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## Shining a light on an adaptable photoinitiator: advances in photopolymerizations initiated by thioxanthenes

Sajjad Dadashi-Silab,<sup>a</sup> Cansu Aydogan<sup>a</sup> and Yusuf Yagci\*<sup>a,b</sup>

Photochemistry plays a central role in synthetic polymer research. Aromatic ketones, examples of which include benzophenone, thioxanthone, camphorquinone, among others, are renowned for their excellent optical characteristics and have been extensively utilized for photochemical induction of polymerization processes. Of particular interest is thioxanthone due to its adaptability for bearing different functionalities and its applications in various modes of photopolymerization, in which it accomplishes photoinitiation in conjunction with other co-initiator compounds; a behavior that is referred to as bi-molecular photoinitiation. In this paper, we review the photochemistry of thioxanthone-based systems and their use in different modes of photoinitiated polymerizations. Citing examples from the literature, the development of various photoinitiating systems based on thioxanthenes along with an understanding of their mechanistic behavior has been elucidated previously.

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### Introduction

The polymer community has witnessed an increasing inclination towards light-mediated polymerization techniques in

recent years. These systems essentially offer the advantage of carrying out reactions efficiently by eliminating the side effects often accompanying the thermally induced counterpart processes of special systems, just to cite one striking example.<sup>1,2</sup> For this reason, photochemical processes are often considered as “green chemistry”.<sup>1,2</sup> Such systems utilize light as the driving force to form suitable initiating sites by absorbing its energy and thereby promoting subsequent photochemical reactions leading to the induction of chemical reactions. Hence, choosing appropriate light absorbing species, *i.e.* photoinitiators or

<sup>a</sup>Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey. E-mail: yusuf@itu.edu.tr; Fax: +90-2122856386; Tel: +90-212 285 3241

<sup>b</sup>Center of Excellence for Advanced Materials Research (CEAMR) and Department of Chemistry, Faculty of Science, King Abdulaziz University, 21589 Jeddah, Saudi Arabia



Sajjad Dadashi-Silab

Sajjad Dadashi-Silab obtained his M.Sc. degree in Chemistry from Istanbul Technical University in 2015, studying under the supervision of Professor Yusuf Yagci. In 2012, he received his B.Sc. degree in Polymer Engineering from Amirkabir University of Technology, Tehran. His graduate research studies were mainly focused on developing new photoinitiating systems for controlled and conventional radical photopolymerizations based on heterogeneous, semiconducting photocatalysis.



Cansu Aydogan

Cansu Aydogan received her B.Sc. degree in Chemistry from Marmara University, in 2011. She completed her M.Sc. studies at the Department of Chemistry in Istanbul Technical University under the supervision of Professor Yusuf Yagci, in 2014. Her research in the Yagci group was essentially focused on benzoxazine chemistry during her M.Sc. She is currently continuing her PhD studies dealing with photoinitiated polymerizations. In particular, thioxanthone-based photoinitiating systems, development of novel polymeric materials, and the synthesis of hyperbranched polymers are the main interests.

photosensitizers, becomes crucial since there has to be good matching of the optical behavior of the photoinitiators with the characteristics of the light source. Photochemical processes have been intensively used in a diverse range of chemical reactions including organic synthesis and materials science, medicinal applications, photocuring and photopolymerization systems.

As the subject of this article, numerous attempts in the area of photoinitiated polymerizations have been undertaken to design new photoinitiating systems, or enhance, improve and expand the scope of existing initiators to fit the many newly emerging needs of advanced technologies.<sup>3</sup> Various types of photoinitiating systems are being developed in academia and applied in industry. Photoinitiators, particularly those involving free radicals and related systems, have been mainly classified in two categories according to their optical behavior: (i) *Type I*, which are also known as  $\alpha$ -cleavage, provide initiating radicals by bond cleavage processes upon absorption of light; (ii) *Type II* undergo photoexcitation followed by an electron or hydrogen transfer process and consequently form initiating species.<sup>4–6</sup> Benzoin and its derivatives are the most widely used *Type I* photoinitiators for radical photopolymerization and are capable of unimolecular bond cleavage on irradiation. As *Type II* photoinitiators, ketone components are of great importance. Examples include benzophenone, thioxanthone, camphorquinone, *etc.*, which exhibit bimolecular photo-behavior in the formation of initiating species. This characteristic behavior arises primarily from photoexcitation of the photoinitiator and its excited state interaction with other components called co-initiators through various transfer processes. *Type II* photoinitiators can be considered advantageous compared with *Type I* as in most cases the energy required for the photoinitiator to undergo bond cleavage is generally high and it necessitates the use of high-energy light sources, *i.e.* with short wavelengths. However, *Type II* photoinitiators exhibit

absorption characteristics at higher wavelengths and can be designed and decorated to manipulate their optical behavior to extend their spectral sensitivity up to the visible range of the electromagnetic spectrum. Such a behavior carries the advantage of using low energy light sources, thus decreasing the cost of processes. Additionally, it provides the possibility of conducting photopolymerization reactions in those systems that are highly sensitive to high-energy exposure, such as those in biological and medical applications. Ultimately, in designing a photoinitiating system, the influence of the special groups used to functionalize the photoinitiators to enhance their photoactivity and lower the cost of the process should be carefully taken into consideration. More important is the influence and critical role of co-initiators which in conjunction with photoinitiators bring about initiating species. Excited state photoinitiators interact with co-initiators according to their redox potentials through reduction or oxidation processes and hence one would expect different excited state interactions in the presence of different types of co-initiator systems.

Traditionally, photoinitiated polymerizations have been employed in free radical,<sup>7,8</sup> cationic<sup>9,10</sup> and, in rare cases, anionic<sup>11</sup> polymerization systems. Applications can be found across a broad spectrum of photocuring, coating, and inking and printing applications, and in medicinal and dental adhesive applications, to fabrication of multidimensional devices and so forth. Despite the tremendous breadth of implementations of these systems, they somehow all lack the ability to provide control of the polymerization process in terms of well-controlled, complex architectures with pre-determined molecular weight properties. Recently, attention has been drawn to the adaptation of light-mediated processes with existing controlled polymerizations such as copper-mediated living radical polymerization techniques,<sup>12–15</sup> reversible addition-fragmentation chain transfer,<sup>16,17</sup> nitroxide-mediated polymerization<sup>18</sup> and so on, or developing novel photocontrolled techniques to achieve photochemically mediated synthesis of well-controlled macromolecular architectures.<sup>19–23</sup> For example, many attempts have been directed towards photochemical induction of the copper-mediated processes, which rely on the photochemical formation of the required copper(I) catalyst by various photochemical means.<sup>24</sup> An important application of such photoinitiation controlled polymerization systems may be the possibility of on-demand-patterning of functionalized surfaces by providing spatio-temporal control.<sup>25</sup>

Our group has long been dealing with investigating, designing, and developing novel photochemical processes for polymer synthesis.<sup>26–28</sup> This review intends to focus on the advent of and progress in photoinitiated polymerization techniques mediated by thioxanthone (TX) and its derivatives. TX-based photoinitiators are an efficient class of photoinitiators widely used in many free radical and cationic polymerization processes. In the first section of this article, we will describe the photochemistry of TX and analogous structures in the formation of suitable initiating sites. The following



**Yusuf Yagci**

*Yusuf Yagci is a professor of Chemistry at Istanbul Technical University (ITU). He received his M.Sc. (1977) and PhD (1979) degrees from Liverpool University (UK). He joined ITU in 1980 where he has remained. He is the recipient of several awards including The Society of Polymer Science, Japan (SPSJ) International Award (2008), the Elginkan Foundation Technology Award (2008), OIC Ministerial COMSTEC Award (2010), and*

*Mustafa Parlar Honorary Award (2013) He was also a member of the Turkish Academy of Sciences (1997–2011). His research interests include all aspects of synthetic polymer chemistry involving photopolymerization and controlled polymerization methods.*

sections will give a comprehensive picture of the advent and development of various TX-based photoinitiating systems including the use of various co-initiator systems, one-component and polymeric photoinitiators. A special focus will be directed towards the mechanistic behavior of each system and their applications for different purposes in macromolecular synthesis. In addition to polymerization systems, in the last section, some miscellaneous applications of TX photosensitizers in different areas of chemistry, materials science and biology will be discussed.

## Photochemistry of thioxanthone: a bimolecular photoinitiator

Photoinitiators are mainly subdivided into the two categories of *Type I* and *Type II* systems. Whilst the formation of radicals in the latter is achieved by a hydrogen abstraction or photo-induced electron transfer processes of the triplet state photoinitiator in the presence of a co-initiator compound, the former undergoes unimolecular fragmentation ( $\alpha$ - or  $\beta$  cleavage) upon absorption of light giving rise to the formation of two initiating radicals (Scheme 1).<sup>29</sup> Depending on the nature of the initiating components, the formation of initiating species in *Type II* systems may well occur through distinct electron transfer reactions or hydrogen abstraction, or a combination of both processes. In the presence of hydrogen-donor co-initiators, like amines, it is mainly believed that an electron transfer process between the triplet state photoinitiator acting as the electron acceptor and the co-initiator as the electron donor primarily forms an ion-pair intermediate of a TX radical anion and a donor radical cation excited state complex (exciplex). Thus, a proton transfer from the  $\alpha$ -position of the co-initiator to the photoinitiator results in the formation of a

ketyl radical derived from the photoinitiator and a radical derived from the co-initiator. Direct abstraction of hydrogen is also possible as in alcohols, ethers and other compounds. Heteroatom-containing co-initiators have been proven to be efficient in the promotion of this process. Amines, thiols, alcohols, ethers, silanes and many others are among the most used co-initiators in such systems with tertiary amines being somehow the most efficient hydrogen donor. Due to the resonance stabilization and steric reasons, the highly conjugated ketyl radicals formed in the aftermath of hydrogen abstraction do not initiate polymerization, but participate in the combination or termination of the growing polymer chains. However, radicals derived from the hydrogen donor compounds are efficient in the initiation process.

Another possibility for the formation of initiating species is the photoinduced electron transfer reaction of a triplet state photoinitiator acting as photosensitizer, with a suitable co-initiator, in which, after a set of subsequent electron transfer and fragmentation reactions, an initiating species including both radicals and/or cations is formed. In this case, an excited state photosensitizer can undergo both oxidation or reduction reactions according to the nature of the co-initiator present and the energy of the absorbed photon. Scheme 2 illustrates the general mechanism of the photoinduced electron transfer reactions of photosensitizers and co-initiators. The excited state photosensitizer is capable of being both more oxidizing or more reducing than the ground state photosensitizer and can be quenched by the respective oxidation or reduction processes. In the oxidative quenching cycle, the excited photosensitizer acts as a reductant as an electron acceptor compound giving rise to the formation of radical anion and radical cation components. In the reductive quenching cycle, however, the excited photosensitizer acts as an oxidant and oxidizes an electron donor compound resulting in the formation of photosensitizer radical anion and co-initiator radical cation species. These radical ions can either directly initiate polymerization or, in most cases, undergo further fragmentation reactions

### Type I photoinitiation:



R: H, alkyl, subs. alkyl

R': H, alkyl, subs. alkyl

### Type II photoinitiation:



R-H (H-donor):

amines, alcohols, ethers etc.

**Scheme 1** Typical representation of the photolysis of the radical photoinitiators based on *Type I* (top) and *Type II* (bottom) systems with the examples of a benzoin derivative and thioxanthone, respectively.



**Scheme 2** General representation of photoinduced electron transfer reactions of photosensitizers (PS) in the presence of electron acceptors (A) or electron donors (D).

bringing about active initiating species. There is also the possibility of reacting the radical ions with some electron donor or electron acceptor to give the ground state photosensitizer and also the corresponding radical or cation species.

These reactions, of course, are thermodynamically feasible if the free energy change of electron transfer ( $\Delta G_{\text{et}}$ ) estimated by the Rehm–Weller equation is negative:

$$\Delta G_{\text{et}} = f_c [E_{1/2}^{\text{ox}}(\text{D}/\text{D}^{+\cdot}) - E_{1/2}^{\text{red}}(\text{A}/\text{A}^{\cdot-})] - E_s + \Delta E_c$$

where,  $f_c$  is the Faraday constant,  $E_{1/2}^{\text{ox}}(\text{D}/\text{D}^{+\cdot})$  and  $E_{1/2}^{\text{red}}(\text{A}/\text{A}^{\cdot-})$  are respectively the redox potentials of the donor (D) and acceptor (A) compounds,  $E_s$  is the singlet state energy of the sensitizer and  $\Delta E_c$  is the Coulombic stabilization energy.

In the following sections, we will deliberate in detail the performance and efficiency of photoinitiated polymerizations by TX derivatives in conjunction with various co-initiator compounds by focusing on the mechanistic explanation of the initiation processes and photoinitiator/co-initiator.

## Two-component photoinitiation

TX-based photoinitiators have become a preferable class of photoinitiators over other similar structures such as benzophenones, primarily because of their spectral characteristics. Their absorption maxima appear in the range of 380–420 nm, laying in the near UV and visible ranges, which reduces the required energy for photoexcitations and subsequent formation of initiating radicals. Although various synthesis methods for TX derivatives have been reported, the usually applied method is based on a simple condensation process of thiosalicylic acids with aromatic hydrocarbons in a concentrated sulfuric acid medium as shown in Scheme 3.<sup>30</sup>

By employing functional components during the synthesis, substituted functional TX compounds can easily be obtained. Substitution of different functionalities can considerably affect the characteristics and optical behavior of TX photoinitiators. These may include further shifting of the absorption band to higher wavelengths, as well as facilitating the photoinitiators' applicability in different media and for various purposes, or enhancement of the photoactivity of the initiator (Table 1). From the practical point of view, it is thought that some drawbacks such as yellowing of the final cured products can be considerably suppressed by using a TX-based photoinitiating system.<sup>4,6</sup>



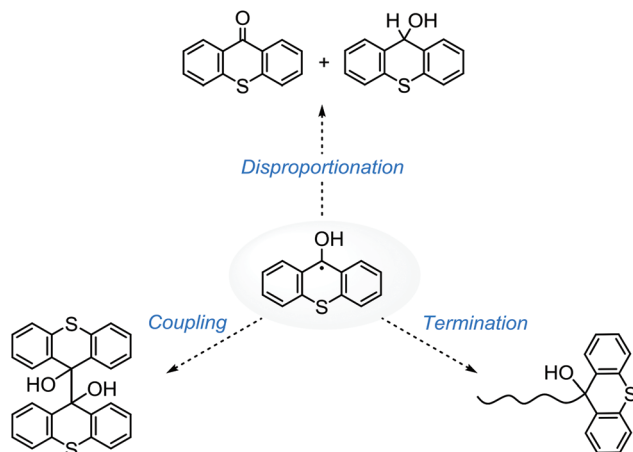
**Scheme 3** Synthesis of thioxanthenes by condensation of thiosalicylic acid and aromatic compounds in the presence of concentrated sulfuric acid.

**Table 1** Absorption characteristics of substituted thioxanthone photoinitiators and the rate constants ( $k_q$ ) of the reactions of their triplets with amine co-initiators<sup>a</sup>

TX derivative	$\lambda_{\text{max}}$ (nm)	$10^{-6} \times k_q$ ( $\text{mol}^{-1} \text{L s}^{-1}$ ) H-donor
	~378	8000 (BMA) 4600 (DEAE)
	~384	6000 (BMA)
	~386	6000 (BMA)
	~400	Rapid self-quenching by hydroxyl group
	~396	580 (DEAE)
	~385	6000 (BMA) 2500 (TEA)

<sup>a</sup> BMA: bis(2-hydroxyethyl)methylamine; TEA: triethylamine; DEAE: 2-(diethylamino)ethanol; data taken from ref. 31, 33 and 42.

Through exploiting various spectroscopic techniques such as laser flash photolysis studies, the mechanism of TX-photo-initiated polymerization has been extensively investigated.<sup>31–40</sup> The process essentially necessitates the presence of a co-initiator to accomplish the formation of initiating species; though quenching can also occur by interaction with low triplet energy monomers or solvents. Amines, for instance, due to their highly reducing properties<sup>41</sup> are commonly used as co-initiators to carry out quenching of triplet TX through the formation of an exciplex or ion pair intermediate between the photoexcited triplet state TX and co-initiator amine, primarily by an electron transfer from the amine to TX which is followed by a proton transfer to the reduced photoinitiator TX. This brings about a free radical on the  $\alpha$ -position of the co-initiator and a thioxanthylyl ketyl radical is formed as well. It was found that the photoactivity of TX-based photoinitiators is highly dependent on the substitution pattern of the photoinitiator as well as the nature of the media and other co-compounds present in the system. Evidently, the presence and type of functionalities can considerably affect the absorption maxima, extinction coefficients and quantum yields of TX during the photoinitiation process. Most importantly, the nature of co-initiators governs the process by which initiation can occur. Table 1 lists some of the studied TX derivatives to illustrate the effect of substitution on the absorption maxima.



Scheme 4 Possible reactions of thioxanthyl ketyl radicals.

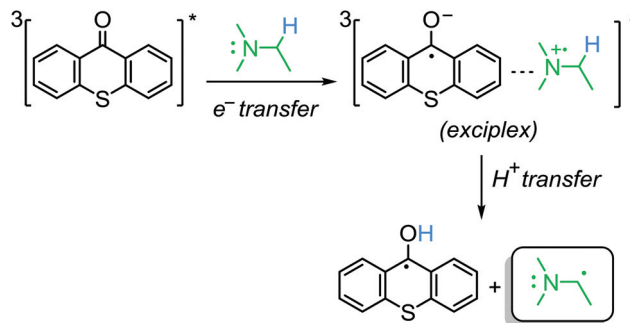
TX derivatives seem to be more efficacious compared with unsubstituted TX in terms of higher absorption maxima and higher extinction co-efficients and applicability for various purposes.

As for the thioxanthyl ketyl radicals formed after the course of hydrogen abstraction, they are believed to rarely add across a monomer and initiate polymerization. Instead, they tend to undergo either a process of disproportionation to return the initial ground state TX and form a thioxanthole species or couple to form a pinacol compound, though with a reduced probability due to the steric factors. Termination of the growing radical chains during the polymerization by the thioxanthyl ketyl radicals has also been reported as one of the reaction possibilities.<sup>43</sup> Scheme 4 depicts the possible reactions of thioxanthyl ketyl radicals.

### Co-initiators

The efficiency of the photoinitiation of polymerization assisted by TX derivatives is chiefly governed by both the properties of the TX photoinitiator as well as by the characteristics of the co-initiator used and its affinity to undergo electron or hydrogen transfer processes. Hydrogen donor compounds such as amines, thiols, alcohols *etc.* have been utilized as co-initiators in quenching the photoexcited triplet state TX and formation of free radicals. Of these, amines have been proven the most efficient hydrogen donor. The hydrogen atom at the  $\alpha$ -position of a heteroatom (N, O, S) is highly likely to be abstracted by the triplet TX and go on to form initiating radicals. The following section gives a comprehensive picture of the types and efficiency of co-initiators used in the presence of TX derivatives with mechanistic explanation of the interaction and initiation processes.

**Amines.** Amine co-initiators are among the most extensively investigated in photopolymerization systems. As noted earlier, the initiation mechanism when using amines as co-initiators in a *Type II* photoinitiation system is thought to proceed primarily through the interaction of the triplet state photo-



Scheme 5 Photoreduction of triplet thioxanthone by amines.

initiator with the non-bonding electrons present in the heteroatom. This process leads to an electron transfer from the amine to the photoinitiator and consequently to the formation of an ion pair intermediate. Subsequent proton transfer from the  $\alpha$ -position then yields a ketyl radical on the photoinitiator and a carbon-centered radical derived from the amine as represented in Scheme 5.<sup>41,44</sup> The formation of this radical anion intermediate on the photoinitiator was further evidenced by the appearance of a new absorption band at 480–510 nm in the end-of-pulse transient absorption spectra.<sup>32</sup> It has been found that the efficiency of this quenching process with amine co-initiators involving electron and proton transfer reactions is highly dependent on the structural properties of the amine that control its propensity to undergo electron transfer and form an exciplex with the triplet ketone and its hydrogen donation properties. The quenching rate has been found to correlate with the ionization potential of the amines.<sup>44</sup> The order of amine photopolymerization efficiency generally increases from primary to secondary and, finally, to tertiary amines. Some amine co-initiators used in combination with TX derivatives are shown in Chart 1.

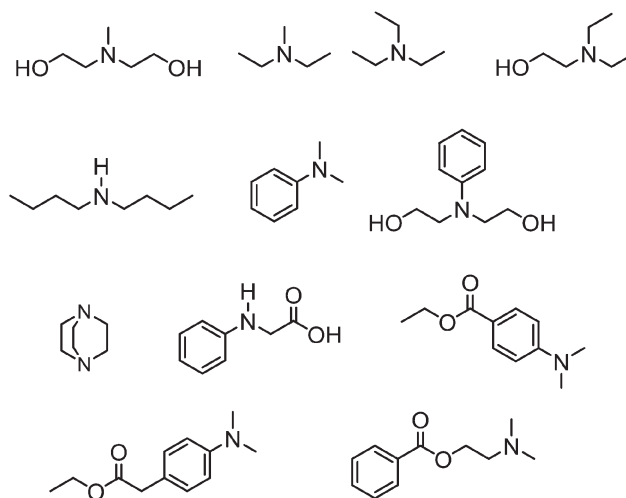


Chart 1 A list of frequently used amine co-initiators in combination with thioxanthone-based photoinitiators.

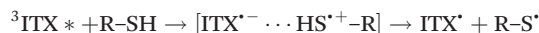


Chart 2 Benzoxazines as co-initiators in Type II photoinitiated polymerization.

**Benzoxazines.** Although in ring form, benzoxazines are structurally similar to substituted aniline compounds and, therefore, can be used as co-initiators in Type II photoinitiation systems (Chart 2).<sup>45</sup> Efficient interaction of benzoxazine with triplet state TX leading to quenching of the photoinitiator by a subsequent electron transfer and hydrogen abstraction from the benzoxazine was evidenced by fluorescence quenching (or Stern–Volmer) studies. The resulting aminoalkyl radicals successfully initiated free radical polymerization of methyl methacrylate with results comparable to triethylamine, which is a commonly used amine co-initiator in such systems. Benzoxazines are an important class of materials that form a network with superior physical and mechanical properties by a ring-opening polymerization process.<sup>46</sup> Treating the obtained polymers initiated by benzoxazine co-initiators with a bi-functional benzoxazine molecule, resulted in a cured network consisting of poly(methyl methacrylate) (PMMA) chains incorporated into the network through the ring opening of the benzoxazine functionality at the PMMA chains.

**Thiols.** Mercaptans or thiol-containing compounds have also been utilized as co-initiators in combination with TX derivatives and other Type II photoinitiating systems. Aromatic thiols are well-known strong quenchers of triplet state photoinitiators.<sup>47,48</sup> The resulting thiyl radicals have been reported to efficiently add across a wide range of double-bonds with the ability of reducing oxygen inhibition in photopolymerization systems. The observed insensitivity of thiol-based systems to oxygen inhibition is due to the ability of peroxy radicals formed by oxygen scavenging to abstract a hydrogen atom from thiols thus giving rise to the formation of a new initiating thiyl radical.<sup>49</sup> Unlike aromatic thiols, the quantum yields of quenching with aliphatic thiols are relatively low.<sup>50</sup> Photo-induced free radical polymerization based on the use of aromatic thiols as co-initiators in conjunction with Type II photoinitiators such as isopropylthioxanthone (ITX) or camphorquinone (CQ) has been reported.<sup>51–54</sup> Investigating the initiation mechanism by laser flash photolysis, Andrzejewska and co-workers observed a rapid quenching of the excited ITX\* by thiol, as the intensity of the transient peak of ITX\* around 640 nm dropped quickly following the appearance of new absorption peaks at 425 and 590 nm. The latter peak was ascribed to the formation of thiyl radicals from the co-initiator thiols while the former arose due to the formation of ketyl radicals. The radical formation was suggested to occur through a photoinduced electron transfer between the triplet state TX and the thiol leading to the formation of an intermediate con-

sisting of a photoinitiator radical anion and co-initiator radical cation. This was followed by a proton transfer to form ketyl and thiyl radicals with the latter being able to initiate the polymerization process as shown below:

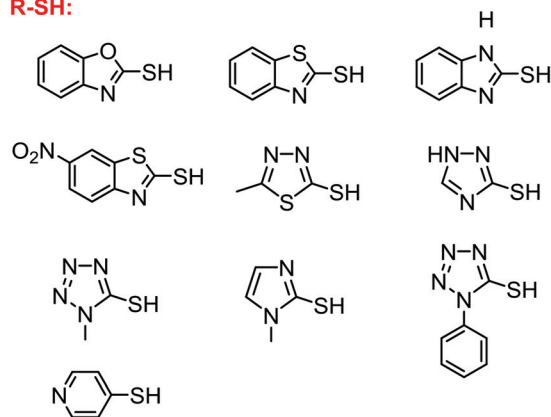
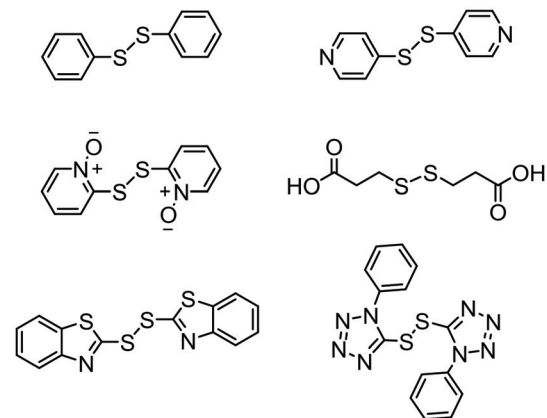


Lalevee and co-workers also have investigated the efficiency of thiols with different functionalities and disulfide components as co-initiators together with various photosensitizers and photoinitiators.<sup>55,56</sup> It was suggested that an energy transfer process between the triplet state TX and the disulfide compound led to the dissociation of the S–S bond, which brought about two sulfur-centered initiating radicals derived from the disulfide:



It should also be noted that the irradiation of disulfides, though at lower wavelengths, could result in the dissociation of the S–S bond, albeit the efficiency was comparatively low as in the case of the photosensitizer/disulfide bi-component system. In the case of thiols, however, the hydrogen abstraction process, as shown above, accounted for the formation of thiyl radicals. Chart 3 shows a list of thiol and disulfide-based co-initiators used for the photoinitiation of free radical polymerizations.

Thiols have also been recognized for their part in thiol–ene reactions in the formation of polymers and networks in a radical-mediated step growth-like polymerization method. The thiol–ene polymerization mechanism is based on propagation and chain transfer processes between the thiol and double bond functional groups.<sup>57,58</sup> Abstraction of a hydrogen atom from the participating thiol by a carbon-centered radical, results in the formation of thiyl radicals capable of adding to a double bond. There follows a radical transfer process from the carbon-centered radical to the thiol functionality. These propagation and chain transfer processes encompass the general mechanism of thiol–ene polymerization. In the photochemical process, the required initial radicals are generated by using various photoinitiator systems. Type I photoinitiators provide radicals by cleaving upon irradiation whereas in the case of Type II systems the interaction of the photoexcited triplet state photoinitiator with the thiol functionality results in hydrogen abstraction from the thiol and subsequently formation of thiyl radicals. Initial investigations in this area were carried out by Morgan and Ketley who used benzophenone as a photoinitiator to form photocured polymers of polyenes and polythiols; the photoexcited benzophenone abstracted the labile hydrogen from the thiol to generate a thiyl radical leading to crosslinking polyene and polythiol.<sup>59</sup> Decker *et al.* studied photo-crosslinking of poly(styrene-*co*-butadiene) rubber with double bonds on the backbone (alkene) or pendant double bonds (vinyl) using the thiol–ene polymerization method in the presence of a multifunctional thiol and a photoinitiator.<sup>60</sup> The reactivity of thiyl radicals to copolymerize with the

**R-SH:****R-S-S-R:**

**Chart 3** Thiol and disulfide compounds used as co-initiators in photo-induced free radical polymerization in the presence of thioxanones.



**Scheme 6** Schematic representation of photo-crosslinking of polymers containing double bonds by using multifunctional thiols.

pendant vinyl groups was found to be 10 times higher than the copolymerization with butene double bonds (Scheme 6).

This kind of thiol-ene reaction is well known as an example of click chemistry that can be triggered *via* either thermal, photo, or redox processes. However, photochemical processes are preferred over the other protocols due to the advantage of spatial and temporal control over the thiol-ene addition process.<sup>28,61</sup> Scheme 7 outlines the overall mechanism of the thiol-ene click chemistry. Yagci and co-workers thoroughly investigated the influence of the type of photoinitiator on the



**Scheme 7** Light-induced thiol-ene click reaction.

photoinitiation of thiol-ene click chemistry for functionalization of polymers.<sup>62</sup> Thiol- or allyl-modified polystyrenes with controlled molecular weight properties were successfully functionalized by an appropriate alkene or thiol functionality in the presence of either *Type I* or *Type II* photoinitiators with excellent yields in both systems. *Type I* photoinitiation appeared to be slightly more efficient than the other one as slightly higher conversion yields were obtained.

**Phenols.** It has been found that phenolic derivatives can efficiently quench triplet state ketones by electron transfer and hydrogen abstraction processes. A quenching mechanism for triplet ketones by phenolic compounds has been proposed using laser flash photolysis studies and is based on the formation of a hydrogen-bonded exciplex between the phenol and triplet state ketone, followed by sequential electron and proton transfer processes resulting in the formation of the ketyl and phenoxyl radicals as depicted in Scheme 8.<sup>63–65</sup> A similar photoreduction mechanism was also reported by Das and Nath using biologically relevant phenolic and indolic hydrogen-donor compounds in sodium dodecyl sulfate micellar medium.<sup>66</sup> In the polymerization processes, however, phenolic compounds are generally used as chain transfer agents to



**Scheme 8** Proposed mechanism of quenching triplet thioxanone by phenolic co-initiators.

control the molecular weight properties of polymer chains.<sup>67,68</sup> The resulting phenoxy radicals are believed to barely initiate the polymerization but rather tend to retard and inhibit initiation or propagation steps of the growing chains.

**Phosphorus compounds.** Phosphorus-containing compounds have been shown to exhibit applicability in *Type II* photoinitiation systems as co-initiators. Lalevee *et al.* investigated photosensitized decomposition of phosphorus compounds by *Type II* photoinitiation in which phosphorus-centered radicals were generated to initiate radical polymerization.<sup>69</sup> A pure hydrogen abstraction process was observed in those compounds bearing a labile hydrogen atom by the photoexcited photoinitiator leading to the corresponding ketyl and phosphorus radicals. No ion-pair intermediate was detected in laser flash photolysis studies ruling out the possibility of the involvement of any electron transfer processes. On the other hand, however, electron transfer processes between the phosphorus co-initiators without any abstractable hydrogen and the triplet photoinitiator resulted in the formation of phosphorus radical cation and ketone radical anion intermediates. Afterwards, this radical cation underwent fragmentation to yield phosphorus-centered initiating species (Scheme 9). Cationic photopolymerization was also attempted with the phosphorus compounds. The combination of ITX and phosphine salts appeared to be the most efficient in ring opening cationic polymerization due to the formation of suitable active cation species when using these phosphorus salts in conjunction with ITX.

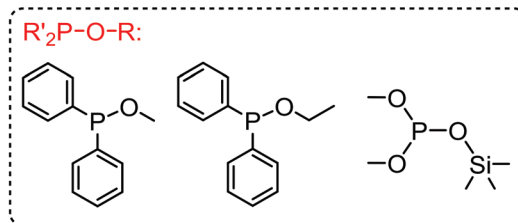
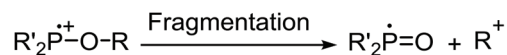
**Silanes.** It has been found that silane compounds can be efficiently employed as co-initiators to initiate photopolymerization in the presence of photoinitiators. The process is based on hydrogen atom abstraction from the Si-H bond leading to silyl radical generation capable of initiating radical polymerization.<sup>70–72</sup> Photoinitiation with disilanes having an Si-Si bond is also possible through electron transfer and Si-Si bond dissociation.<sup>73</sup> The striking feature of silane co-initiators lies in the ability of the resulting silyl radical to proceed in the presence of oxygen to the point that, in some cases, even an enhancement in the rate of polymerization in the presence of oxygen was observed – up to 2-fold – compared to deaerated media. Various silane-type co-initiators including silylamines, silyloxyamines and others have been reported.<sup>74–78</sup>

**Germanes and stannanes.** It has been shown that some germane and stannane compounds bearing a labile hydrogen bond can be efficient co-initiators in combination with *Type II* photoinitiated polymerization (Chart 4).<sup>79,80</sup> Following a similar mechanism to that of silanes, abstraction of the labile hydrogen forms the corresponding germyl and stannyl radicals.

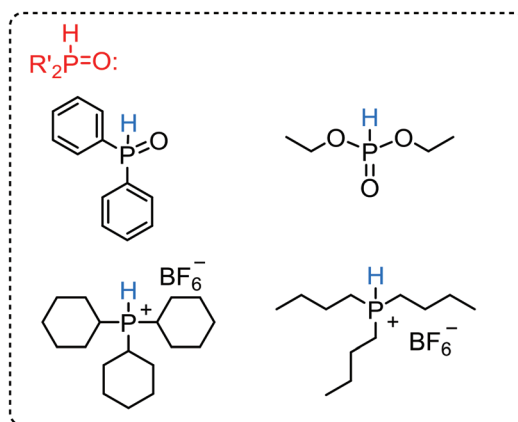
These radicals were efficient in the photoinitiation of both free radical polymerization and free radical promoted cationic polymerization. In the latter case, the resulting radicals were oxidized to form active cationic species with the help of an iodonium salt to initiate the cationic polymerization.<sup>81–84</sup>

**Onium salts.** Cationic photopolymerizations initiated by onium salt photoinitiators have become well-established pro-

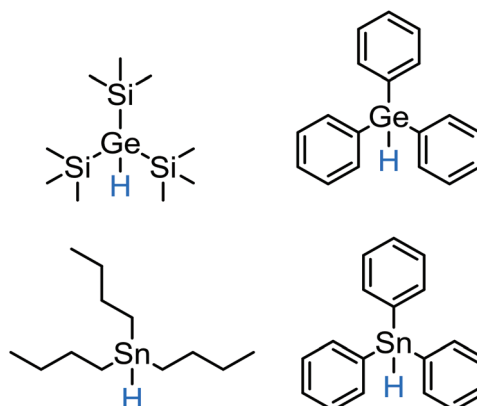
*Electron transfer:*



*Hydrogen abstraction:*



**Scheme 9** Phosphorus-containing compounds as co-initiators in *Type II* photoinitiated polymerization.



**Chart 4** Germane and stannane co-initiators.

cesses in commercial applications and academic research. Iodonium, sulfonium, and phosphonium salts are amongst the most utilized onium salt photoinitiators, which in

**Table 2** Redox potentials of thioxanthone and the free energy change of electron transfer with some onium salts calculated by the Rehm–Weller equation

Photosensitizer			$\Delta G^a$ (kcal mol <sup>-1</sup> )		
Compound	$E_{1/2}^{ox}(D/D^+)$ (eV)	$E_s$ (kcal mol <sup>-1</sup> )			
TX	1.7	277	-92	+4	-44.2

<sup>a</sup> Energy changes calculated by the Rehm–Weller equation.

common with each other contain a heteroatom with a cationic center and an inorganic metal complex anion as the counter anion part, such as  $BF_4^-$ ,  $PF_6^-$ , and  $SbF_6^-$ . Photolysis of onium salts may occur through both heterolytic or homolytic bond cleavage of the photoexcited onium salt resulting in the formation of cation or radical cation species, respectively.<sup>85</sup> Most onium salts absorb light in the short wavelength region of the UV spectrum around 300 nm and below. In order to activate the photolysis of onium salts in the near UV and visible regions of the electromagnetic spectrum, photosensitization by aromatic compounds through photoinduced electron or energy transfer processes is proposed. In addition to the spectral sensitivity shift, the photosensitization approach in essence would significantly contribute to enhancing the efficiency of photoinitiation and increasing the rate of polymerization. In principle, an electron transfer occurs between the excited state photosensitizer, as the electron donor, to the ground state onium salt, acting as an electron acceptor. The possibility of the process is therefore governed by the redox potentials of the photosensitizer and onium salts. From the point of view of thermodynamics, the feasibility of this process can be estimated by the Rehm–Weller equation, which calculates the energy change in the electron transfer reaction ( $\Delta G_{et}$ ). The more negative  $\Delta G_{et}$ , the more feasible the possibility of electron transfer.

Taking diphenyliodonium, triphenylsulfonium, and *N*-ethoxy-2-methylpyridinium as examples of commonly used onium salts, the Gibbs free energy for electron transfer with TX calculated by the equation above is given in Table 2. Iodonium and pyridinium salts appear to be more efficient than sulfonium salts as the energy of electron transfer in sulfonium salts is rather positive.

A wide range of efficient onium salts and photosensitizers were developed by Crivello, Fouassier, and Yagci. Mechanistic investigations of quenching triplet TX-based photosensitizers by onium salts further proved the involvement of the electron transfer process and formation of TX radical cation and onium radical species. Additionally, in the presence of a hydrogen-donor, the radical cation can abstract a hydrogen atom yielding a Brønsted acid and ground state photosensitizer (Scheme 10). These radical cation or Brønsted acid species are believed to initiate the cationic polymerization of the related

**Scheme 10** Photosensitized cationic polymerization using onium salts.

monomers including cyclohexene oxide, isobutyl vinyl ether, tetrahydrofuran, *N*-vinylcarbazole *etc.* In addition to TX derivatives, other triplet photosensitizers such as benzophenone, anthracene, perylene, phenothiazine, dyes and analogous structures have been shown to undergo a similar quenching with onium salts.<sup>86–96</sup> Some prominent onium salts which have been employed in photoinitiated polymerizations are depicted in Chart 5.

Onium salts have also appeared in three-component photoinitiating systems consisting of a photosensitizer, an electron donor (mostly an amine or a silane), and an electron acceptor (onium salt) component.<sup>97–104</sup> The three-component photoinitiation systems are aimed to enhance the rate and efficiency of the photopolymerization process in two simultaneously occurring reaction pathways. Direct interaction of the onium salt with the triplet photosensitizer, as mentioned above, generates a neutral onium-centered radical and a photoinitiator radical cation by an electron transfer process, which can then correspondingly initiate free radical or cationic polymerizations. This also requires the simultaneous interaction of the amine co-initiator with the triplet photoinitiator, which forms an initiating radical through sequential electron and proton transfer reactions. The second pathway, on the other hand, involves participation of all three initiating components wherein two of the three components react with one another after which the third component then reacts with the resultant of the prior



**Chart 5** Some onium salts utilized in photopolymerization initiated by *Type II* photoinitiators.

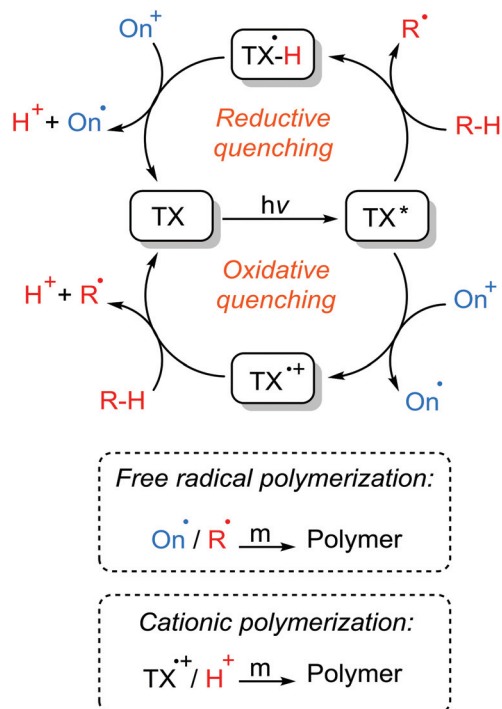
reaction. Plainly, the radical cation formed in the course of the electron transfer between onium salt and photoinitiator can abstract a hydrogen atom from the amine co-initiator to form an aminoalkyl radical while regenerating the ground state photosensitizer.

The reverse also holds true. The irreversible oxidation of the generated radicals in amine–photoinitiator interactions, especially non-propagating ketyl radicals, by onium salt leads to a neutral onium radical for the initiation of radical polymerization as well as a protonic acid capable of initiating cationic polymerization while regenerating the initial ground state photosensitizer. Both free radical<sup>101,105,106</sup> and cationic<sup>84,107,108</sup> polymerizations are applicable in three-component photoinitiation systems since they form appropriate active radical and cation centers to initiate target radical or cationic

polymerizations. Regeneration of the initial photosensitizer, the possibility of the formation of both radical and cationic species by various interactions for the initiation of different modes of polymerization, and converting terminating agents to active initiating sites (oxidation of ketyl radicals to form initiating radical or cationic species) all make three-component photoinitiation systems highly efficacious and promising for many target applications. Scheme 11 illustrates the reaction mechanisms involved in the three-component photoinitiation systems of free radical and cationic polymerizations.

## One-component photoinitiation

The research focus in *Type II* photoinitiation has been to design new classes of photoinitiators capable of acting as both



**Scheme 11** Three-component photoinitiation of free radical and/or cationic polymerizations in the presence of thioxanthone photosensitizer, amine hydrogen donor (R-H), and onium salt ( $\text{On}^+$ ) components: triplet thioxanthone is quenched through either oxidation by the onium salt or reduction by the amine hydrogen donor.

photoinitiator and co-initiator at the same time. Chemical incorporation of various co-initiators into the structure of photoinitiators makes one-component photoinitiators exhibit double functionality. Without the need for additional co-initiators, one-component *Type II* photoinitiators form initiating species through intramolecular and/or intermolecular interactions between the triplet state chromophore core and co-initiator part of the photoinitiator. Some disadvantages have been encountered using individual co-initiators, which may cause strong odors or yellowing and migration of the photolysis byproducts in cured films. These disadvantages associated with additional co-initiators can be suppressed to some extent by linking the co-initiator functionality to the photoinitiator structure. In this regard, amine-, thiol-, and ether-like hydrogen donors have been incorporated into photoinitiator structures to make one-component photoinitiating systems.

As part of preliminary work in one-component TX photoinitiators, 2-mercaptothioxanthone (TX-SH), a thiol substituted derivative of TX, has been extensively utilized as an efficient one-component *Type II* photoinitiator.<sup>109–111</sup> It was synthesized by reacting thiosalicylic acid with thiophenol as the starting materials in a concentrated sulfuric acid media. As revealed by laser flash photolysis studies, an intermolecular interaction between triplet  $^3\text{TX-SH}^*$  and ground state TX-SH molecules results in the formation of thiyl radicals through consecutive electron transfer and hydrogen atom abstraction processes.

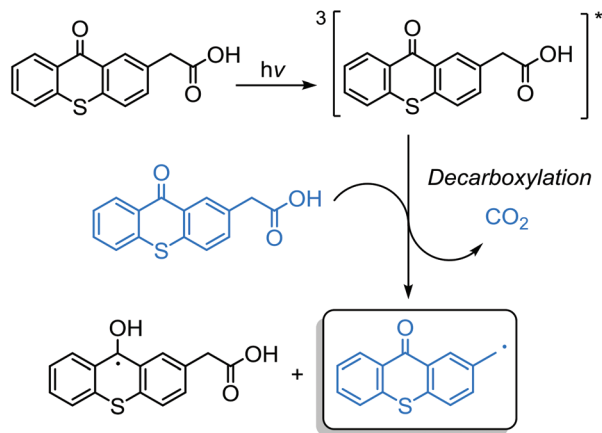


**Scheme 12** Photoinitiation mechanism of the formation of initiating radicals by 2-mercaptothioxanthone.

Intramolecular interaction is unlikely to happen due to the rigidity of the spacer group between the carbonyl and thiol functionalities and therefore the dominant reaction is through an intermolecular hydrogen abstraction process (Scheme 12). Thiyl radicals are insensitive towards oxygen inhibition and can initiate polymerization in both the absence and presence of air. While initiating a polymerization process, TX functionalities are incorporated into the polymer chain and thus can further contribute in the photoinitiation processes.<sup>112</sup> Another striking advantage of the TX-SH photoinitiator involves its applicability to styrene-based monomer formulations. Indeed, aromatic ketone/amine combinations appear to be effective photoinitiator systems for the polymerization of acrylates or methacrylates, whereas they have low reactivity toward styrenic monomers by virtue of the high quenching rate of the monomer and the reduced reactivity of the resulting  $\alpha$ -amino radicals with styrene. It has been proven that the efficiency of the TX-SH photoinitiator for the polymerization of styrene is far higher than that with TX and amine co-initiator combinations.

TX-SH was also reported to behave as an efficient photosensitizer for *Type I* photoinitiators. As demonstrated by Jockusch, Arsu, and co-workers, the energy transfer between excited triplet TX-SH and acylphosphine oxide derivatives as  $\alpha$ -cleavable *Type I* photoinitiators, leads to excitation of acylphosphine oxide photoinitiators and subsequently bond cleavage to yield initiating radicals. In addition to facilitating the energy transfer and excitation of acylphosphine oxide photoinitiators by improving the efficiency of light absorption, TX-SH serves as an oxygen insensitive species thus enabling photopolymerizations in the presence of air without any significant inhibitory effect of oxygen.<sup>113</sup>

The versatility of the synthesis route for TX derivatives has made it possible to incorporate desired functionalities into the structure of TX using functional aromatic compounds as start-



**Scheme 13** Photoinitiation mechanism of the formation of initiating radicals by carboxylic acid-functionalized thioxanthone.

ing materials. Carboxylic acid-functionalized TX photoinitiators have been prepared and utilized efficiently for free radical photopolymerization systems.<sup>114</sup> Acting as a one-component *Type II* photoinitiator, the mechanism of the formation of initiating free radicals in carboxylic acid-functionalized TX occurs through the abstraction of the acidic hydrogen by the triplet excited state TX core, which further results in a decarboxylation process to evolve carbon dioxide yielding initiating radicals. Intermolecular hydrogen abstraction has been reported as the dominant reaction pathway (Scheme 13). This decarboxylation was proved visually by a model reaction employing a solution of sodium carbonate in the presence of phenolphthalein, which was connected to a tube containing carboxylic acid TX solution. The experiment was designed so that the evolving carbon dioxide gas resulting in decarboxylation on irradiation could be directed to the other tube containing sodium carbonate solution. The pink colored sodium carbonate solution turned into a colorless solution upon contact with the evolved carbon dioxide.

Several other carboxylic acid-functionalized TX compounds able to act as one-component *Type II* photoinitiators have been reported with different spacer lengths capable of affecting the efficiency of photoinitiation process.<sup>115,116</sup> For example, thioacetic acid TX was shown to undergo intramolecular electron transfer yielding an ion exciplex intermediate that resulted in hydrogen abstraction and subsequently decarboxylation processes.<sup>117</sup> The flexibility of carboxylic acid moieties due to longer spacer length favors intramolecular electron and hydrogen transfer processes (Scheme 14). This is supported by the short triplet lifetime of thioacetic acid TX (65 ns) due to the involvement of intramolecular quenching processes, as compared to unsubstituted TX. It has been also found that the photoinitiation efficiency can be increased further by introducing a second acetic acid substituent to the photoinitiator.<sup>118</sup>

Arsu and co-workers investigated the influence of substitution pattern and position on the photoinitiation activity of

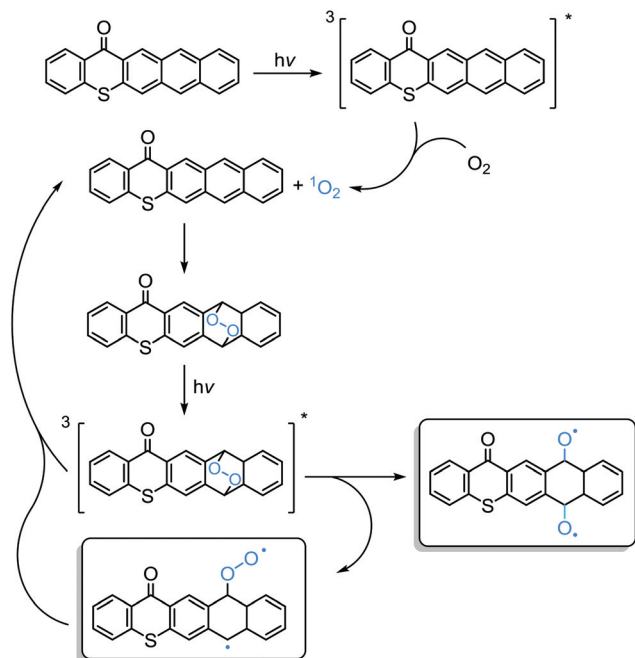


**Scheme 14** Photoinitiation mechanism of thioacetic acid thioxanthone.

carboxylic acid-functionalized TX derivatives.<sup>119</sup> Photoinitiators with carboxylic acid functionalities at the 1-position of TX appeared to be inefficient for photoinitiation of polymerization in certain environments. With these compounds, intramolecular hydrogen bonding results in rapid excited state quenching and deactivation. Additionally, it was observed that the nature of solvents could significantly affect the initiation mechanism. Apparently, using acetonitrile as the solvent, intramolecular hydrogen bonding occurs which prevents the possibility of any electron transfer and formation of initiating radicals. No polymerization occurred in this solvent. However, when the solvent was replaced with hydrogen-bond-disrupting solvents such as dimethylformamide or dimethyl sulfoxide, which form intermolecular hydrogen bonds, the polymerization efficiently proceeded through consecutive electron and proton transfer and decarboxylation processes. For reactions in acetonitrile, the addition of a small amount of hydrogen-bond-disrupting solvent to suppress intramolecular hydrogen bonding seemed necessary for successful polymerization.

On the other hand, photoinitiators with substitutions at the 2-position were reported to efficiently form initiating radicals and initiate polymerization process due to a sterically unfavorable intramolecular hydrogen-bonding interaction.

An anthracene incorporated TX (TX-A) exhibits a photoinitiation mechanism different from that of the other hydrogen-abstraction *Type II* photoinitiators.<sup>120,121</sup> The anthracene moiety is a well-known photosensitizer by itself and when combined with TX, shifts the absorption maxima to higher wavelengths up to visible light. The proposed mechanism of the photoinitiation relies on the photoexcitation of the TX-A photoinitiator and quenching of the triplet excited state primarily by molecular oxygen to form singlet oxygen species. Singlet oxygen then reacts with the anthracene moiety of TX-A to generate an endoperoxide intermediate. The endoperoxide



**Scheme 15** Proposed photoinitiation mechanism by thioxanthone-anthracene photoinitiator in the presence of oxygen.

thus formed undergoes photochemical or thermal decomposition resulting in the formation of initiating radicals. Free radical polymerization of methacrylate and styrene based monomers were efficiently initiated using TX-A as one-component photoinitiator in the presence of oxygen. Scheme 15 depicts the photoinitiation mechanism by TX-A. The necessity of oxygen molecules for the TX-A photoinitiator to form free radicals makes this photoinitiator highly advantageous in terms of the possibility of overcoming oxygen inhibition problems in free radical systems. Substituted TX-A photoinitiators have also been synthesized and efficiently used in photopolymerization reactions.<sup>122,123</sup>

A panchromatic behavior was observed when using thio-salicylic acids with *N*-phenylglycine to form a glycine-functionalized TX photoinitiator. Allonas, Arsu and co-workers demonstrated that the absorbance of the glycine-functionalized TX (Chart 6) was shifted to longer wavelengths up to 600 nm covering a wide range of the UV and visible light parts of the electromagnetic spectrum. This shift to longer wavelengths was attributed to the formation of hydrogen bonding facilitated by glycine functionalities. Photopolymerizations



**Chart 6** Glycine-functionalized thioxanthone showing panchromatic characteristics.



**Chart 7** Some nitrogen-containing thioxanthone-based compounds as one-component Type II photoinitiators.



**Chart 8** Carbazole-thioxanthones as one-component photoinitiators.

were successfully achieved using different light sources at 392, 473, 532, and 635 nm wavelengths with increasing photoinitiation efficiency with decreasing irradiation wavelength, consistent with increasing the absorption coefficient at shorter wavelengths.<sup>124</sup>

Several other nitrogen-containing one-component photoinitiators bearing abstractable hydrogen sites have also been synthesized and utilized for the photoinitiation of polymerization (Chart 7).<sup>125–127</sup>

Carbazole functionalities were also taken advantage of for forming one-component TX photoinitiators with extended conjugation. In this regard, for example, carbazole and ethylcarbazole functionalized TX photoinitiators (Chart 8) have been reported.<sup>84,128–130</sup> Due to the extended conjugation contributed by the incorporation of carbazole moieties, these photoinitiators exhibit a strong absorption band in the visible region (>400 nm) where both TX and carbazole chromophores have no significant absorption characteristics. Bearing abstractable hydrogen sites, free radical polymerization was achieved using carbazole TX photoinitiators without the use of hydrogen donors; though supplying additional co-initiators contributed to enhancing the efficiency of the process. Ethylcarbazole-attached TX was reported to be highly soluble in a diverse range of both polar and nonpolar solvents due to the presence of the ethyl group of the carbazole functionality.

Additionally, free radical promoted cationic photopolymerization was achieved using ethylcarbazole TX in conjunction with onium salt-based oxidants. The free radicals formed in the course of the photolysis of carbazole TX interacted with the onium salt compounds while being oxidized to form the corresponding cationic species. Applicability of the initiation process to suitable cyclic and vinylic monomers was demonstrated.<sup>84,128</sup>



**Chart 9** A selection of some-water soluble thioxanthone-based photoinitiators.

## Water-soluble TX photoinitiators

In order for photoinitiators to be water compatible, water-solubilizing groups have to be incorporated in the skeleton of oil-soluble photoinitiators. Various methodologies have been proposed to introduce hydrophilic substituents to convert non-water-soluble photoinitiators to water-soluble. In this regard, ammonium derivatives, sulfonic and other acidic groups, or several water-soluble macromolecules, among others, have been successfully taken advantage of for making water-soluble photoinitiators (Chart 9).<sup>131</sup> The photochemistry of these water-soluble photoinitiators is principally similar to their oil-soluble counterparts and they follow the same trend in interacting with co-initiators for the formation of initiating radicals.<sup>32</sup> There might be some expected changes in the optical properties of water-solubilized photoinitiators causing extension of light absorption maxima to higher wavelengths.

Complexation of photoinitiators with water-soluble agents has also been used to make water-soluble photoinitiators.<sup>132</sup> Cyclodextrins consisting of a hydrophobic cavity and a hydrophilic outer space have been used to form host-guest complexes with oil-soluble photoinitiators.

## Two-photon initiated photopolymerization

TX derivatives have also found their place in two-photon initiated polymerization systems. Two-photon initiated photopolymerizations are distinguished from commercial one-photon induced photopolymerizations by their distinctive ability to absorb the energy of two photons of the irradiating light as opposed to one-photon absorbing commercial photoinitiators. Two-photon photopolymerizations are especially unique and powerful techniques for the micro-fabrication of three-dimensional (3D) subtle, fine objects.

Crucial for the highly efficient two-photon absorbing behavior of photoinitiators is the presence of electron-donor and/or electron-acceptor groups with extended conjugation properties. Malval *et al.* reported the enhancement of the two-photon absorption characteristics of TX by introducing an

anthracene group to TX in a chevron-shaped architecture which in combination with an amine co-initiator was capable of exhibiting excellent two-photon absorption properties for the fabrication of 3D structures.<sup>133</sup> Gryko and co-workers recently studied two-photon absorption characteristics of the  $\pi$ -expanded donor-acceptor photoinitiators of TX moieties.<sup>134</sup> Dialkylamino groups as electron-donor components were substituted to TX with a significant enhancement of the optical properties. Those possessing aryethylene and aryethynyl linkages (C=C or C≡C bonds, respectively) showed favorable two-photon absorption properties with remarkable two-photon absorption cross section compared to the bare TX or non-conjugated photoinitiators.

## Macrophotoinitiators

To empower the (photo)activity of photoinitiators and incorporate different functionalities into their structure, an efficient way is to design and construct polymeric photoinitiators, also known as macrophotoinitiators.<sup>135</sup> Polymeric photoinitiators bearing photoinitiator sites are prepared through various polymerization methods of suitable monomers, including step-growth<sup>136–141</sup> and addition<sup>142</sup> (co)polymerization, functionalization by click chemistry techniques, dendrimerization and other functionalization methodologies. In addition to their enhanced photoactivity by virtue of incorporating functional groups, the main idea of the formation of polymeric photoinitiators would probably deal with overcoming some of the disadvantages encountered with small molecule photoinitiators, which cause migration or volatility, yellowing and other drawbacks in the final cured products. Yin and co-workers reported a string of TX-containing macrophotoinitiators by step-growth polymerization methods. Containing in-chain TX and amine groups, these macrophotoinitiators were reported to act as one-component photoinitiators.<sup>138–140,143,144</sup>

Using glucamine as the co-monomer, which contains tertiary amine groups as suitable hydrogen-donor sites, made the resulting TX macrophotoinitiators water-soluble.<sup>140</sup> Examples of some TX macrophotoinitiators prepared by step-growth polymerization are collected in Chart 10.

Alternatively, functionalization of supramolecular or hyper-branched polymeric structures containing amine or etheric functional groups as hydrogen donating groups<sup>145</sup> with photoinitiator moieties have been used to form one-component macrophotoinitiators.<sup>146,147</sup> As an example, dendritic or hyper-branched supramolecular amines were reacted with an epoxy functional TX molecule resulting in the formation of dendritic structures with their TX end functional groups exhibiting photoinitiation activity much higher than small molecular weight photoinitiating systems.<sup>148–150</sup> In this context, hyper-branched poly(ethylene imine) or dendritic poly(propylene imine) have been utilized for the formation of TX-bearing dendritic macrostructures (Scheme 16).

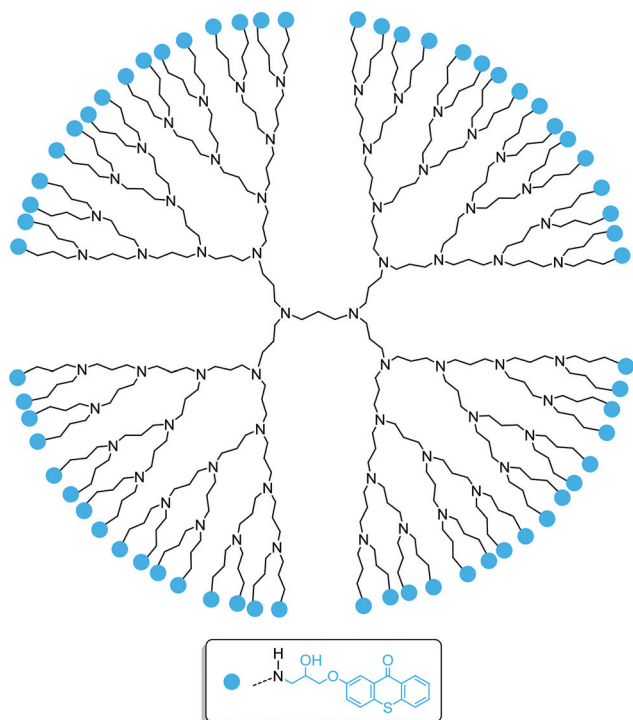
Post-modification of polystyrene as a polymeric backbone by treating it with thiosalicylic acid, which leads to the thio-



**Chart 10** A selection of thioxanthone-based, one-component polymeric photoinitiators prepared by step-growth polymerization techniques.



**Scheme 17** Synthesis of polystyrene-based macrophotoinitiator with thioxanthone groups using double click reactions.



**Scheme 16** Dendritic poly(propylene imine) end-functionalized with thioxanthone moieties as a one-component *Type II* macrophotoinitiator.

xanthone of polystyrene, has been reported to prepare macrophotoinitiators with pendant TX groups.<sup>151</sup> Additionally, this process can bring about water-soluble polystyrene-based polymeric photoinitiators by performing a sulfonation during the thioxanthone process in a one-pot manner.<sup>152</sup> An amine co-initiator was necessary for polymerization to occur.

Click chemistry techniques, examples of which include copper-catalyzed azide–alkyne cycloaddition (CuAAC) or Diels–Alder click reactions, offer unique possibilities for the preparation of functional polymeric photoinitiators, which efficiently enable the incorporation of suitable photoinitiator sites

into polymeric supports. For example, using both CuAAC and Diels–Alder techniques together, an alkyne-functionalized maleimide group was linked to a polystyrene backbone with side-chain azide groups using CuAAC technique (Scheme 17).<sup>153</sup> The maleimide group possessing alkyne as well as protected norbornene functionalities was used as a double-functional click linker to facilitate incorporation of TX groups to the azidated polystyrene. TX-A group was then clicked to the polystyrene through the maleimide linker using a Diels–Alder click reaction occurring between the anthracene and norbornene functionalities. The resulting TX-incorporated polystyrene with double click chemistry techniques showed similar optical characteristics to that of bare TX with excellent photoinitiation efficiency. However, different absorption characteristics compared to the precursor TX-A were observed probably due to the loss of the aromaticity of the anthracene group in the course of the Diels–Alder click reaction.

Owing to its good solubility in aqueous media and its possession of etheric hydrogen abstraction sites in its structure, poly(ethylene glycol) (PEG) has been widely used as a building block to prepare macrophotoinitiators. Using Diels–Alder click chemistry, for instance, anthracene–TX was linked to a maleimide-functionalized PEG support yielding a water-soluble, one-component polymeric photoinitiator (Scheme 18).<sup>154</sup> A variety of water-soluble monomers were polymerized using



**Scheme 18** Synthesis of thioxanthone end-functionalized poly(ethylene glycol) by Diels–Alder click reaction.



**Scheme 19** Synthesis of thioxanthone end-functionalized poly(ethylene oxide) by counterion exchange.



**Scheme 20** Synthesis of poly(vinyl alcohol) thioxanthone macrophotoinitiator.

this PEG-TX photoinitiator through a grafting method due to the formation of initiating free radicals onto the PEG backbone as a result of the etheric hydrogen abstraction process by the triplet state TX.

Counterion incorporation of TX to poly(ethylene oxide) (PEO) support through a straightforward acid–base salt formation has also been reported. Reacting an  $\alpha$ -amino functional PEO with a carboxylic acid functionalized TX group led to the formation of a polymeric salt with ionically attached TX groups (Scheme 19).<sup>155</sup> Polymerization of water-soluble monomers was initiated upon counterion sensitization to triplet state TX abstracting a hydrogen atom from the PEO segment.

More recently, poly(vinyl alcohol) (PVA) was used as a polymeric support for the incorporation of a TX chromophore (Scheme 20).<sup>156</sup> An aldehyde functional TX was initially synthesized and then linked to PVA through a simple acetylation process yielding PVA with pendant TX groups. Bearing several abstractable hydrogen sites, this macrophotoinitiator was reported to act as a one-component photoinitiator with efficient photoactivity and applicability in both organic and aqueous media for the photopolymerization of vinyl monomers including acrylamide and methyl methacrylate as model water soluble and oil-soluble monomers, respectively.

## Heterogeneous TX networks

Porous materials having high accessible active surface area have been widely used in a broad range of photocatalysis applications. With respect to polymerization processes, semiconducting nanoparticles or organic porous networks have been reported as heterogeneous photoinitiators for various modes of polymerization techniques.<sup>157–161</sup> Given the heterogeneous

nature of this type of macrophotoinitiator, which makes them easily separable from the reaction media eliminating any contamination problems associated with by-products, heterogeneous photochemical processes become of great importance. They often offer the advantage of being reused in promoting reactions multiple times while preserving their reactivity, which is a desirable and significant behavior from the point of view of economic and environmental issues.

In this regard, the groups of Thomas and Yagci recently developed a new strategy to generate TX-based heterogeneous networks as potential macrophotoinitiators for conducting photopolymerization.<sup>162</sup> Using various cross-coupling processes such as Sonogashira–Hagihara or Friedel–Crafts alkylation techniques (the latter being also referred to as “knitting” process), conjugated microporous networks of TX with specific surface areas of up to  $750 \text{ m}^2 \text{ g}^{-1}$  were obtained employing TX along with other suitable co-monomers. Dibromothioxanthone and triethynylbenzene were subjected to the Sonogashira–Hagihara coupling reaction to form a microporous network of TX with a pore size of 1.4 nm and a microporosity of  $500 \text{ m}^2 \text{ g}^{-1}$ . Using the Friedel–Crafts alkylation method, TX and benzene (or triphenylmethane) were “knitted” together. It was found that these macrophotoinitiators being two or three-dimensional networks had strong absorption characteristics in the visible region which were reasoned to be due to the strong  $\pi$  interactions of the highly conjugated nature of the networks. Free radical and cationic photopolymerizations were achieved in the presence of different co-initiators under visible or sun light irradiation. In free radical polymerization of vinyl monomers, a hydrogen abstraction from the amine co-initiator produced an initiating free radical species whereas in the presence of an onium salt co-initiator (diphenyl iodonium hexafluorophosphate,  $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ ) electron transfer reactions brought about the initiating species. In the latter case, as explained earlier, the photoexcited TX moieties reduce the onium salt through electron transfer reactions forming a diphenyl iodonium radical which further decomposes to give a phenyl radical capable of initiating polymerization of vinyl monomers. Ring-opening cationic polymerization of cyclic ethers was achieved by a free radical promoted cationic process in the presence of the iodonium salt and an amine (dimethylaniline) or an ether (tetrahydrofuran) hydrogen donor. The so-formed radical species *via* hydrogen abstraction processes were responsible for the reduction of the onium salt to generate suitable cationic species as well as the other above-mentioned mechanisms, which form active cationic components to initiate ring-opening cationic polymerization. Reusability was found for all three types of microporous TX networks in both free radical and cationic polymerizations.

## Miscellaneous applications

In addition to their widespread use in photopolymerization systems, TX photoinitiators have found substantial applicability in other areas of materials science and (photo)chemistry.

In this section, we briefly evaluate the fields in which the photochemical behavior of TX derivatives has been taken advantage of for carrying out target reactions.

One interesting area concerns the photochemical formation of metal nanoparticles such as silver (Ag) or gold (Au) based on photochemical reduction of metal ions by electron-donor radicals from different photoinitiators. Malval *et al.* studied the photo-generation of silver nanoparticles by carboxylate derivatives of TX (TX-O-CH<sub>2</sub>-COO<sup>-</sup> Na<sup>+</sup> and TX-S-CH<sub>2</sub>-COO<sup>-</sup> Na<sup>+</sup>) in the presence of amine hydrogen donors.<sup>163</sup> While silver nanoparticles form by reduction of silver cations by photogenerated radicals as a result of interaction of triplet state TX with amine co-initiator, these nanoparticles can be capped by the carboxylate functionality of TXs acting as a ligand to stabilize nanoparticles. It was found that the substitution pattern had a significant impact on the formation, stability and morphology of the final nanoparticles. For example, when using a bare TX, a rapid aggregation of silver metal was observed. However, carboxylate-derivatives of TX suppressed this aggregation significantly owing to their ligand effect, uniformly capping the generated nanoparticles through carboxylate functional groups, which in turn resulted in the formation of uniform individual nanoparticles. This capping behavior was considerable in the case of TX-S-CH<sub>2</sub>-COO<sup>-</sup> as compared with TX-O-CH<sub>2</sub>-COO<sup>-</sup>, by which homogeneous silver nanoparticles with narrow size distributions were obtained. Similar redox processes can also be achieved by cleavage type photoinitiators providing that they yield electron donor radicals.<sup>164–166</sup>

Our group recently reported a new TX-based copper catalyst for the photochemical conduction of the CuAAC click reaction.<sup>167</sup> CuAAC is known to be promoted by photochemical processes in which the required copper(I) catalyst for CuAAC is achieved by photoreduction of copper(II) species.<sup>28</sup> Using a TX carboxylate which was converted to its sodium salt by treatment in sodium hydroxide media, copper(II) ions were bonded to the TX (Cu(TX)<sub>2</sub>) by an ion exchange process between TX sodium and copper(II) triflate (Scheme 21). The reduction of copper(II) species in the obtained Cu(TX)<sub>2</sub> catalyst was observed by irradiation of the catalyst in a dimethylformamide solution without the use of any additional ligand or hydrogen donor compounds. The solubility of the catalyst was due to the solubility of the TX part, which in turn eliminated the need for additional ligands. This was attributed to the intramolecular photoinduced electron transfer reactions between the triplet TX and copper(II) ions which resulted in the reduction of copper(II). CuAAC was successfully catalyzed in a ligand-free manner under soft irradiation conditions using the Cu(TX)<sub>2</sub> photocatalyst providing the advantage of temporarily controlling the process.

Alonso and Bach developed a photosensitization approach for the induction of enantioselective [2 + 2] photocycloaddition reactions using a chiral TX as the organocatalyst compound.<sup>168</sup> They reported that the intramolecular [2 + 2] photocycloaddition of quinolones, which generally exhibit absorbance in the UV region around 300 nm, could be efficiently realized under



**Scheme 21** Synthesis of copper(II) thioxanthone carboxylate photocatalyst (a) and its use as a ligand-free photocatalyst for copper(I)-catalyzed azide–alkyne cycloaddition (b).



**Scheme 22** Photosensitization of [2 + 2] photocycloaddition by a chiral thioxanthone photosensitizer through energy transfer process.

visible light irradiation of TX by a triplet energy transfer process to the quinolones to sensitize their intermolecular cycloaddition (Scheme 22). The reactions were conducted in a non-hydrogen donating media (*i.e.* trifluorotoluene) so as to eliminate the probability of hydrogen abstraction and further decomposition of TX. After the reaction, though not completely, TX photoinitiator was successfully recovered signifying the preservation of TX functionality after the triplet charge transfer process.

TX derivatives are also known for their excellent biological and pharmaceutical activities.<sup>169</sup> Some biologically relevant applications concerning drug development, anti-cancer and tumor treatment<sup>170–172</sup> or protein damage<sup>173</sup> induced and mediated by TX photosensitizers have been reported in this context.

## Conclusion

In this paper, we have reviewed recent advances of photopolymerizations initiated by TX derivatives. We have discussed in detail the conceptual aspects of the photochemistry of TX molecules, explaining how they would behave under light and interact with the additional reaction components (*i.e.* in the presence of co-initiators) to form suitable initiating sites of interest. In this regard, the applicability of various co-initiators in combination with TXs has been explained by providing a comprehensive picture of their mechanistic behavior. Developments of specially designed TX-based photoinitiators involving one- and two-component, water-soluble, and polymeric photoinitiators obtained through various processes have been exemplified for macromolecular synthesis. In addition, some miscellaneous applications of TX photoinitiators in promoting and photosensitizing other chemical reactions and biological events have been reviewed.

The field of photopolymerization is gaining more and more research interest across a broad range of polymers and a wide realm of the chemistry and science communities. For more than three decades, our laboratory has been engaged in designing, developing, and taking advantages of photochemical strategies for the synthesis of polymers having specific characteristics. A great deal of effort has gone into “softening” polymerization conditions or enhancing the efficacy of photoinitiation reactions. This would be through, for instance, the use of photoinitiating systems insensitive to oxygen inhibition problems, especially in large-scale industrial applications or photoinitiating systems efficiently working in the visible range of the electromagnetic spectrum with newly emerging light sources like Light Emitting Diodes (LED) or natural sunlight, which would significantly contribute to lowering the cost of such processes as well as suppressing some of the disadvantages that high energy sources may cause to some special systems.

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