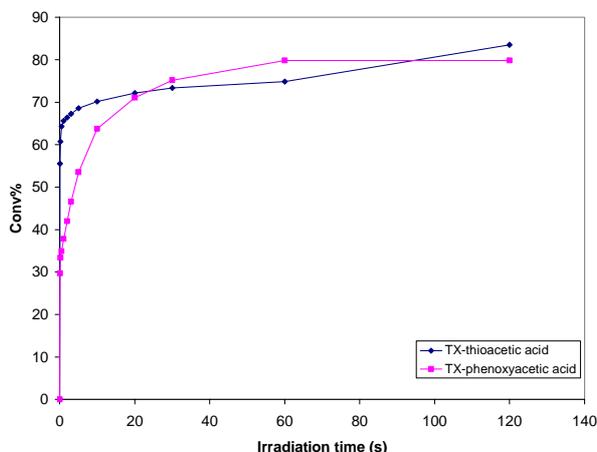


Figure 9. Kinetic profiles demonstrating the photopolymerization of PEG-6 and Photomer 3038 (Epoxyacrylate+25% Tripropyleneglycoldiacrylate) containing different photoinitiators with polychromatic light. Photoinitiator (1 %): (◆)TX-thioacetic acid (■) TX-phenoxyacetic acid

As a new approach, the synthesis and the use of novel one component photoinitiator systems are still under of our interest .

ACKNOWLEDGEMENT

Author thank to Prof.Yusuf Yagci for his extremely valuable help and support and Dr.Meral Aydin, Dr.Steffen Jockusch and Prof. Nicholas Turro for their contribution.

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