Visible Light Initiating Systems for Photopolymerization: Status, Development and Challenges

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Visible Light Initiating Systems for Photopolymerization: Status, Development and Challenges

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Free radical and cationic photopolymerizations have been greatly utilized in various conventional and emerging applications, such as coatings, electronic circuits, digital storage and 3D precision machining. Compared with ultraviolet light induced photopolymerization, visible light induced photopolymerization presents significant advantages in irradiation safety, curing depth and equipment cost. In this paper, the advancement in visible light induced initiating systems using free radical, cationic and hybrid photoinitiators is reviewed. Chemical structures of the photoinitiators or photosensitizers, photochemical reactivity of photoinitiating systems, and initiating mechanisms of these photoinitiating systems with different activation modes are introduced. The characteristics and limitations of some visible light initiating systems are compared and discussed in terms of the initiating efficiency, excitation wavelength, material cost and safety. The recent promising development of free radical and cationic hybrid initiating systems is also highlighted with their complementary properties in initiating performance and mechanical properties of the cured products.

1. Introduction

Photopolymerization reactions are based on the chemical reactions of excited molecules with light as the energy source. Compared with conventional thermally induced polymerization, photopolymerization has a number of unique advantages, such as low energy consumption, low environmental pollution, fast polymerization rate, low polymerization temperature, wide adaptability. Therefore, the photopolymerization technologies have recently been widely applied in coatings[1-3], electronic circuits[4-7], digital storage[8], solar cells[9], and 3D precision machining[10].

Among the photopolymerization technologies, the ultraviolet (UV) light induced polymerizations have been industrially applied in the fields of UV inks[11-13], UV printings[14, 15] and UV adhesives[16, 17] with the high-energy irradiation of UV light. And numerous works[18-22] have been overviewed in the chemistry, excited-state processes and reactivity of photoinitiators; the components, properties and mechanisms of photopolymerization reactions; and the practical applications of the photopolymerization in various fields. It is noteworthy that some issues associated with UV induced photopolymerizations, such as the generation of ozone, the radiation safety and the curing depth, hindered their further applications. In order to address these issues, visible light induced photopolymerizations were proposed in 1970s and then commercially applied only in dentistry[23] with the metal halide lamp as the light source. Although the light from the metal halide lamp has negligible radiation hazards, it suffers from the irradiation heat from the infrared part of the emission spectrum after a lengthy curing process. In the 1990s, the visible light emitting diode (LED) came out with the advent of the LED technologies. Compared with the ultraviolet lamp, visible light LEDs, such as the blue light LED, have some significant advantages in irradiation safety and energy utilization efficiency[24].

The visible light initiating systems can generate active species under visible light irradiation, which then initiate the polymerization or crosslink reaction of the monomers or oligomers. According to the initiating mechanisms, the visible light initiating systems can be mainly divided into two groups: the free radical initiating systems and the ionic initiating systems. With the growing interdisciplinary collaboration between polymer chemistry and photochemistry, plus the LED technology, the visible light induced photopolymerization has attracted great interest recently. And the components, mechanism and reactivity aspects of visible light photopolymerization have been introduced.[25-27] In this review, some typical and emerging visible light initiating systems for the free radical and cationic photopolymerizations and their associated problems are presented. In addition, some feasible solutions are discussed.

2. Visible light initiating systems for the free radical photopolymerization

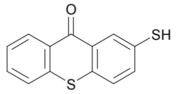
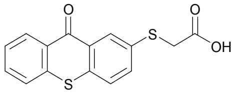
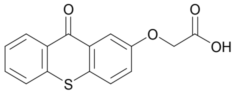
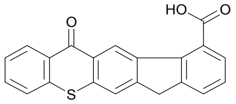
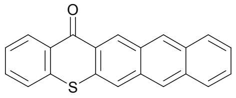
The development of free radical initiating systems has a long history and is quite mature nowadays. The exploitation of novel photoinitiators or photosensitizers is the main research direction for visible light induced free radical polymerization. Some visible light photoinitiators are based on the modification of the existing UV photoinitiators by the introduction of various auxochromes, such as amino, halogen or by the extension of their conjugation structure. The absorption spectrum of modified photoinitiators, such as anthraquinone derivatives, can be shifted from UV to the visible region. Some novel visible light photosensitizers have been successively exploited with better visible light absorption characteristics, achieving more efficient initiating systems in conjunction with a co-initiator. However, the charge-transfer states of these modified photoinitiators are changed by some introduced substituents, resulting in a low initiating efficiency.[28]

2.1 Visible light initiating system based on organic dyes

Some dyes, such as acridine orange, eosin B, erythrosin B, rose bengal, rhodamine B, and methylene blue used as visible light photosensitizers have been previously reported.[28, 29] In a photochemical reaction, a photosensitizer plays a key role in absorbing photons, and then transferring the energy to a co-initiator (hydrogen donor) by a hydrogen abstraction reaction. During the hydrogen abstraction reactions between the excited photosensitizers and the hydrogen donors, both active radical species and photosensitizer radicals are generated. The active radical species initiate the free radical polymerization, whereas the photosensitizer radicals do not have the same initiating ability and even possibly coupled with the active radical species, thus reducing the initiating efficiency.

In order to improve the efficiency of these two-component initiating systems based on dyes/hydrogen donors, Padon *et al.* found that the initiating efficiency of these systems could be enhanced by adding an onium salt as a third component, such as the methyl blue/amine/onium salt system[30], the eosin/amine/onium salt system[31] and the squaraine dyes/iodonium salts[32]. As an electron acceptor, the onium salt has an important role in the initiating process. On one hand, the chain terminating agents (dye radicals) can be oxidized by the onium salt back to original dyes state and re-participate in a hydrogen abstraction reaction. On the other hand, active phenyl radicals are generated upon the photolysis of the onium salt. Grotzinger *et al.* found that 2-(methoxyphenyl)-4,6-bis (trichloromethyl)-1,3,5- triazine (TA) could be also used as a third component to improve the initiating efficiency of dye/amine systems with erythrosine B (ERB), acridine orange (AO), acridine yellow (AF), phenol safraniny (PS) as a photosensitizer. Furthermore, its role in different dye/amine systems was discussed from the thermodynamic point of view.[33]

Table 1 Thioxanthone derivatives as visible light photoinitiators.

Structure	Interaction mode	Absorption region	Ref.
	Intermolecular	320-420nm	34
	Intramolecular	330-450nm	35
	Intramolecular	340-450nm	35
	Intramolecular and intermolecular	340-650nm	36
	Form endoperoxides	300-450nm	37

Thioxanthones are one kind of efficient UV photoinitiators, with their absorption spectra between 370-385nm, while the absorption spectrum of some thioxanthone derivatives can be extended to 450nm. The modification of thioxanthones as visible light photoinitiators can be dated back to the 1970s. In early times, Fouassier *et al.* attempted to increase the photosensitivity of thioxanthone derivatives in the visible region by introducing a carboxyl, an ester or a halogen group into the benzene structure.[38] Other substituent groups, such as sulfhydryl, acetic acid derivatives, and fluorenecarboxylic acid, shown in Table 1, were recently incorporated onto the thioxanthones to extend their absorption to the visible region by Yagci and coworkers. Interestingly, if there is a hydrogen-donating site on these introduced groups, one-component initiating system can be achieved by the intramolecular or intermolecular hydrogen donating reaction[36] shown in Fig. 1. It is worth noting that these one-component initiating systems usually have a higher initiating efficiency than those two-component initiating systems. In this case, the dye not only transfers the excitation, it also participates in the initiation mechanism as a photoinitiator.

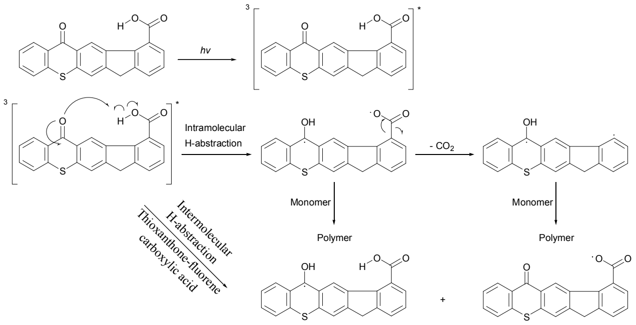


Fig. 1 Photopolymerization mechanism of thioxanthone-fluorenecarboxylic acid through intramolecular hydrogen abstraction. Reprinted with permission from Ref. [36]. Copyright 2010 American Chemical Society.

Apart from these small molecule photoinitiators, the development of polymeric photoinitiators has become an important research direction. Due to their macromolecular chain structure, polymeric photoinitiators displayed many unique advantages. They overcame the compatibility and odour problems existing with some small molecule photoinitiators.[39] Thanks to the "click chemistry" synthesis method, Akat *et al.*[40] grafted the poly(ethylene glycol) maleic anhydride onto the thioxanthone structure, shown in Fig. 2. In addition, the water solubility and initiating performance of the poly(ethylene glycol)-thioxanthone polymeric photoinitiator could be improved by introducing some hydrophilic monomers, such as acrylic acid, acrylamide, hydroxymethyl acrylate and vinyl piperidine.

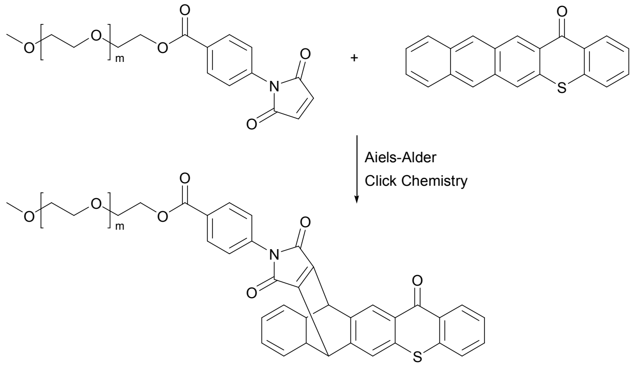


Fig. 2 Poly(ethylene glycol)-Thioxanthone as Macroinitiator. Reprinted with permission from Ref. [40]. Copyright 2010 Wiley Periodicals, Inc.

2.2 Visible light initiating system based on organometallic compounds

Many organic metal compounds have been recognized for their high photoreactivity. Besides, due to the d-d transitions of the metal ions[41], some of them usually show an adequate absorption in the visible region. However, some organic metal initiators suffer from storage stability and toxicity issues. In the early 1880s, some metallocene initiators, such as bis(cyclopentadienyl) titanium, bis(cyclopentadienyl) zirconium, were proposed because of their good thermal stability and broad absorption response in the UV-vis region. Among them, fluorinated diphenyl titanocene (trade name Ciba Irgacure 784) and bis(pentafluorophenyl) titanocene have a wide range of industrial applications due to their high initiating activity, high storage stability, low toxicity, and broad absorptions up to 500nm. In addition, both of them are suitable for the polymerization of acrylates because of the low yellowing index and deep curing depth of the cured products. The Norish I free radical initiating mechanism of Irgacure 784 as a representative compound in the metallocene group is shown in Fig. 3.

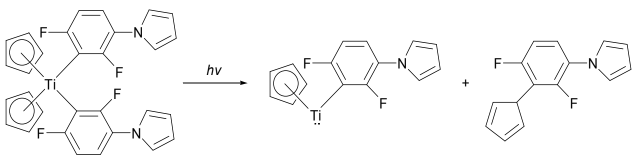


Fig. 3 The initiating mechanism of Bis(2,6-difluoro-3-(1-hydropyrro-1-yl)-phenyl)titanocene.

In addition to the metallocene based initiators, a new class of germanium-containing organic ketone photoinitiators deserves special discussion. As a cleavage-type free radical initiator, diacyltrimethylgermane can be used as a one-component free radical photoinitiator[42], as shown in Fig. 4. The initiating performance of diacyltrimethylgermane was systematically studied and compared with some commercially available photoinitiators, such as 2,4,6-trimethyl-benzoyldiphenylphosphine oxide (MAPO) and camphorquinone/ethyl 4-dimethylaminobenzoate.[43] One of the findings was that the diacyltrimethylgermane has a good stability and photobleaching property, and has an equal reactivity with the camphorquinone/dimethyl amine borane initiating system. Other organic germanium compounds such as triphenylgermanium hydride and tris(trimethylsilyl)germanium hydride can be used as co-initiators in free radical initiating systems due to their hydrogen donating property. Lalevée *et al.*[44] found that these two germanium-containing co-initiators have a similar or even better initiating efficiency than a tertiary amine.

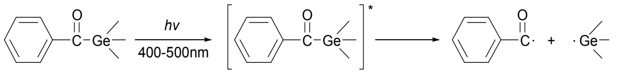


Fig. 4 The photoinitiating cleavage mechanism of diacyltrimethylgermane. Reprinted with permission from Ref. [42]. Copyright 2008 Elsevier Ltd.

Some transition metal complexes are applied as photocatalysts in photovoltaic and photodynamic therapy fields owing to their excellent absorption capacity in the visible region. A series of Ru(II)[45, 46], Pt(II)[47-49], Ir(III)[50] and other transition metal complexes were designed and prepared by Zhao and coworkers. Some transition metal complexes were proposed to be applied in photocatalysis due to their strong photosensitivity in the visible region and a long excited state lifetime.[51] However, few of them have been yet found practical in the visible light induced free radical polymerization. It is believed that, with further exploration and improvement, these transition metal-based complexes will be undoubtedly of great importance in visible light induced photopolymerization.

2.3 Anti-oxygen inhibition in free radical initiating systems

Although free radical initiating systems have been widely applied in photopolymerization owing to their high efficiency and low cost, one of the major drawbacks of free radical polymerization is related to the well-known oxygen inhibition.[52-57] First of all, the excited state of the photoinitiator or photosensitizer can be quenched by molecular oxygen hindering the generation of active radicals. Secondly, the initiating radicals can be oxidized by the molecular oxygen to peroxy radicals, which do not possess the initiating ability. Thirdly, the propagating radicals can also be oxidized to peroxy radicals, which cannot participate in any further polymerization reaction.

In order to overcome the oxygen inhibition in free radical polymerization, some physical and chemical measures have been tried. For example, using an inert gas, such as nitrogen or carbon dioxide[58], is the main measure to isolate the oxygen via a physical method. In addition, liquid wax[59] can also be used to cover the surface of the polymerization system. These physical measures are effective, but the associated high cost in large-scale production restricts their further application. In industrial production, some simple and operational strategies have been developed to eliminate or reduce the oxygen inhibition by increasing the dosage of the photoinitiators or raising the irradiation intensity. Besides, using oxygen scavengers, such as tertiary amine, thiol, organic silane, organic phosphorus compounds is another versatile route to combat the oxygen inhibition. These oxygen scavengers react with the molecular oxygen faster than the active radicals, and the resultant peroxy radicals can be converted into active radicals by a hydrogen abstraction reaction with the oxygen scavengers.

Among those oxygen scavengers, tertiary amines are a class of widely applied co-initiators in the free radical photopolymerization, and their oxygen scavenging mechanism[60, 61] is shown in Fig. 5. The tertiary amine radical, generated by a hydrogen donating reaction between the excited photosensitizer and the tertiary amine, reacts with the oxygen to form a peroxy radical, which subsequently regenerates a new tertiary amine radical and a peroxy acid by a hydrogen abstraction reaction with a second tertiary amine. In this recycling process, the oxygen is continuously consumed and new active radicals are generated. Therefore, the increased dosage of the tertiary amine can efficiently counteract the oxygen inhibition. It is noteworthy that, some side effects such as yellowing, poor stability, odour and safety issues would appear by using tertiary amines as oxygen scavengers.

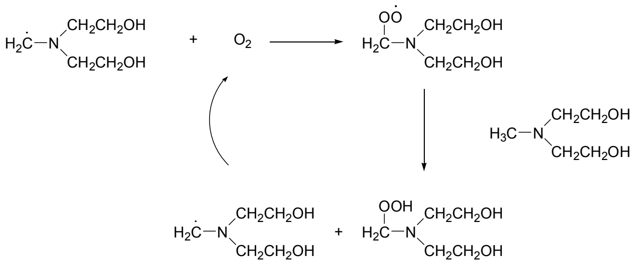


Fig. 5 The anti-oxygen inhibition mechanism of tertiary amine. Reprinted with permission from Ref. [61]. Copyright 2000 John Wiley & Sons, Inc.

The earliest thiol-ene studies on their effects on photopolymerization can be traced back to the 1930s-1950s.[62] Due to the fast polymerization rate, high final conversion, low volume shrinkage and uniform network structure, the study on thiol-ene chemistry has become an attractive field.[63] Additionally, low oxygen sensitivity is another prominent advantage of the reaction of thiols in the free radical polymerization[64] as the thiols can convert the peroxy radicals into active radicals by the hydrogen donating reaction, depicted in Fig. 6. Bowman and coworkers found that a small amount of thiol (1-10 wt%) is sufficient to significantly reduce the oxygen inhibition and to reduce the volume shrinkage in the acrylate polymerization system[57]. Crivelloa and coworkers also reported that the addition of a small amount of thiols could reduce the oxygen inhibition and increase the polymerization rate of the methacrylates in a titanium-containing initiating system under blue light.[65]

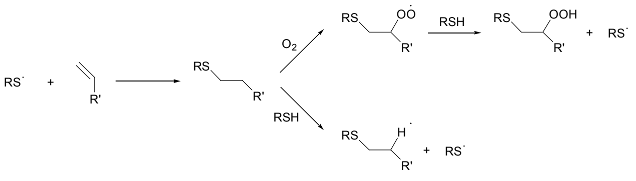


Fig. 6 Oxygen-scavenging mechanism for free radical polymerization in the presence of aliphatic thiols. Reprinted with permission from Ref. [64]. 2004 Wiley Periodicals, Inc.

Organic silane modifiers now are widely applied to improve the flexibility and weatherability of the polymer materials. New features and new uses of the organic silane compounds have been constantly developed. Due to the strong hydrogen donating ability, some silanes such as tris(trimethylsilyl)silane (TTMSS) and tetraphenyl silane (TPDS) can react with some nitrogen-, carbon-, oxygen-, sulfur-centered free radicals to form silicon radicals capable of initiating free radical polymerization.[66] TTMSS also showed an excellent co-initiating performance in free radical initiating systems with some visible light photosensitizers like isopropyl thioxanthone, camphorquinone and eosin.[67] The polymerization results demonstrated that the co-initiating performance of TTMSS is better than the commonly used co-initiator ethyl 4-dimethylaminobenzoate.

Based on the strong hydrogen donating property of these organic silane compounds, Lalevée *et al.* proposed the role of TTMSS in reducing oxygen inhibition[68] as demonstrated in Fig. 7. New active silicone radicals, which show excellent initiating performance for the free radical polymerization, are generated via a hydrogen abstraction reaction between TTMSS and peroxy radicals. Besides, some phosphorus-containing compounds such as methyl diphenylphosphinite, dimethyltrimethylsilyl phosphate, and diethyl phosphonate also have the similar roles in minimizing the oxygen inhibition.[69]

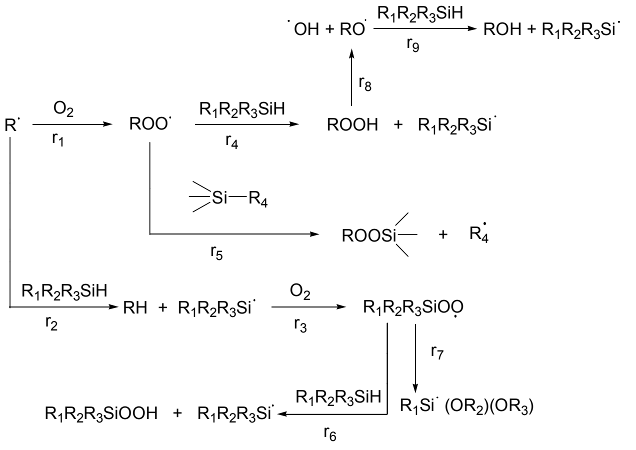


Fig. 7 The anti-oxygen inhibition mechanism of silane. Reprinted with permission from Ref. [68]. Copyright 2011 Elsevier Ltd.

Apart from these hydrogen donors, thioxanthone-Anthracene (TX-A) shows a unique anti-oxygen inhibition mechanism[37, 70] and can photochemically produce active radicals in the absence of any hydrogen donor, as shown in Fig. 8. The triplet excited states of TX-A are quenched by the molecular oxygen to produce singlet oxygen, which then reacts with the anthracene moiety of TX-A to form an endoperoxide. The endoperoxide intermediate undergoes a photochemical or thermal decomposition to generate active radicals for initiating the free radical polymerization. Moreover, TX-A possesses excellent optical absorption properties in the visible region extending to about 450nm and can be used as a visible light photoinitiator without oxygen inhibition.

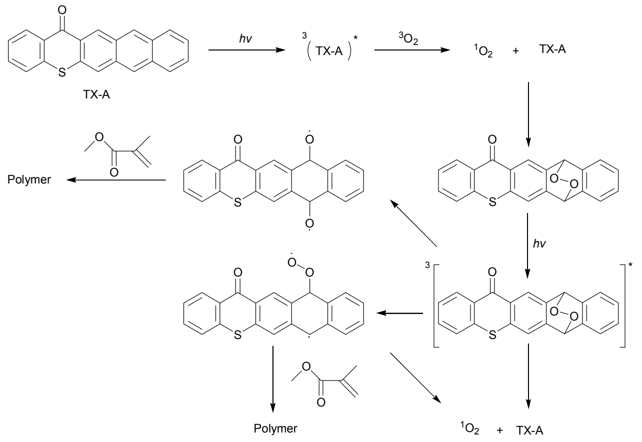


Fig. 8 The free radical initiating mechanism of TX-A under oxygen. Reprinted with permission from Ref. [37]. Copyright 2011 American Chemical Society.

Inspired by enzyme catalysis, a new biological catalysis method with glucose oxidase (GOx) and β-D-glucose (G) as redox components was introduced to overcome the oxygen inhibition in photoinitiated free radical polymerization. The GOx catalyzes the oxidation of β-D-glucose to D-glucono-δ-lactone in the presence of oxygen in aqueous solution, as shown in Fig. 9. During this process, the oxygen in the polymerization system is consumed constantly, preventing the oxidation of the free radicals. The polymerization results indicated that, the polymerization rate and final conversion of monomers increased in the presence of GOx and G redox components. In addition, a shorter induction time was observed in such formulations. However, limited by the solubility of the GOx/G components in organic systems, these anti-oxygen inhibition components can be only applied in waterborn applications.[71]

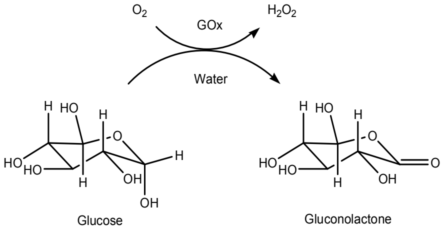


Fig. 9 Oxidation of β-D-glucose (G) to D-glucono-δ-lactone in the presence of molecular oxygen. Reprinted with permission from Ref. [71]. Copyright 2013 Wiley Periodicals, Inc.

3. Visible light initiating systems for cationic photopolymerization

Although free radical photopolymerization technologies have been widely applied in numerous industrial fields, they still suffer from oxygen inhibition, curing shrinkage, insufficient conversion, and unitary monomer type. The development of cationic photopolymerization technologies was relatively late and proposed in the 1970s. In the cationic initiating process, upon photolysis of the cationic initiator, a protonic acid or a Lewis acid forms and then initiates the cationic polymerization. Compared with free radical photopolymerization, the cationic photopolymerization systems have the following characteristics:

1. A variety of cationic monomers. The chain propagation of the free radical photopolymerization is mainly accomplished by the double bond addition reaction of acrylates, while many monomers are available for the double bond addition reaction or the ring-opening reaction in cationic photopolymerizations. Accordingly, the physical and mechanical properties of the cationically cured products are easily tweakable with different kinds of monomers, such as vinyl, epoxy, cyclic ethers, sulfides, acetals.
2. Insensitivity to the oxygen inhibition. The oxygen inhibition is one of the major drawbacks of the photoinitiated free radical polymerization. However, the cationic photopolymerization is insensitive to oxygen. It is necessary to point out that the cationic polymerization can be inhibited by moisture. Fortunately the humidity in practical applications can be easily controlled.
3. Dark reaction. "Dark reaction" is a unique phenomenon of the cationic photopolymerization. Once the active cations are generated by the excitation of the irradiation, they can initiate the cationic polymerization of monomers until complete conversion, even if the irradiation is ceased. Dark reaction is featured with its high final conversion leading to a wide application in coatings, inks, and adhesives.

These features of the cationic polymerization indicate its attractive application prospects. Nevertheless, the cationic photopolymerization still has some shortcomings. In contrast to the free radical photoinitiators, fewer cationic photoinitiators are commercially available. Onium salts are one of the commercial cationic photoinitiators with stable chemical properties and good compatibility with most cationic monomers. However, onium salts have some spectral limitations in the visible region, which restrict their further applications. Therefore, the development of visible light cationic photoinitiators has an important practical significance to the progress and application of the cationic photopolymerization technology.

Nowadays, the development of the visible light cationic initiating systems has attracted much interest. Some novel visible light cationic photoinitiators and cationic initiating mechanisms are being developed and proposed. According to the initiating mechanism, visible light cationic initiating systems can be divided into the direct mode and indirect mode.[72] In the direct initiating mode, the active cations form from the photolysis of the cationic photoinitiator under irradiation, and then initiate the cationic polymerization. Whereas, in the indirect initiating mode, the photosensitizers firstly absorb the visible light to form their exited states, then active cations are produced via an electron transfer process between the excited photosensitizer and cationic initiator. Since the absorption spectrum of the cationic initiating system can be adjusted by changing the photosensitizer, the indirect cationic initiating mode is seemingly more versatile and feasible under visible light.

3.1 The direct visible light induced cationic initiating systems

In the past two decades, onium salts are a class of widely applied cationic initiators. A variety of new onium salts have been developed including iodonium, sulfonium, and alkoxypyridinium. The spectrum response of most onium salts locates in the far-ultraviolet or ultraviolet region, thus their further applications under visible light were restricted. In order to broaden the spectral absorption of onium salts to the visible region, structural modification is applied to extend their conjugated structure with conjugated groups or chromophores. Some derivatives of sulfonium salts, such as anthracene-bound sulfonium salts[73], alkyl phenyl (9-phenyl thioanthracenyl)-10-sulfonium salts and arylbenzylmethylsulfonium[74] were synthesized with a long wavelength absorption spectrum extending to the visible region. Hamazu *et al.* modified the structure of aryl phenyl methyl sulfonium salt, and analyzed the effect of the positions and the types of the substitutes on the initiating activity. The results showed the cationic initiating activity of the sulfonium salt could be noticeably improved by introducing the electron withdrawing group on aryl group.[75] In the works of Crivello and coworkers, five different multi-ring aromatic compounds with long conjugated structures were applied to extend the conjugation of phenyl dihydrocarbyl benzoylthio onium salt. With the extension of the conjugated structure, the absorption wavelength of the modified onium salt gradually increased[76], while the cationic initiating activity generally decreased. Gaud *et al.* also pointed out that, in order to enhance the photosensitivity of the onium salts, it is better to choose 4-thiophenoxy triarylsulfonium, the alkylaryl derivatives (9-phenylthioanthracenyl)-10 sulfonium, or the bisiodonium salts covalently connected with oxygen, carbon or sulfur as the modification parent.[77] Although some successful modification cases were achieved with the peak absorption shifted to the visible region, the structure modification strategy has the following drawbacks. First, the molar absorption coefficient or the fluorescence emission intensity may be reduced by simply increasing the conjugated structure of the cationic initiator.[78] Second, a complex and costly synthesis process is needed for the structural modification of the onium salts. Third, the spectral properties of the modified products sometimes cannot be obtained as expected.

Apart from the modified onium salts, organometallic compounds are another class of visible light cationic initiators, which mainly include ferrocene[79, 80], zirconocenes[81-83], and organoaluminum compounds[84-86]. The cationic initiating mechanism of a ferrocenium initiator can be described as follow: The trivalent ferric ions become bared after the photodegradation of the ferrocenium initiator, and then initiate the ring-opening complexing reaction with the oxygen atom of the epoxy compound. Wang *et al.* synthesized a series of ferrocene salt cationic initiators based on a sandwiched iron-arene complexe, shown in Table 2, and drew the following conclusions: (1) The synthetic yield of the ferrocene salt initiators could be enhanced by introducing of a methyl group on the ferrocene parent; (2) The absorption wavelength and the photosensitivity of the ferrocene salt initiators could be increased by introducing a longer conjugated structure with benzene ring or biphenyl; (3) The photosensitivity and the photolysis rate of the ferrocene salt initiators could be increased by introducing a strong electron-withdrawing group; (4) The absorption wavelength of the ferrocene salt initiators could be red shifted by introducing an ether bond, and (5) the solubility of the aryl ferroceniums could be improved with the enhancement of their polarity.

3.2 The indirect visible light induced cationic initiating systems

The indirect visible light cationic initiating systems usually contain two or three major components, a visible light photosensitizer, a cationic initiator (often onium salts), and sometimes a hydrogen donor. According to different initiating mechanisms, the indirect visible light cationic initiating systems can be divided into three groups: energy transfer between the photoexcited sensitizer and an onium salt, electron transfer in photoexcited charge transfer complexes, and oxidation of free radicals by onium salts (free radical promoted cationic polymerization).[87]

The energy transfer is one form of the photosensitive processes. According to the energy transfer mechanism, the photosensitizer firstly forms its excited state by absorbing light energy. Then, the energy is transferred from the excited photosensitizer to an onium salt. During the energy transfer process, the onium salt simultaneously forms its excited state while the excited photosensitizer is returning to its ground state for another excitation and energy transfer cycle. It is worth pointing out that, a high triplet energy (>70kcal/mol) is needed for a photosensitizer to intersystem-cross to its triplet state. Furthermore, the energy transfer photosensitization between a photosensitizer and an onium salt also needs a high oxidation potential which prevents the occurence of an electron transfer process. However, the 70 kcal/mol triplet energy, which is equal to the radiation energy with 400nm wavelength[88], cannot be obtained under visible light irradiation. Therefore, owing to the energy limit of the visible light irradiation, the triplet energy transfer between an excited photosensitizer and an onium salt under visible light cannot be realized theoretically.[89] In the works of Durmaz and coworkers, the cationic initiating mechanism of benzoyltrimethylgermane (BTG)/onium salt system under visible light was discussed. From the fluorescence and phosphorescence spectrum analysis, the energy transfer mechanism from both excited singlet and triplet BTG to the iodonium salt was disproved.[90]

The charge transfer mechanism is a common form of indirect cationic photopolymerization. The charge transfer complex (CTC) forms from the interaction between the electron donor and the electron acceptor after irradiation. Then the active species capable of initiating polymerization are generated after the photolysis of the CTC.

Pyridinium salts mixing with donors of aromatic compounds[91-94] or thiophene derivative[95] are typical cationic photoinitiating systems, which follow the charge transfer mechanism. Radical cations of donors, formed by excitation of pyridinium salts/aromatic donors CTC, can directly initiate cationic polymerization or they undergo hydrogen abstraction yielding Brønsted acid capable of initiating cationic polymerization. The absorption range of the charge transfer complexes mainly depends on the structure of the electron donor and the pyridinium salt. Interestingly, Hizal and coworkers found that the CTC of alkoxy pyridinium salts such as N-ethoxy-p-cyanopyridinium hexafurophosphate with electron donor aromatic compounds such as 1,2,4-trimethoxybenzene[96] or hexamethylbenzene[97] possess a absorption wavelength extending to 600 nm, while the absorption maxima of any constituents alone is lower than 300 nm. The applications of organic dyes as visible light photosensitizers have been widely realized. These organic dyes can initiate the cationic photopolymerization under visible light by combining with cationic initiators such as iodonium salts, piperidine salts or sulfonium salts. In dye/onium salt cationic initiating systems, the dye forms its excited state by absorbing the light with a suitable wavelength and then is oxidized by the onium salts to generate the radical cations capable of initiating the cationic polymerization[98], shown in Fig. 10. In this initiating system, the dye is actually a bi-functional component acting as both photosensitizer and photoinitiator.

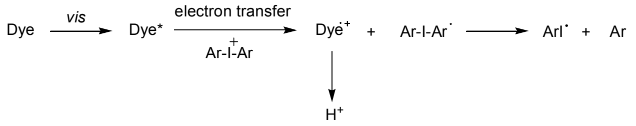


Fig. 10 Photosensitization of iodonium salts. Reprinted with permission from Ref. [98]. Copyright 2010 Elsevier Ltd.

Excellent studies on dyes as photosensitizers were carried out by Podsiadły and coworkers to overcome some application limitations of conventional cationic initiators regarding the photosensitive wavelength range and the initiating rate. The structural modifications of some dyes, such as 12H-Quinoxalino[2,3-b][1,4]benzothiazine derivatives, fluoflavin, diazobenzo[a]fluorine, and quinoxaline derivatives were performed to adjust their spectral absorption and molar absorption coefficient by the introduction of some electron donating or withdrawing groups, as shown in Table 3.

Bulut *et al.* synthesized some derivatives of benzotriazole[99], quinoxaline[100], dibenzophenazine[101] with long conjugation structures, which have strong absorptions in the visible region and their absorption range could be extended to 450nm, 550nm, 600nm respectively. The photopolymerization experiments demonstrated that the quinoxaline derivatives have a satisfied initiating efficiency and it can initiate the photopolymerization even under the sunlight.

Two thiophene derivatives[102] were synthesized by Yagci and coworkers as novel visible light photosensitizers, whose maximum absorption peaks are located at 480nm, and their photosensitive range could be extended to about 600 nm. Moreover, the cationic initiating mechanism of these two thiophene derivatives was investigated in depth. The initiating mechanism in Fig. 11 shows that the excited photosensitizer is oxidized by iodonium salt to produce radical cations, which can directly initiate the cationic polymerization. On the other hand, the radical cations of photosensitizers can also initiate the cationic polymerization by a self coupling interaction or a hydrogen transfer reaction with the hydrogen donor.

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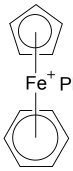
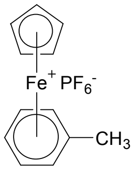
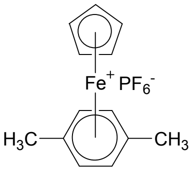
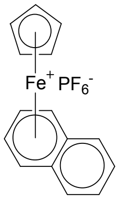
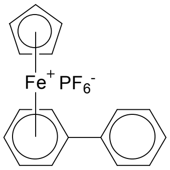
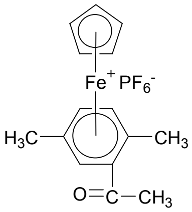
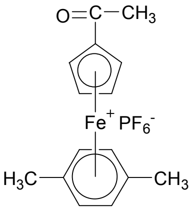
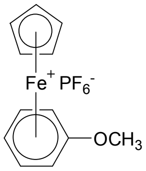
ARTICLE TYPE

Table 2 The structure and absorption spectrum data of aryl ferrocenium salts in dichloromethane solution.[103-105]

No.	Name	structure	The main absorption peak (nm)	Molar absorption coefficient (mol^{-1} cm^{-1})
1	[Cp-Fe-benzene]$^+$		239 370 450	1.39×10^{4} 111 79
2	[Cp-Fe-toluene]$^+$		239 375 455	1.24×10^{4} 75 59
3	[Cp-Fe-xylene]$^+$		238 375 455	1.22×10^{4} 68 52
4	[Cp-Fe-naphthalene]$^+$		233 249 307 355 480	1.25×10^{4} 1.15×10^{4} 2.33×10^{4} 893 362
5	[Cp-Fe-biphenyl]$^+$		233 253 300 389 442	1.36×10^{4} 1.89×10^{4} 1.22×10^{4} 277 138
6	[Cp-Fe-(2,5-dimethylhypnone)]$^+$		240 365 460	0.91×10^{4} 638 63
7	[(acyl-Cp)-Fe-(p-xylene)]$^+$		238 360 490	1.08×10^{4} 1.43×10^{3} 438
8	[Cp-Fe-anisole]$^+$		242 396 466	1.47×10^{4} 136 72

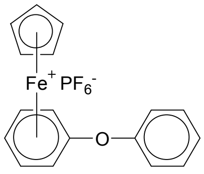
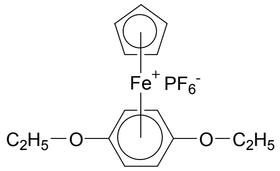
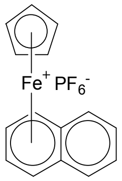
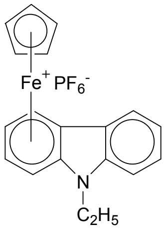
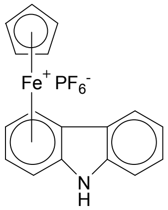
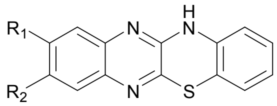
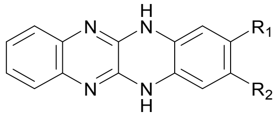
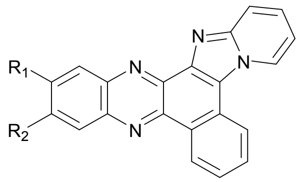
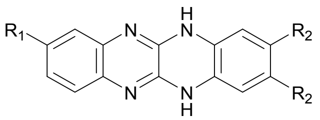
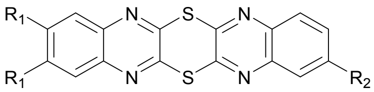
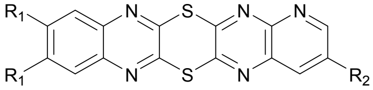
9	[Cp-Fe-diphenylether]$^+$		243 394 466	1.97×10^4 140 75
10	[Cp-Fe-p-diethoxybenzene]$^+$		242 404 468	1.68×10^4 146 76
11	[Cp-Fe-aminonaphthalene]$^+$		213 242 376 546	2.16×10^4 2.01×10^4 2.38×10^3 9.67×10^2
12	[Cp-Fe-n-ethylcarbazole]$^+$		219 259 352 429	2.37×10^4 2.87×10^4 2.32×10^3 1.87×10^2
13	[Cp-Fe-carbazole]$^+$		219 259 347 421	2.41×10^4 2.62×10^4 2.17×10^3 2.67×10^2

Table 3 The maximum absorption wavelength and molar absorption coefficient of dye based photosensitizers.

Structure	R_1	R_2	λ_{max} (nm)	ε (mol^{-1}cm^{-1})
 12H-Quinoxalino[2,3-b][1,4]benzothiazine derivatives[106] in EtOH	H	H	421	6600
	CH_3	CH_3	424	6500
	Cl	Cl	442	5000
 Fluoflavin dye derivatives[98, 107] in CHO	H	H	413	-
	H	Br	416	-
	H	Cl	416	-
	H	CH_3	415	-
	CH_3	CH_3	417	-
 Diazobenzo[a]fluorene derivatives[108] as in chloroform	H	-	443	9800
	CH_3	-	443	11100
	Cl	-	460	10700
	Br	-	462	8300
 8-halogeno-5,12-dihydroquinoxalino[2,3-b]quinoxaline derivatives[109] in 1-methyl-2-pyrrolidone	Br	H	418	24050
	Br	CH_3	417	21200
	Br	Cl	420	23170
	Cl	H	418	25910
	Cl	CH_3	417	25670
	Cl	Cl	420	24100
	OCH_3	H	421	26600

	H	H	456	-
Dithiinoquinoxaline derivatives[110] in 1-methyl-2-pyrrolidone	CH_3	H	466	-
	H	H	455	-
	H	Cl	484	-
	H	Br	486	-
	CH_3	H	459	-
Dithiinoquinoxaline derivatives[110] in 1-methyl-2-pyrrolidone	CH_3	Cl	500	-
	CH_3	Br	502	-

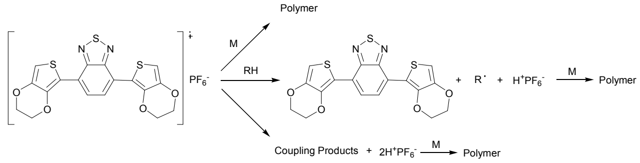


Fig. 11 The cationic initiating mechanism of 4,7-Di(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole radical cations. Reprinted with permission from Ref. [102]. Copyright 2009 American Chemical Society.

Apart from these dye-based visible light photosensitizers, some other unique compounds are applied with onium salts as cationic initiating systems. Fullerene is an aromatic compound with a hollow spherical structure. It has attracted great interest in photochemical, superconducting and electromagnetic fields since the 1990s. Owing to its wide photosensitive range in the visible region (400-650 nm), a new cationic initiating system based on fullerene and onium salt was studied to initiate the cationic polymerization of ethylene oxide and vinyl monomers under visible light.[111] The initiating mechanism of the fullerene based cationic initiating system is shown in Fig. 12.

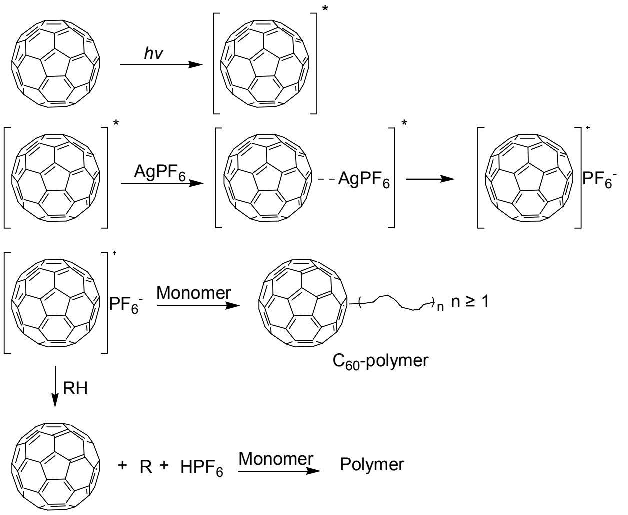


Fig. 12 Visible Light Induced Cationic Polymerization by Fullerene Sensitization. Reprinted with permission from Ref. [111]. Copyright 2012 American Chemical Society.

The cationic initiating mode based on oxidation of free radicals by onium salts (also called free radical promoted cationic polymerization process) has been recognized as a versatile method. The free radicals, generated from Norish I or Norish II free radical initiating process, was oxidized by onium salts to produce active cations. According to this initiating mechanism, the potential difference between radicals and onium salts is an important factor in the initiating efficiency. Since the commonly used cationic initiators usually have a high oxidation potential, most free radicals can be oxidized to their corresponding cations which can subsequently initiate the cationic polymerization.

Organometallic initiators are an important part of the visible light free radical initiators. Some organometallic initiators including dimanganese decacarbonyl[112, 113], dirhenium decacarbonyl[114], (benzene)tricarbonylchromium[115], carbonyl ferrocene compounds and titanocene compounds[116, 117] can also been applied in initiating cationic polymerization under visible light in the presence of onium salts. Benzoyl germanium and iodonium salts are taken as an example[90] to illustrate the initiating mechanism of organic metal compound involved in the free radical promoted cationic polymerization in Fig.13.

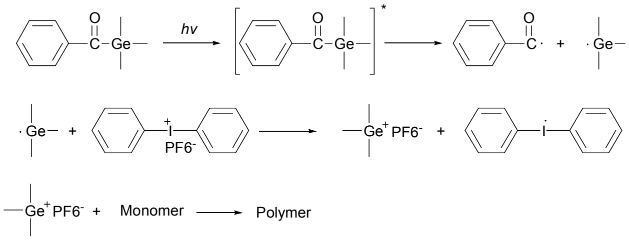


Fig. 13 The oxidation of trimethyl germyl radicals by $Ph_2I^+PF_6^-$. Reprinted with permission from Ref. [90]. Copyright 2008 American Chemical Society.

The free radicals generated in these organometallic photoinitiators follow a Norish I type split mechanism. Of course, free radicals from Norish II mechanism still work in the free radical promoted cationic photopolymerization. 1,2-diketones[118], aryl ketones and quinones[119] were applied as effective photosensitizers for diaryl iodonium salts in cationic photopolymerization of epoxides and vinyl ethers under visible light. Yilmaz *et al.* proposed a free radical promoted cationic initiating system using thioxanthone-fluorene carboxylic acid, tetrahydrofuran and hexafluorophosphate iodonium salt. This three-component cationic initiating system showed a high initiating efficiency, which could be attributed to the generation of multiple active cations. In this initiating process, thioxanthone-fluorene carboxylic acid firstly absorbs the visible light to form its excited state, followed by the hydrogen donating reaction with a tetrahydrofuran to produce two free radicals. Both thioxanthone-fluorene carboxylic acid and tetrahydrofuran based radicals can be oxidized to their corresponding cations for further cationic polymerization[120], as shown in Fig. 14. In addition, when the monomer isobutyl vinyl ether participates in this cationic polymerization, the free radicals generated in free radical addition reaction process can be also oxidized to active cations, as shown in Fig. 15. Such similar initiating mechanism can also work for monomer vinyl carbazole monomer.[121]

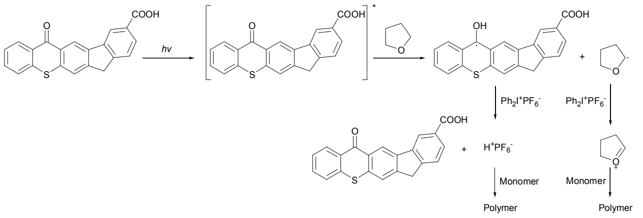


Fig. 14 Free radical promoted cationic polymerization using thioxanthone-fluorene carboxylic acid in the presence of $Ph_2I^+PF_6^-$. Reprinted with permission from Ref. [120]. Copyright 2011 Wiley Periodicals, Inc.

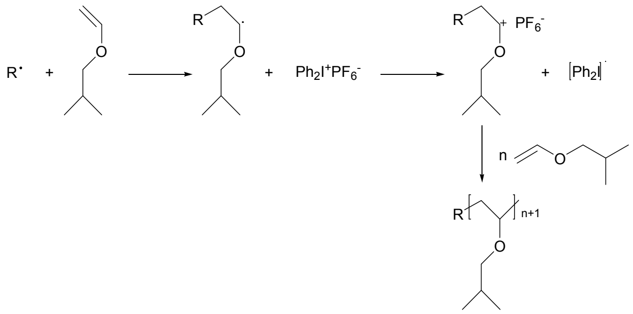


Fig. 15 Free radical promoted cationic polymerization of isobutylvinylether. Reprinted with permission from Ref. [120]. Copyright 2011 Wiley Periodicals, Inc.

The above examples indicate that the visible light free radical promoted cationic initiating systems are practical and versatile. However, as this cationic initiating process is based on the free radical initiating process, the free radical promoted cationic initiating systems also suffer from oxygen inhibition. The free radicals can be converted to peroxyl radicals, which are stable and difficult to be oxidized by the onium salts due to their high oxidation potential. The oxygen inhibition in free radical promoted cationic initiating process can greatly reduce the quantity of the free radicals, eventually resulting in a small number of active cations.

Fortunately, in the photosensitizer/diphenyl iodonium salt free radical promoted cationic initiating system, Lalevée *et al.* found that a high final conversion of the cationic monomers in air can be achieved by adding a third component tris(trimethylsilyl)silane.[122] In addition, other silanes with one or more benzene rings substituents were also applied and compared in free radical promoted cationic polymerization under visible light. The results indicated that the initiating performance of the three-component cationic initiating system containing tris(trimethylsilyl)silane is far superior to the others. Furthermore, it was pointed out that the initiating performance of these systems mainly depend on the hydrogen transfer process and the redox reaction, which are related to the structure of organic silicone.[123]

In order to further explore the role of organosilane compounds in free radical promoted cationic initiating systems, Lalevée *et al.* applied tris(trimethylsilyl)silane in some free radical promoted cationic initiating systems with 9,10-bis[(triisopropylsilyl)ethynyl]anthracene[124, 125], organic transition metal iridium[126, 127], ruthenium[128], and platinum[129] complexes as visible light photosensitizers. It was exciting to find that the cationic photopolymerization in these systems show a high initiating efficiency even under some soft visible light. Moreover, tris(trimethylsilyl)silane was confirmed as a real cationic active species with a high initiating performance.[130, 131] Combined with the role of tris(trimethylsilyl)silane in anti-oxygen inhibition shown in Fig. 7, the role of tris(trimethylsilyl)silane in free radical promoted cationic initiating systems can be summarized in Fig. 16. Owing to its strong hydrogen-donating property, tris(trimethylsilyl)silane experiences a hydrogen transfer reaction with an excited photosensitizer or a free radical (photolysis products) to form a silyl radical, which can be easily oxidized by an onium salt leading to an efficient initiating species silylium cations. On the other hand, the anti-oxygen inhibition effect of tris(trimethylsilyl)silane can be ascribed to the conversion of stable peroxyl radicals into new active silyl radicals, which can be oxidized to silylium cations capable of initiating the cationic polymerization[132, 133].[132, 133]

$$PS + hv \longrightarrow {}^*PS$$

$$^*PS + (TMS)_3SiH \longrightarrow PSH^{\bullet} + (TMS)_3Si^{\bullet}$$

$$(TMS)_3Si^{\bullet} + Ph_2I^+ \longrightarrow (TMS)_3Si^+ + Ph^{\bullet} + PhI$$

$$Ph^{\bullet} + (TMS)_3SiH \longrightarrow PhH + (TMS)_3Si^{\bullet}$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$(TMS)_3Si^{\bullet} + O_2 \longrightarrow (TMS)_3SiOO^{\bullet}$$

$$ROO^{\bullet} + (TMS)_3SiH \longrightarrow ROOH + (TMS)_3Si^{\bullet}$$

$$(TMS)_3SiOO^{\bullet} + (TMS)_3SiH \longrightarrow (TMS)_3SiOOH + (TMS)_3Si^{\bullet}$$

Fig. 16 The role of tris(trimethylsilyl)silane in free radical promoted cationic initiating system. Reprinted from an open access and re-usable paper Ref. [132].

In above examples, the cationic initiator onium salt plays a very important role in free radical promoted cationic initiating system. Kahveci *et al.* found that some vinyl halides and Lewis acids could be used to initiate the cationic polymerization of vinly ether-based monomers even in the absence of onium salts. The initiating mechanism of vinyl halides is shown in Fig. 17. Vinyl cation and bromide ion are generated from the breakage of the carbon-bromine bonds under irradiation and subsequently the electron transfer process. The vinyl cation then directly reacts with a vinly ether monomer to form a new vinyl cation and is then neutralized by the bromide ion. The chain growth process proceeds with the coordination effect of zinc iodide.[134] Some long conjugated vinyl halides were synthesized to extend/shift their photosensitive region, because the spectral absorption of the original vinyl halides with three aryls or anisoles as substituent was under 400 nm. As a new initiating mechanism for cationic polymerization, it is still worthy of further study.

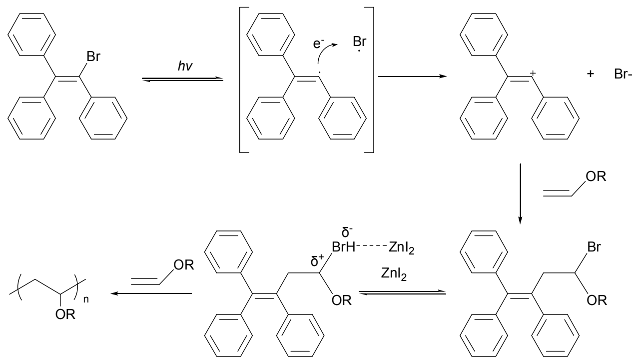


Fig. 17 Photoinitiated cationic polymerization of vinyl ethers by irradiation of PPPVB in the presence of ZnI_2. Reprinted with permission from Ref. [134]. Copyright 2009 American Chemical Society.

4. Visible light initiating systems for free radical/cationic hybrid photopolymerization

As a well-developed photopolymerization technology, free radical photopolymerization is well known for its fast curing speed and numerous raw materials for the polymerization such as photoinitiators and monomers. However, the free radical photopolymerization suffers from oxygen inhibition, and low final conversion rate. Since the forces between the monomers or oligomers are changed from van der Waals forces before the polymerization to covalent bonds after polymerization, the distance between the monomers/oligmers molecules is shortened resulting in a noticeable volume shrinkage and poor adhesion. Compared with the free radical photopolymerization, the cationic photopolymerization technology can offer many unique advantages, such as no oxygen inhibition, low curing shrinkage, and dark curing behavior, which complement the free radical photopolymerization.[135] Of course, the cationic photopolymerization still has its limitations on cost, curing speed and humidity inhibition. In order to combine the advantages of both the free radical and cationic photopolymerizations, a hybrid photopolymerization was proposed to be initiated by both the free radicals and cations simultaneously. Not only is the overall performance of the hybrid photopolymerization improved including the reduced sensitivity to oxygen and moisture, the increased polymerization rate, and the reduced volume shrinkage, but also the physical and mechanical properties such as hardness, elasticity, flexibility of the resultant polymer are more easily adjustable. Therefore, the synergistic effect of the hybrid polymerization is beneficial to improving the polymerization performance in a broad application field.

Due to the great potential of the free radical/cationic hybrid photopolymerization, the development of a mixture system with both began in the 1970s. However, Cirvello *et al.*[136] found that the simple mixing of two photopolymerization systems has a limitation on the spectral matching of different photoinitiator types. This mismatching issue was then solved by the synthesis of a cleavage-type hybrid initiator, which combines the characteristic structure of benzophenone and diphenyl iodonium salt and has a high initiating efficiency[137, 138].[137, 138] Owing to the narrow spectral absorption of benzophenone and diphenyl iodonium salt, the hybrid initiator can only be applied under ultraviolet light. In order to extend the spectral range of such hybrid initiator, Wang *et al.* designed a cleavage-type hybrid initiator with the structures of benzophenone and ferrocenium (η6-3-benzoyl-4-chloro-diphenylamine) (η5-cyclopentadienyl) iron hexafluorophosphate (Fc-NBP)[139, 140].[139, 140] Due to the n-π * transitions of the carbonyl group and the d-d transitions of the iron arene complexes in Fc-NBP, the photosensitive range of Fc-NBP can be extended to 550nm, which just matches the emission wavelength of the halogen lamp. The photolysis process of Fc-NBP can proceed in two ways to generate free radical and cation speices, as shown in Fig. 18. In one way, after absorbing the light, the arene ligand is removed from the Fc-NBP structure and can initiate the cationic polymerization. Residual structure of Fc-NBP undergoes photolysis reactions to produce benzoyl radicals capable of initiating free radical polymerization. In the other way, the excited state of the Fc-NBP directly photocleaved into two active radicals, both of which can initiate the free radical polymeriztion. In addition, benzoyltrimethylgermane(BTG) also has a similar initiating process, whereas the generation of the active cations needs the presence of onium salts.[141]

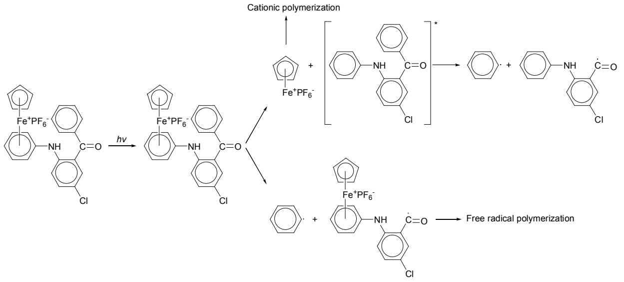


Fig. 18 Mechanism of photoinitiation of acrylate irradiated by Fc-NBP. Reprinted with permission from Ref. [124]. Copyright 2010 Elsevier Ltd.

As mentioned above for the free radical promoted cationic initiating systems, the cations are generated by the oxidation of free radicals. It means that both active free radicals and cations concurrently exist during the initiating process. Therefore, some free radical promoted cationic initiating systems can also be used as free radical/cationic hybrid initiating systems as the active free radicals and cations are presented simultaneously. Some organic dyes[26], such as Eosin Y, methylene blue, Rose Bengal, camphorquinone[142] ,5,12-dihydroquinoxalino[2,3-b]quinoxaline, 5,12-dihydroquinoxalino[2,3-b]pyridopyrazine[143] and some transition metal compounds, such as $Ru(bpy)_3^{2+}$ [127], $Ru(phenanthroline)_3^{2+}$ [144] ,Ir(ligand)$_3$[128, 133] have been applied as visible light photosensitizers or photoinitiators in the free radical/cationic hybrid photopolymerization in the presence of onium salt.

Among above free radical/cationic hybrid initiating systems, the transition metal compounds gain great interest as visible light photosensitizers or photoinitiators, due to their broad absorption in the visible region and high initiating efficiency. However, most of these transition metal compounds are based on noble metals. Compared with these transition metal compounds, some organic photosensitizers or photoinitiators have advantages in cost, toxicity and stability. Many new organic photosensitizers or photoinitiators, such as 9,10-bis-[(triisopropylsilyl)ethynyl]anthracene[124], truxene and tris(aza)pentacene derivatives[145], and thioxanthone derivatives, have been synthesized and applied in free radical/cationic hybrid photopolymerizaiton, demonstrating excellent initiating efficiency. Thioxanthone-ethylcarbazole(TX-EC)[146] is a novel visible photoinitiator with three typical characteristics. (1) It has an excellent absorption between 400-450 nm, and its spectral response can be extended to 500 nm. (2) It exhibits high solubility in common polar and nonpolar solvents, and monomers. (3) It displays one-component nature owing to its hydrogen donating sites on the carbazole group and acts as an efficient photoinitiator.

Recently, Durmaz *et al.* proposed that diethoxy-azobis(pyridinium) could initiate the free radical and cationic photopolymerization without onium salts.[147] diethoxy-azobis(pyridinium) has a photoisomerization characteristic with two spectral absorptions located at 459 and 360 nm. The excited trans form of diethoxy-azobis(pyridinium) splits to produce both the free radical and cationic species capable of initiating respective polymerizations. The polymerization experiments verified that the trans form of diethoxy-azobis(pyridinium) is much more efficient than the cis form. The photoisomerism and initiating mechanism of diethoxy-azobis(pyridinium) are shown in Fig. 19.

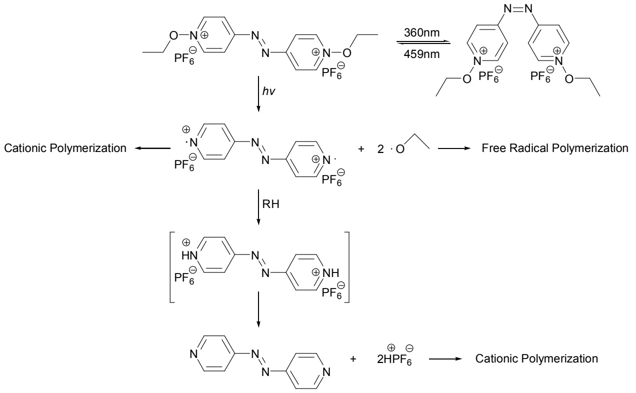


Fig. 19 Absorbance changes with visible light and UV light of DEAP and its radical and cationic polymerization mechanism. Reprinted with permission from Ref. [133]. Copyright 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

5. Conclusions

Compared with the ultraviolet light induced photopolymerization, the visible light induced photopolymerization has noticeable advantages against the UV photopolymerization regarding ozone and radiation hazards. However, visible light induced photopolymerization is still in its infancy. Many visible light initiating systems suffer from the narrow absorption and low molar absorbance coefficient in the visible region. Encouragingly, a lot of beneficial works has been carried out in the areas of the synthesis of visible light photosensitizers for matching various visible light sources, the exploration of one-component initiating systems for simplified systems, the optimization of additives for adaptability and efficiency. There is no doubt that, the development of visible light photopolymerization technologies will bring about a broad range of applications-driven effort for new polymeric materials.

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Notes and references

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