

Polymer Chemistry

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Polymer Chemistry

REVIEW

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Shining a Light on an Adaptable Photoinitiator: Advances in Photopolymerizations Initiated by Thioxanthenes

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Photochemistry has been playing a central role in the synthetic polymer community. Aromatic ketones, examples of which include benzophenone, thioxanthone, camphorquinone, among others, are renowned for their excellent optical characteristics and have been extensively taken advantage of photochemically induction of polymerization processes. Of particular interest is thioxanthone due to its adaptability for bearing different functionalities and applications in various modes of photopolymerization which 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 literature, the development of various photoinitiating systems based on thioxanthenes along with an understanding of their mechanistic behavior has been elucidated in advance.

Introduction

The polymer community has witnessed an increasing inclination towards light-mediated polymerization techniques in recent years. These systems essentially offer advantages of carrying out reactions leniently by eliminating side effects often accompanied in thermally induced counterpart processes of special systems, just to cite one striking example. For this reason, photochemical processes are often considered as "green chemistry".^{1, 2} Such systems utilize light as the driving force to the formation of suitable initiating sites by absorbing its energy and promotion of subsequent photochemical reactions leading to the induction of chemical reactions. Hence, choosing appropriate light absorbing species, *i.e.* photoinitiators or photosensitizers, becomes crucial since there has to be a well matching of the optical behavior of photoinitiators with the characteristics of lightning source. Photochemical processes have been intensively used in as diverse range of chemical reactions as 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 for designing new photoinitiating systems, or enhance, improve and expanding the scope of the existing initiators to fit in many newly emerging needs and advanced technologies.³ 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 α -cleavage and provide initiating radicals by a bond cleavage processes upon absorption of light, and (ii) *Type II* which undergo photoexcitation followed by an electron or hydrogen transfer processes and consequently formation of initiating species.⁴⁻⁶ Benzoin and its derivatives are the most widely used *Type I* photoinitiators for radical photopolymerization capable of unimolecular bond cleavage on irradiation. As *Type II* photoinitiator, ketone components are of great importance. Examples include benzophenone, thioxanthone, camphorquinone etc. exhibiting a bimolecular photo-behavior in the formation of initiating species. This characteristic behavior lies primarily on 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.* lights at 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 visible ranges of the electromagnetic spectrum. Such a behavior carries the advantages of using low energy lightning 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 exposures such as biological and medical applications. Ultimately, in designing a photoinitiating system, the influence

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of some special groups used to functionalize photoinitiators on enhancing their photoactivity and lowering the costs 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 potential through reduction or oxidation processes and hence one would expect different excited state interactions in the presence of different types of co-initiator systems.

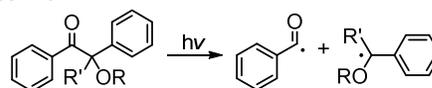
Traditionally, photoinitiated polymerizations have been employed in free radical,^{7, 8} cationic^{9, 10} and, in rare cases, anionic¹¹ polymerization systems. Applications can be traced in a broad spectrum of photocuring, coatings, inks and printings, adhesives to medicinal and dental applications to fabrication of multidimensional devices and so forth. Despite tremendous implementations of these systems, they somehow lack the ability of providing control in polymerization process in terms of well-controlled, complex architectures with predetermined molecular weight properties. Recently, attention has drawn to adaptation of light-mediated processes with the existing controlled polymerizations such as copper-mediated living radical polymerization techniques,¹²⁻¹⁵ reversible addition-fragmentation chain transfer,^{16, 17} nitroxide-mediated polymerization¹⁸ and so on, or developing novel photocontrolled techniques to achieve photochemically mediated synthesis of well-controlled macromolecular architectures.¹⁹⁻²³ For example, many attempts have been directed towards photochemically induction of the copper-mediated processes which lies on the photochemically formation of the required copper(I) catalyst by various photochemical means.²⁴ An important application of such photoinitiated controlled polymerization systems may be the possibility of on-demand-patterning of functionalized surfaces by providing spatiotemporal control.²⁵

Our group has long been dealing with investigating, designing, and developing novel photochemical processes for polymer synthesis.²⁶⁻²⁸ This review intends to focus on the advent of and progress in the 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 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 of macromolecular synthesis. In addition to polymerization systems, in the last section, some miscellaneous applications of TX photosensitizer in different areas of chemistry, materials science and biology will be discussed.

Photochemistry of Thioxanthone: A Bimolecular Photoinitiator

Photoinitiators are mainly subdivided into two categories of *Type I* and *Type II* systems. Whilst the formation of radicals in the latter is achieved by a hydrogen abstraction or photoinduced electron transfer processes of triple state photoinitiator in the presence of a co-initiator compound, the former undergoes unimolecular fragmentation (α - or β cleavage) upon absorption of light giving rise to the formation of two initiating radicals (Scheme 1).²⁹ Depending on the nature of the initiating components, formation of initiating species in *Type II* systems may well be through distinct paths of 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 TX radical anion and donor radical cation excited state complex (exciplex). Thus, a proton transfer from the α -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 efficient in the promotion of this process. Amines, thiols, alcohols, ethers, silanes and many others are among the mostly 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 aftermath of hydrogen abstraction do not initiate polymerization, but participate in combination or terminating growing polymer chains. However, radicals derived from the hydrogen donor compounds are efficient in the initiation process.

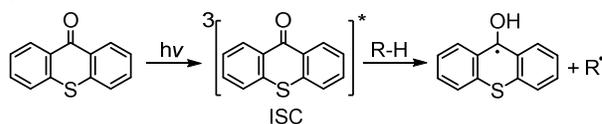
Type I photoinitiation:



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 on the example of a benzoin derivative and thioxanthone, respectively.

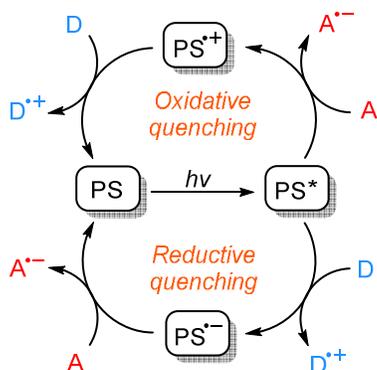
initiating species and are accounted for the successful initiation of polymerization.

Another possibility for the formation of initiating species is the photoinduced electron transfer reactions of triplet state photoinitiator acting as photosensitizer, with suitable co-initiator in which after a set of subsequent electron transfer and fragmentation reactions forms initiating species including both radicals and/or cations. In this case, 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 reacts as a reductant with 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 bringing about active initiating species. There is also the possibility of reacting radical ions with some electron donor or electron acceptor to give the ground state photosensitizer and also corresponding radical or cation species.

These reactions, of course, are thermodynamically feasible if the free energy change of electron transfer (ΔG_{et}) estimated by the Rehm-Weller equation is negative:

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

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



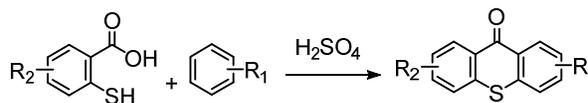
Scheme 2 General representation of photoinduced electron transfer reactions of photosensitizers (PS) in the presence of electron acceptors (A) or electron donors (D).

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 mechanistically 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 at near UV and visible ranges, reduces the required energy for photoexcitation, 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 thioalicyclic acids with aromatic hydrocarbons in a concentrated sulfuric acid medium as shown in Scheme 3.³⁰ 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 the absorption band shifting further to higher wavelengths as well as facilitating their applicability in different media and for various purposes, or enhancing 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 TX-based photoinitiating system.^{4,6}

Exploiting various spectroscopic techniques such as laser flash photolysis studies, the mechanism of the photoinitiated polymerization by TX was extensively investigated.³¹⁻⁴⁰ The process essentially necessitates the presence of a co-initiator to accomplish the formation of initiating species. Though, quenching can also occur by interacting with low triplet energy monomers or solvents. Amines, for instance, due to their highly reductant properties⁴¹ are commonly used co-initiators to carry out quenching triplet TX through the formation of an exciplex or ion pair intermediate between the photoexcited triplet state TX and co-initiator amine by primarily 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 α -position of the co-initiator and a thioxanthyl 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 photoinitiators 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,

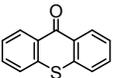
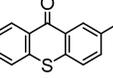
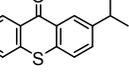
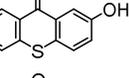
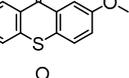
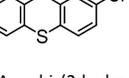


Scheme 3 Synthesis of thioxanthenes by condensation of thioalicyclic acid and aromatic compounds in the presence of concentrated sulfuric acid.

REVIEW

Polymer Chemistry

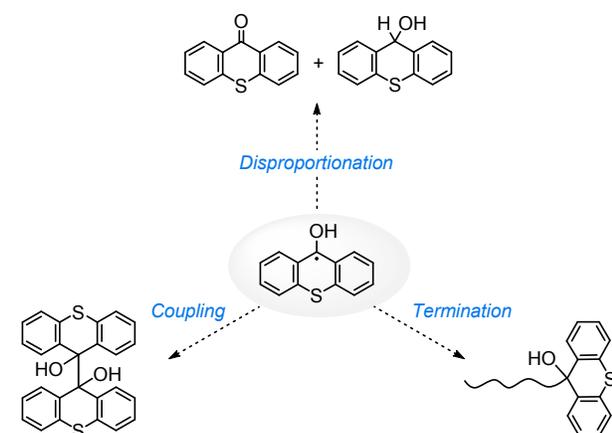
Table 1 Absorption characteristics of substituted thioxanthone photoinitiators and the rate constants (k_q) of the reaction of their triplets with amine co-initiators.

TX derivative	λ_{\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)

BMA: bis(2-hydroxyethyl)methylamine; TEA: triethylamine; DEAE: 2-(diethylamino)ethanol; data taken from ref. ^{31, 33, 42}

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 with the effect of substitution on the absorption maxima. TX derivatives seem to be more efficacious compared with none-substituted TX in terms of higher absorption maxima and higher extinction efficiency and applicability for various purposes.

As of the thioxanthyl ketyl radicals formed after the course of hydrogen abstraction, they are believed to rarely add across monomer and initiate polymerization. Instead, they tend to undergo either a process of disproportionation to return the initial ground state TX and form thioxanthole species or couple to form a pinacol compound, though with relatively less

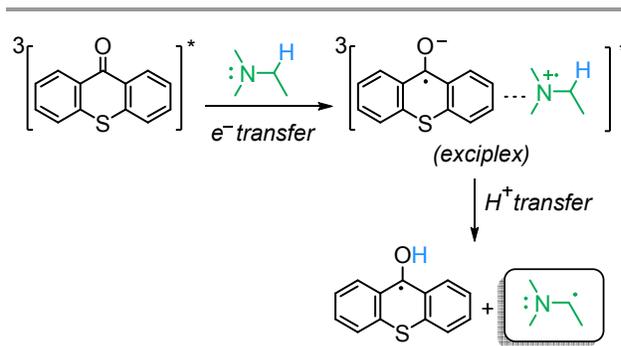
**Scheme 4** Possible reactions of thioxanthyl ketyl radicals.

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.⁴³ 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 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-initiator in quenching the photoexcited triplet state TX and formation of free radicals. Of these, amines have been proven the most efficient hydrogen donor. Hydrogen atom at the α -position of a heteroatom (N, O, S) is highly potential to be abstracted by the triplet TX and formation of 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 mechanistically explanation of the interaction and initiation processes.

Amines. Amine co-initiators are among the most extensively investigated ones in photopolymerization systems. As noted earlier, the initiation mechanism using amines as co-initiators in *Type II* photoinitiation system is thought to proceed primarily by the interaction of the triplet state photoinitiator with the non-bonding electrons present in 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 α -position then yields a ketyl radical on the photoinitiator and a carbon-centered radical derived from the amine as represented in Scheme 5.^{41, 44} 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.³² 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 to undergo electron transfer and form an exciplex

**Scheme 5** Photoreduction of triplet thioxanthone by amines.

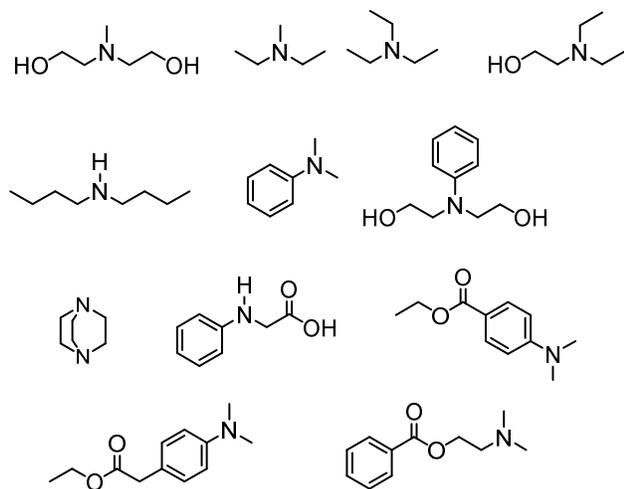


Chart 1 A list of frequently used amine co-initiators in combination with thioxanthone-based photoinitiators.

with the triplet ketone and its hydrogen donation properties. The quenching rate has been found to correlate with the ionization potential of the amines.⁴⁴ The order of photopolymerization efficiency with amines 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.

Benzoxazines. Although in the ring form, benzoxazines represent structural similarity to substituted aniline compounds and, therefore, can be used as co-initiator in *Type II* photoinitiation systems (Chart 2).⁴⁵ Efficient interaction of the benzoxazine with the triplet state TXs leading to quenching 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 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.⁴⁶ 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 to the network through the ring opening of the benzoxazine functionality at the PMMA chains.

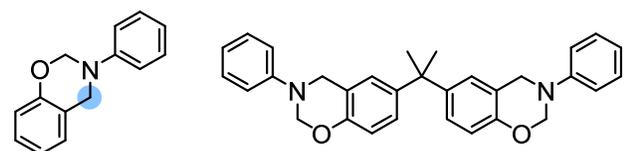


Chart 2 Benzoxazines as co-initiator in *Type II* photoinitiated polymerization.

Thiols. Mercaptans or thiol-containing compounds have also been utilized as co-initiator in combination with TX derivatives and other *Type II* photoinitiating systems. Aromatic thiols are well-known strong quenchers of the triplet state photoinitiators.^{47, 48} 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 the thiols thus giving rise to the formation of a new initiating thiyl radical.⁴⁹ Unlike the aromatic thiols, the quantum yields of quenching with aliphatic thiols are relatively low.⁵⁰ Photoinduced free radical polymerization based on the use of aromatic thiols as co-initiator in conjunction with *Type II* photoinitiators such as isopropylthioxanthone (ITX) or camphorquinone (CQ) has been reported.⁵¹⁻⁵⁴ Investigating the initiation mechanism by laser flash photolysis, Andrzejewska and co-workers observed a rapid quenching of the excited ITX* with the thiols as 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 be through the photoinduced electron transfer between the triplet state TX and thiols leading to the formation of an intermediate consisting 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:



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

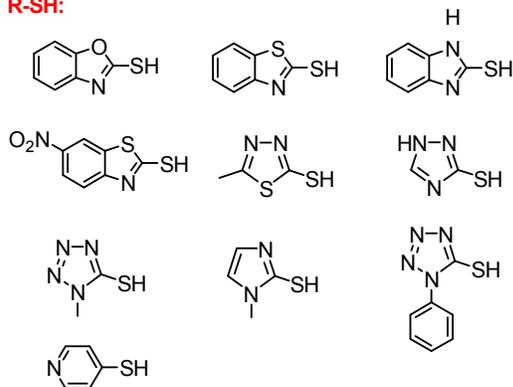


It should also be noted that the irradiation of disulfides, though at lower wavelengths, could result in the dissociation of S-S bond, albeit the efficiency was comparably low as in the case of photosensitizer/disulfide bi-component system. In the case of thiols, however, the hydrogen abstraction process, 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

REVIEW

Polymer Chemistry

R-SH:



R-S-S-R:

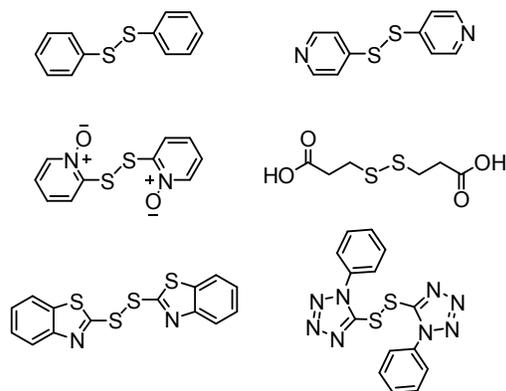
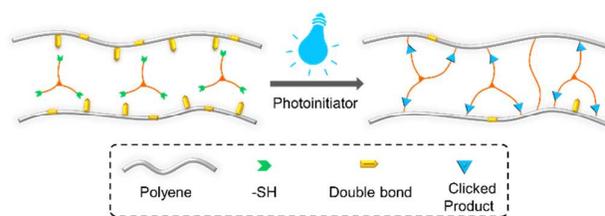


Chart 3 Thiol and disulfide compounds used as co-initiator in photoinduced free radical polymerization in the presence of thioxanthenes.

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.^{57, 58} Abstraction of a hydrogen atom from the participating thiol by a carbon-centered radical, results in the formation of thiyl radicals capable of adding over 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 encounter the general mechanism of thiol-ene polymerization. In the photochemical processes, the required initial radicals are generated by using various photoinitiator systems. *Type I* photoinitiators provide the 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 the 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 the photoinitiator to form photocured polymers of polyenes and polythiols in which the photoexcited benzophenone abstracted the labile hydrogen from the thiol to generate thiyl radical leading to crosslinking polyene and polythiol.⁵⁹ Decker et al. studied photo-crosslinking of poly(styrene-co-butadiene) rubber with double

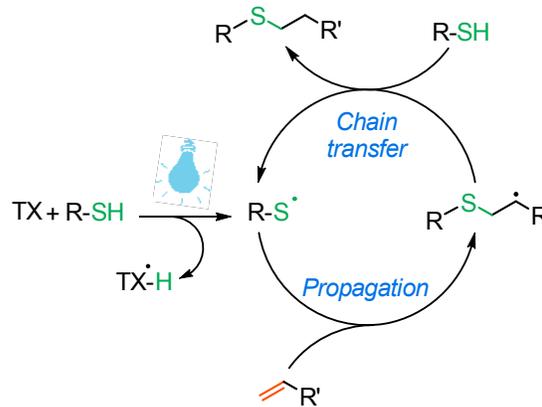


Scheme 6 Schematic representation of photo-crosslinking of polymers containing double bonds by using multifunctional thiols.

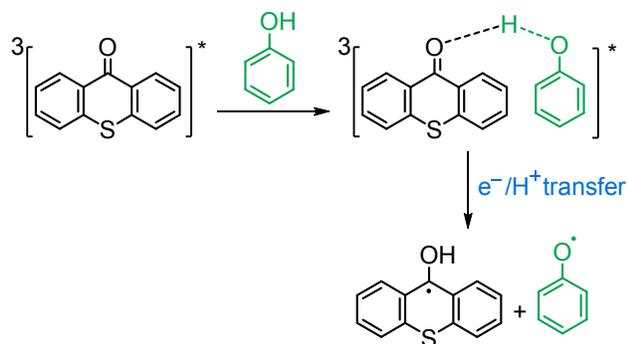
bonds on the backbone (alkene) or pendant double bonds (vinyl) using thiol-ene polymerization method in the presence of a multifunctional thiol and a photoinitiator.⁶⁰ The reactivity of thiyl radicals to copolymerize with the pendant vinyl groups was found to be 10 times higher than the copolymerization with butene double bonds (Scheme 6).

This kind of thiol-ene reaction has been well known as an example of click chemistry that can be triggered *via* either thermal, photo, or redox processes. However, the photochemical processes are more preferred over other protocols due to the advantage of spatial and temporal control over the thiol-ene addition process.^{28, 61} 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 photoinitiation of thiol-ene click chemistry for functionalization of polymers.⁶² 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 a little higher conversions 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 of triplet ketones by phenolic compounds has been proposed



Scheme 7 Light-induced thiol-ene click reaction.

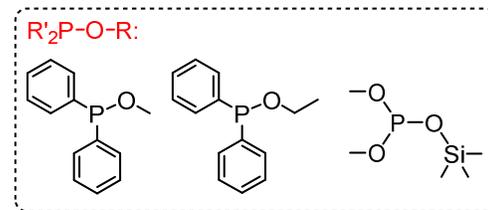
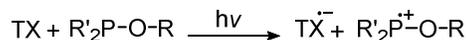


Scheme 8 Proposed mechanism of quenching triplet thioxanthone by phenolic co-initiators.

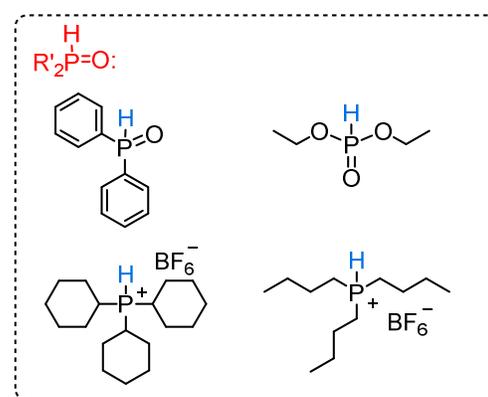
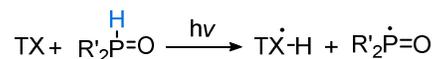
using laser flash photolysis studies based on the formation of a hydrogen-bonded exciplex between the phenol and triplet state ketone, which was followed by sequential electron and proton transfer processes resulting in the formation of the ketyl and phenoxy radicals as depicted in Scheme 8.⁶³⁻⁶⁵ A similar photoreduction mechanism was also reported by Das and Nath using biologically relevant phenolic and indolic hydrogen-donor compounds in sodium dodecyl sulfate micellar medium.⁶⁶ In the polymerization processes, however, phenolic compounds are generally used as chain transfer agents to control the molecular weight properties of polymer chains.^{67, 68} 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-initiator. Lalevee et al. investigated photosensitized decomposition of phosphorus compounds by *Type II* photoinitiation in which phosphorus-centered radicals were generated to initiate radical polymerization.⁶⁹ 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 probability of involvement of any electron transfer processes. On the other hand, however, electron transfer processes between the phosphorus co-initiators without any abstractable hydrogen and 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.

Electron transfer:



Hydrogen abstraction:



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

Silanes. It has been found that silane compounds can be efficiently employed as co-initiator to initiate photopolymerization in the presence of photoinitiators. The process is based on the hydrogen atom abstraction from the Si-H bond leading to silyl radical generation capable of initiating radical polymerization.⁷⁰⁻⁷² Photoinitiation with disilanes having an Si-Si bond is also possible through electron transfer and Si-Si bond dissociation.⁷³ 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-folds compared to deaerated media. Various silane-type co-initiators including silylamines, silyloxyamines and others have been reported.⁷⁴⁻⁷⁸

Germanes and Stannanes. It has been shown that some germanes and stannanes compounds bearing a labile hydrogen bond can be efficient co-initiators in combination with *Type II* photoinitiated polymerization (Chart 4).^{79, 80} In a similar mechanism to silanes, the abstraction of the labile hydrogen formed the corresponding germyl and stannyl radicals.

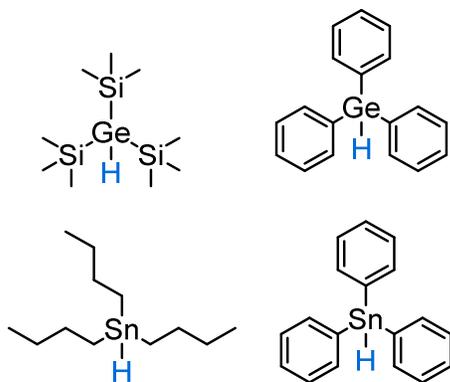


Chart 4 Germane and stannane co-initiators.

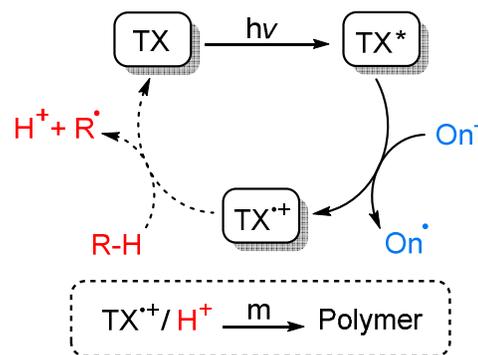
These radicals were efficient in the photoinitiation of both free radical polymerization and free radical promoted cationic polymerization. In the latter case, the resulted radicals were oxidized to form active cation species with the help of an iodonium salt to initiate the cationic polymerization.⁸¹⁻⁸⁴

Onium salts. Cationic photopolymerizations initiated by onium salt photoinitiators have become well-established processes in commercial applications and academic research areas. Iodonium, sulfonium, phosphonium salts are amongst the mostly utilized onium salt photoinitiator which in common contain a heteroatom with the 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.⁸⁵ Most onium salts absorb light at the short wavelengths region of the UV spectrum around 300 nm and below. In order to activate the photolysis of onium salts at 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 electron donor part 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 points of thermodynamics, the feasibility of this process can be estimated by the Rehm-Weller equation, which calculates the energy changes of the electron transfer reaction (ΔG_{et}). The more negative is ΔG_{et} , the more feasible becomes the possibility of electron transfer.

Taking diphenyliodonium, triphenylsulfonium, and *N*-ethoxy-2-methylpyridinium as examples of mostly 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 the sulfonium salt as the energy of electron transfer in sulfonium salt 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 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 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 the onium salts.⁸⁶⁻⁹⁶ Some prominent onium salts which have been employed in photoinitiated polymerizations are depicted in Chart 5.



Scheme 10 Photosensitized cationic polymerization by using onium salts.

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

Compound	Photosensitizer		ΔG (kcal mol ⁻¹) ^a		
	$E_{1/2}^{\text{ox}}(\text{D}/\text{D}^+)$ (eV)	E_s (kcal mol ⁻¹)			
TX	1.7	277	-92	+4	-44.2

^a Energy changes calculated by the Rehm-Weller equation

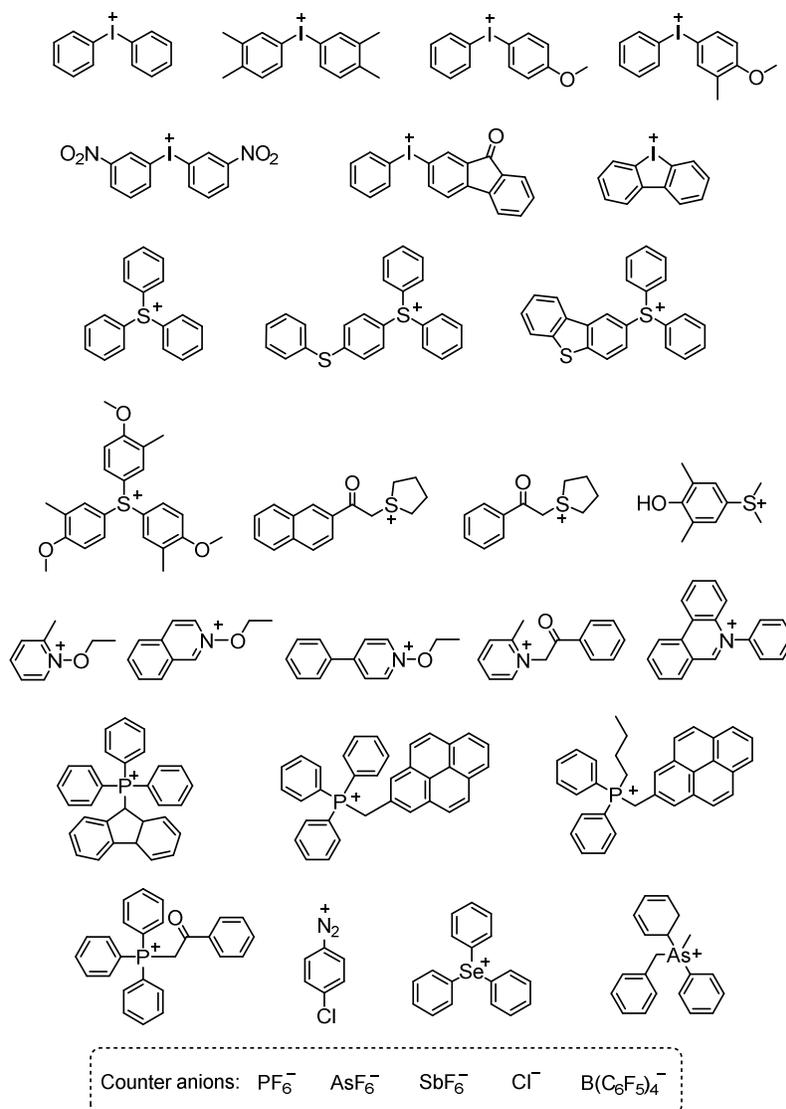
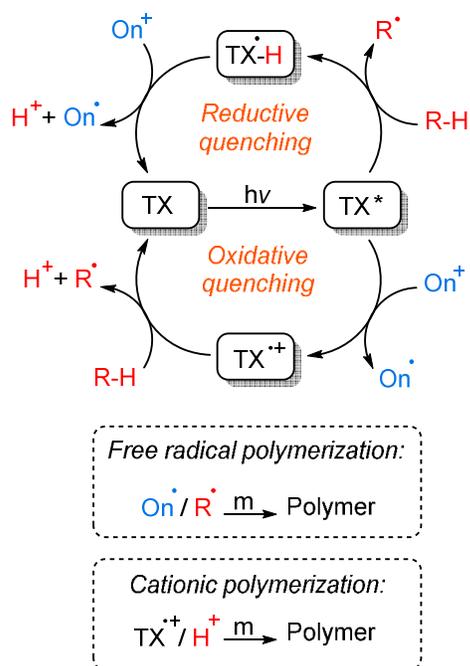


Chart 5 Some onium salts utilized in photopolymerization initiated by Type II photoinitiators.

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.⁹⁷⁻¹⁰⁴ The three-component photoinitiation systems are aimed to enhance the rate and efficiency of 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. For this, should also be added the simultaneous interaction of the amine co-initiator with the triplet photoinitiator, which forms an initiating radical through a 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 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 aminoalkyl radical while regenerating the ground state photosensitizer.

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



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 (On^+) components: triplet thioxanthone is quenched through either oxidation by the onium salt or reduction by the amine hydrogen donor.

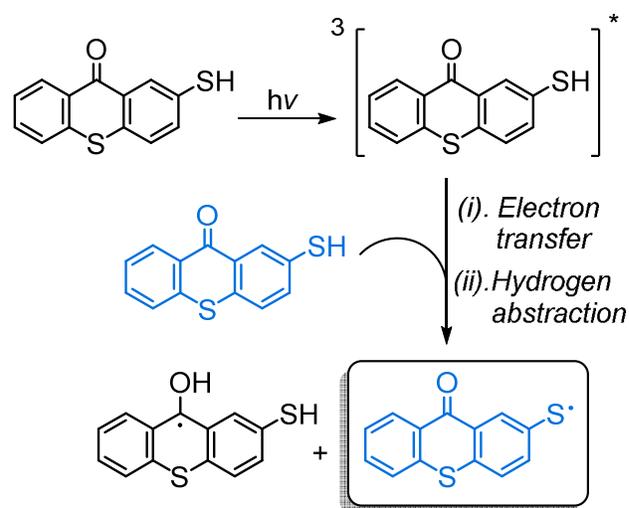
polymerizations. Regeneration of the initial photosensitizer, the possibility of formation of both radical and cationic species by various interactions for the initiation of different modes of polymerization, and converting terminating agents to active initiating sites (oxidation of ketyl radicals to form initiating radical or cationic species) 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 focus on *Type II* photoinitiation has been to design new classes of photoinitiators capable of acting both photoinitiator and co-initiator functionalities at the same time. Chemically incorporation of various co-initiators into the structure of photoinitiators makes one-component photoinitiators exhibit double functionality. Without the need of additional co-initiators, one-component *Type II* photoinitiators form initiating species through intramolecular and/or intermolecular interactions between triplet state chromophore core and co-initiator part of the photoinitiator. There have been encountered some disadvantages of using individual co-initiators which may bring strong odor or cause 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, ether-like hydrogen donors have been incorporated to the photoinitiator structure to make one-component photoinitiating systems.

As a preliminary work in one-component TX photoinitiators, 2-mercaptothioxanthone (TX-SH), a thiol substituted derivative of TX, has been extensively utilized as efficient one-component *Type II* photoinitiator.¹⁰⁹⁻¹¹¹ 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 $^3\text{TX-SH}^*$ with a ground state TX-SH molecule results in the formation of thiyl radicals through a consecutive electron transfer and hydrogen atom abstraction processes. Intramolecular interaction is unlikely to happen due to the rigidity of the spacer group between 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 polymerization process, TX functionalities are incorporated into the polymer chain and thus can further contribute in the photoinitiation processes.¹¹² Another striking preference of the TX-SH photoinitiator involves with its applicability to styrene-based monomer formulations. Indeed, aromatic ketone/amine combinations appear to be an effective photoinitiator system for the polymerization of acrylates or methacrylates, whereas they represent low reactivity toward styrenic monomers in virtue of the high quenching rate of the monomer and the less reactivity of resulting α -amino radicals with styrene. It has been proven that the efficiency of TX-SH photoinitiator for the polymerization of styrene is by far higher than with the TX and amine co-initiator combinations.

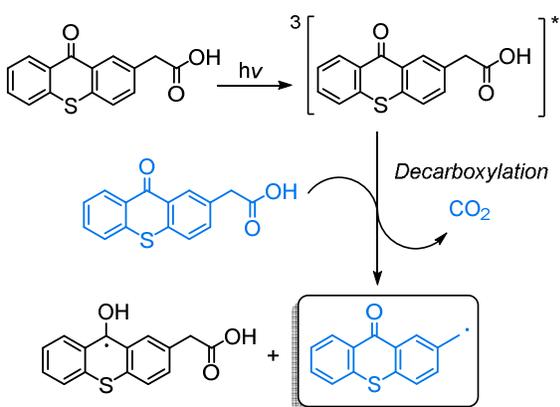


Scheme 12 Photoinitiation mechanism of the formation of initiating radicals by 2-mercaptothioxanthone.

TX-SH was also reported to behave as 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 α -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 oxygen insensitive species thus enabling photopolymerizations in the presence of air without any significant inhibitory effect of oxygen.¹¹³

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 starting materials. Carboxylic acid-functionalized TX photoinitiators have been prepared and utilized efficiently for free radical photopolymerization systems.¹¹⁴ Acting as one-component *Type II* photoinitiator, the mechanism of the formation of initiating free radicals in carboxylic acid-functionalized TX is 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 the decarboxylation on irradiation could be directed to the other tube containing sodium carbonate solution. The pink colored sodium carbonate solution turned to a colorless solution upon getting in contact with the evolved carbon dioxide.

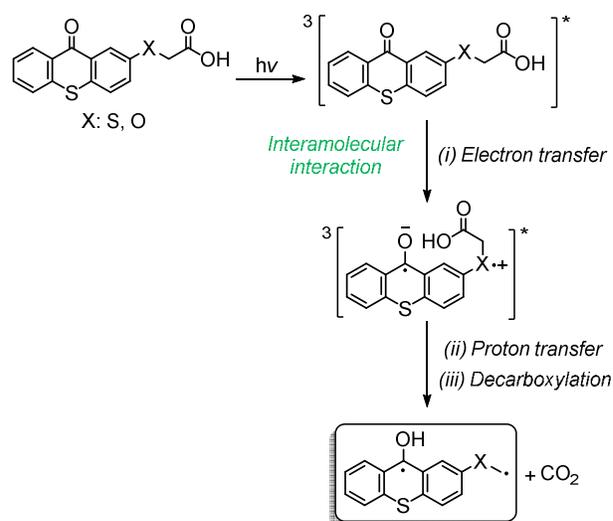
Several other carboxylic acid-functionalized TX compounds as one-component *Type II* photoinitiator having different spacer length capable of affecting the efficiency of photoinitiation



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

process were reported.^{115, 116} 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.¹¹⁷ The flexibility of carboxylic acid moieties due to longer spacer length favors intramolecular electron and hydrogen transfer processes (Scheme 14). This was supported by a short triplet lifetime of thioacetic acid TX (65 ns) due to the involvement of intramolecular quenching processes, as compared to an 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.¹¹⁸

Arasu and co-workers investigated the influence of the substitution pattern and their position on the photoinitiation activity of carboxylic acid-functionalized TX derivatives.¹¹⁹ Photoinitiators with carboxylic acid functionalities at the 1-position of TX appeared to be inefficient for the photoinitiation of polymerization in certain environments. With these compounds, intramolecular hydrogen-bonding results in a 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 bonding, the polymerization efficiently proceeded through consecutive electron and proton transfer and decarboxylation processes. For reactions in acetonitrile, addition of small amount of hydrogen-bond-disrupting solvents to suppress intramolecular hydrogen bonding seemed necessary for successful polymerization.



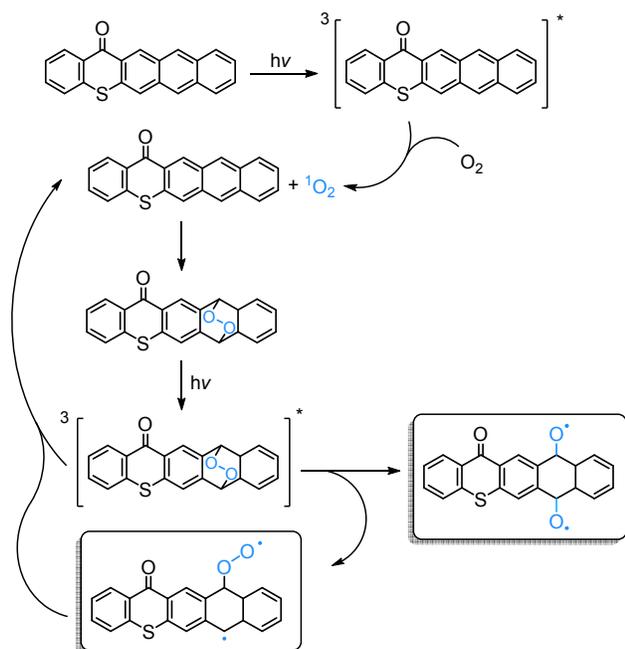
Scheme 14 Photoinitiation mechanism of thioacetic acid thioxanthone.

REVIEW

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

An anthracene incorporated TX (TX-A) exhibits photoinitiation mechanism different from that of the other hydrogen-abstraction *Type II* photoinitiators.^{120, 121} 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 TX-A photoinitiator and quenching 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 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 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.^{122, 123}

A panchromatic behavior was observed when using thiosalicylic acids with *N*-phenylglycine to form glycine-



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

Polymer Chemistry

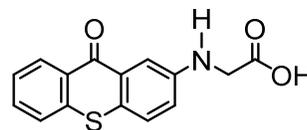


Chart 6 Glycine-functionalized thioxanthone showing panchromatic characteristics.

functionalized TX photoinitiator. Allonas, Arsu and co-workers demonstrated that the absorbance of the glycine-functionalized TX (Chart 6) was shifted to higher wavelengths up to 600 nm covering a wide range of UV and visible light of electromagnetic spectrum. This shift to higher wavelengths was attributed to the formation of hydrogen bonding facilitated by glycine functionalities. Photopolymerizations were successfully achieved using different light sources of at 392, 473, 532, and 635 nm wavelengths with increasing the photoinitiation efficiency by decreasing the irradiation wavelength in consistent with increasing absorption coefficient at lower wavelengths.¹²⁴ Several other nitrogen-containing one-component photoinitiators bearing abstractable hydrogen sites have also been synthesized and utilized for the photoinitiation of polymerization (Chart 7).¹²⁵⁻¹²⁷

Carbazole functionalities were also taken advantage of forming one-component TX photoinitiators with extended conjugation. In this regard, for example, carbazole and ethylcarbazol functionalized TX photoinitiators (Chart 8) have been reported.^{84, 128-130} Due to the extended conjugation contributed by the incorporation of carbazole moieties, these photoinitiators exhibit 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 ethyl group of the carbazole functionality. Additionally, free radical promoted cationic photopolymerization was achieved using ethylcarbazole TX in conjunction with onium salts-based oxidants. The free radicals formed in the course of the photolysis of carbazole TX interacted with the onium salts compounds while being

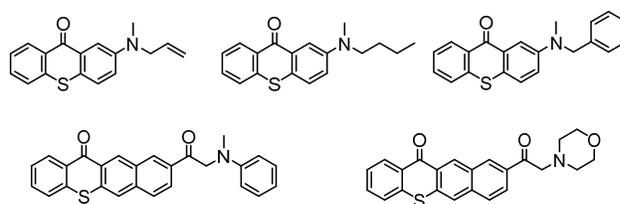


Chart 7 Some nitrogen-containing thioxanthone-based compounds as one-component *Type II* photoinitiator.

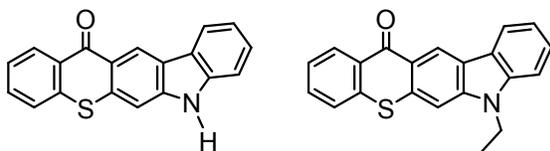


Chart 8 Carbazole-thioxanthenones as one-component photoinitiators.

oxidized to form corresponding cationic species. Applicability of the initiation process to the suitable cyclic and vinylic monomers was demonstrated.^{84, 128}

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 making water-soluble photoinitiators (Chart 9).¹³¹ 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.³² 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.¹³² 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. The two-photon initiated photopolymerizations are distinguished from the commercial one-photon induced photopolymerizations by their distinctive ability to absorb the energy of two photons of the irradiating

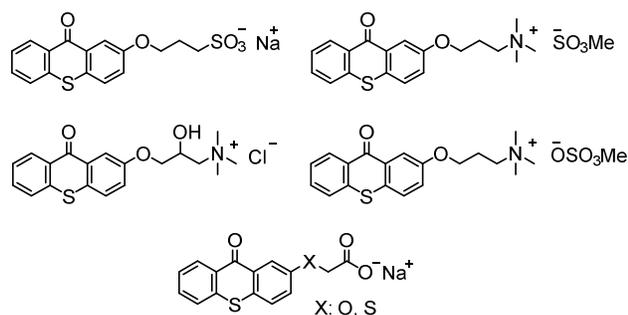


Chart 9 A selection of some-water soluble thioxanthenone-based photoinitiators.

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.¹³³ Gryko and co-workers recently studied two-photon absorption characteristics of the π -expanded donor-acceptor photoinitiators of TX moieties.¹³⁴ Dialkylamino groups as electron-donor components were substituted to TX with a significant enhancement of the optical properties. Those possessing arylethylene and arylethynyl linkages (C=C or C \equiv 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.¹³⁵ Polymeric photoinitiators bearing photoinitiator sites are prepared through various polymerization methods of suitable monomers, including step-growth¹³⁶⁻¹⁴¹ and addition¹⁴² (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 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

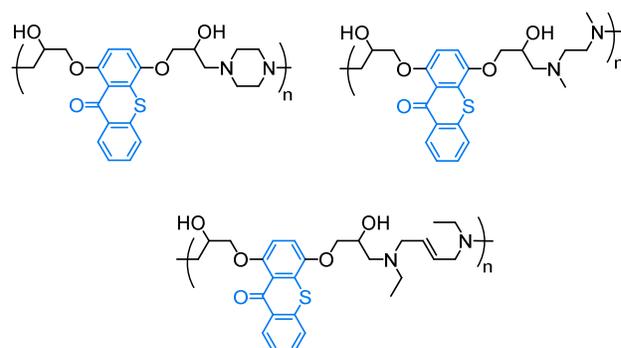


Chart 10 A selection of thioxanthenone-based, one-component polymeric photoinitiators prepared by step-growth polymerization techniques.

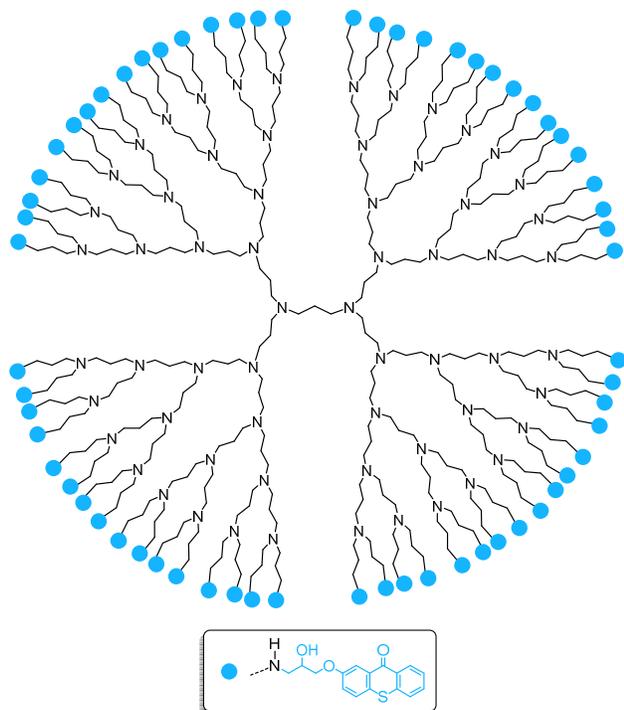
REVIEW

macrophotoinitiators by step-growth polymerization methods. Containing in-chain TX and amine groups, these macrophotoinitiators were reported to act as one-component photoinitiator.^{138-140, 143, 144}

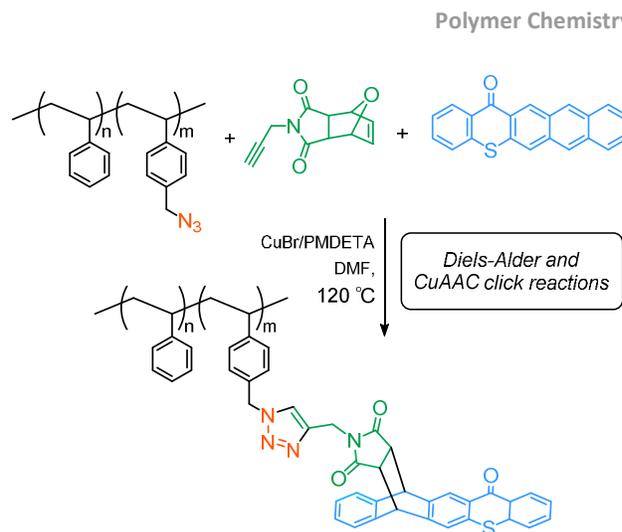
Using glucamine as the co-monomer which contains tertiary amine groups as suitable hydrogen-donor sites, made the resulting TX macrophotoinitiators water-soluble.¹⁴⁰ Examples of some TX macrophotoinitiators prepared by step-growth polymerization are collected in Chart 10.

Alternatively, functionalization of supramolecular or hyper-branched polymeric structures containing amine or etheric functional groups as hydrogen donating groups¹⁴⁵ with photoinitiator moieties have been used to form one-component macrophotoinitiators.^{146, 147} As an example, dendritic or hyperbranched supramolecular amines were reacted with an epoxy functional TX molecule resulting in the formation of dendritic structures with TX end functional groups exhibiting photoinitiation activity much higher than small molecular weight photoinitiating systems.¹⁴⁸⁻¹⁵⁰ 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 thioxanthone of polystyrene, has been reported to prepare macrophotoinitiators with pendant TX groups.¹⁵¹ 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.¹⁵² An amine co-initiator was necessary for polymerization to occur.



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

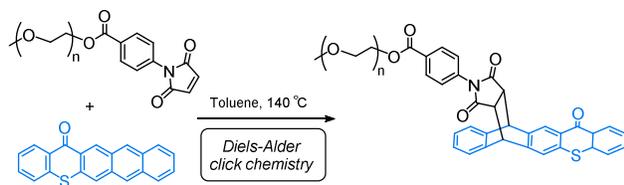


Scheme 17 Synthesis of polystyrene-based macrophotoinitiator with thioxanthone groups using double click reactions.

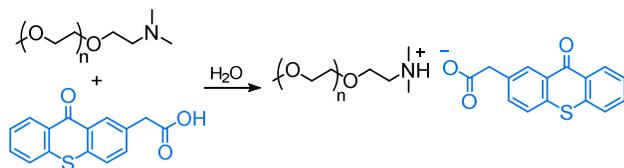
Click chemistry techniques, examples of which include copper-catalyzed azide-alkyne cycloaddition (CuAAC) or Diels-Alder click reactions, offer unique possibilities for the preparation of functional polymeric photoinitiators, which efficiently enable the incorporation of suitable photoinitiator sites 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).¹⁵³ 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 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 aromaticity of anthracene group in the course of Diels-Alder click reaction.

Owing to its good solubility in aqueous media and possessing etheric hydrogen abstraction sites in the 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).¹⁵⁴ A variety of water-soluble monomers were polymerized using this PEG-TX photoinitiator through a grafting from method due to the formation of initiating free radicals onto the PEG backbone as a result 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



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



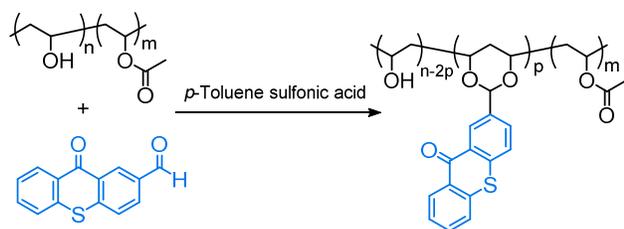
Scheme 19 Synthesis of thioxanthone end-functionalized poly(ethylene oxide) by counterion exchange.

has also been reported. Reacting an α -amino functional PEO with a carboxylic acid functionalized TX group led to the formation of polymeric salt with ionically attached TX groups (Scheme 19).¹⁵⁵ 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 TX chromophore (Scheme 20).¹⁵⁶ 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 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.¹⁵⁷⁻¹⁶¹ Given the



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

heterogeneous nature of this type of macrophotoinitiators, 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 for multiple times while preserving their reactivity, which is a desirable and of significant behavior from the point 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 macrophotoinitiator for conducting photopolymerization.¹⁶² 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 Sonogashira-Hagihara coupling reaction to form a microporous network of TX with the pore size of 1.4 nm and 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 at visible region which were reasoned to the strong π 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 the 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 initiating species. In the latter case, as explained earlier, the photoexcited TX moieties reduced the onium salt through electron transfer reactions forming diphenyl iodonium radical which further decomposes to give 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 formed radical species *via* hydrogen abstraction processes were responsible for the reduction of the onium salt to generate suitable cationic species as well as 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 massive 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

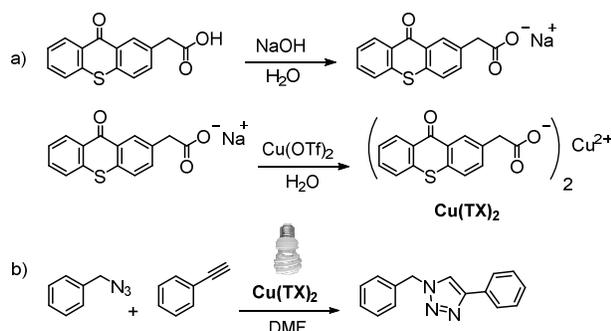
REVIEW

Polymer Chemistry

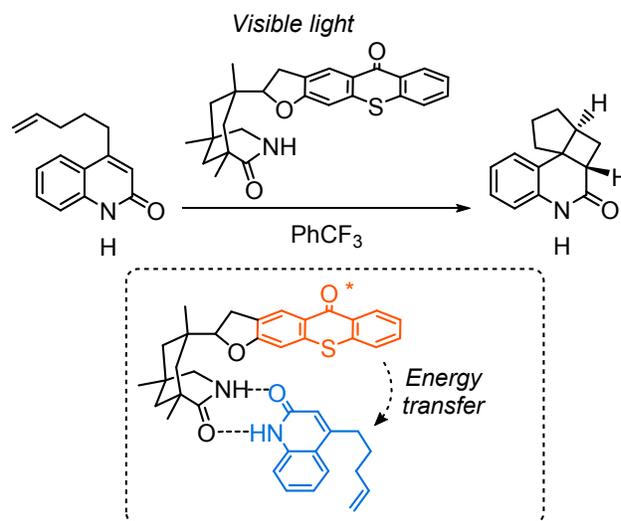
photochemical behavior of TX derivatives has been taken advantage of carrying out target reactions.

One interesting area concerns with the photochemically formation of metal nanoparticles such as silver (Ag) or gold (Au) which is based on photochemically 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-CH₂-COO⁻ Na⁺ and TX-S-CH₂-COO⁻ Na⁺) in the presence of amine hydrogen donors.¹⁶³ While silver nanoparticles form by reduction of the silver cations by the 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 the ligand to stabilize nanoparticles. It was found that the substitution pattern had significant impact on the formation, stability and morphology of 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 and capping the generated nanoparticles through carboxylate functional groups, which in turn uniform, resulted in the formation of uniform individual nanoparticles. This capping behavior was considerable in the case of TX-S-CH₂-COO⁻ as compared with TX-O-CH₂-COO⁻, 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.¹⁶⁴⁻¹⁶⁶

Our group recently reported a new TX-based copper catalyst for the photochemically conduction of CuAAC click reaction.¹⁶⁷ 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.²⁸ Using a TX carboxylate which was converted to its sodium salt by treating in sodium hydroxide media, copper(II) ions were bonded to the TX (Cu(TX)₂) 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)₂ 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



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.

solubility of TX part, which in turn eliminated the need of 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)₂ photocatalyst providing the advantage of temporarily control of 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.¹⁶⁸ They reported that the intermolecular [2+2] photocycloaddition of quinolones, which generally exhibit absorbance at UV region around 300 nm, could be efficiently realized under 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 have also been known for their excellent biological and pharmaceutical activities.¹⁶⁹ Some biologically relevant applications concerning drug development, anti-cancer and tumor treatment¹⁷⁰⁻¹⁷² or protein damage¹⁷³ 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 with 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 interests from a broad realm of polymers, chemistry and science community. 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 efforts has gone into “softening” polymerization conditions or enhancing 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 lightning sources like Light Emitting Diodes (LED) or natural sunlight, which would significantly contribute to lowering the cost of processes as well as suppressing some disadvantages that high energy sources may cause to some special systems.

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REVIEW

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REVIEW

Polymer Chemistry

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Table of Content

Shining a Light on an Adaptable Photoinitiator: Advances in Photopolymerizations Initiated by Thioxanthenes

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This review focuses on the advancements and progress in the photoinitiated polymerizations techniques mediated by thioxanthone (TX) and its derivatives.

