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Photoinitiators for UV and visible curing of coatings: mechanisms and properties

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Abstract

The radiation curing industry is one of the most rapidly developing fields in the entire coatings industry. The low toxicity, cheapness, speed, control and ease of formulation and operation are some of the main advantages of this growing technology. UV and/or visible light radiation is used to induce photochemical polymerization or crosslinking of a monomer, oligomer or prepolymer formulation containing a certain type of unsaturation, such as an acrylic group, and an appropriate initiator. The latter is used to absorb the light energy and transform it into active species, such as radicals or ions, capable of inducing such reactions. Applications extend to general coatings for paper, board, wood, tapes, compact discs and holograms, inks, photoresists for imaging processes and adhesives for welding and sealing in electronic circuit boards. The photoinitiator is the key to the control of these processes and, in recent years, has seen many new developments. These include the need for water-soluble, co-reactive and polymeric structures with low migration rates, as well as cheaper UV/visible sensitizers with enhanced speed. New and effective cationic systems are also on the scene and, although expensive, are attracting significant academic and commercial interest.

Keywords: Coatings; Curing; Photoinitiator; UV/visible light

1. Introduction

Over the last 25 years, radiation curing science and technology has grown from a subject of esoteric research specialities into a major industrial development and is now a field of central importance in polymer science and technology. Applications include resists, barrier coatings, paper, board and metal coatings, dentistry, imaging science and printing. Inherent in these technologies is the use of a photoactivator system which is capable of absorbing the incident UV and/or visible radiation wavelengths employed for converting a monomer or prepolymer system into a crosslinked network [1–5]. In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiator molecules with more desirable properties, such as higher activity coupled with greater speed and a low migration rate to the surface of the cured coating in order to reduce loss of adhesion and to minimize toxicity where food contact is important. Two areas of importance in this regard are the development of monomeric and polymeric photoinitiators with reactive functionalities capable of co-reaction and extension of the absorption spectrum, thus imparting greater spectral sensitivity to the visible region of the spectrum [6]. The latter is now of utmost importance, particularly for laser-induced polymerizations and holography [7].

2. The coating

Over the years, several types of UV/light-curable monomers and prepolymers have been developed [8]. The main objective is to produce a molecule which contains unsaturation that is capable of reacting with other unsaturated molecules when subjected to UV/visible light energy to produce a solid coherent film. In the industry, there are two basic types of system. The first (diluent monomers) is divided into what may be called first and second generation types. First generation types are typical simple monofunctional and difunctional structures, such as 2-ethylhexyl acrylate, methyl methacrylate and styrene. The second generation types are usually difunctional and multifunctional acrylates, such as glycerol propoxylate triacrylate. The former type is now rarely used due to the strong odour, toxicity (often referred to in the industry by a Draize value) and slow speed. These diluent monomers are used, as their name implies, for the control of the viscosity of a liquid prepolymer, which, in turn, controls the film properties for application, adhesion and degree of flexibility as well as speed of cure. The prepolymers are often complex structures based on, for example, epoxy-acrylates, urethane acrylates, polyether urethane acrylates, polyester acrylates, polyether acrylates and acrylated oils. The structures and formulations of diluent monomers and

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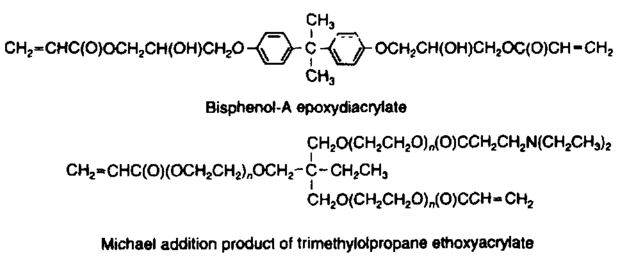

Fig. 1. Examples of acylated resins used in UV curing formulations.

prepolymers may be varied to suit a particular application and property requirement (e.g. hardness, speed of cure and solvent/chemical resistance as well as oil and water miscibility). A typical bisphenol-A epoxydiacrylate prepolymer is shown in Fig. 1, together with a diluent aminated trimethylolpropane ethoxyacrylate. The latter is normally prepared from the triacrylate via a Michael addition reaction with diethylamine and will be discussed later. Generally, acrylated structures are used today since they exhibit the highest reactivity. The following order in reactivity has been established [1,2]: vinyl < allyl < methacrylic < acrylic groups.

3. Photoinitiators and mechanisms

In order to induce the photopolymerization or photocrosslinking of an acrylated system, two types of initiator are available. The first induces a free radical chain process in which low molecular weight monomers and prepolymers are converted by the absorption of UV/visible light into highly crosslinked, solvent and chemically resistant films. The second type of initiator polymerizes via an ionic mechanism (usually cationic) and has the advantage in this respect of being oxygen insensitive; it is widely used for ring opening reactions, i.e. epoxy resins. Developments in both of these areas are highlighted here. Measurements of the rates of curing or crosslinking vary enormously from the simplistic, such as the thumb screw test/pencil and pendulum hardness methods, through to the more scientific methodologies involving real-time Fourier transform IR (FTIR) and photocalorimetry. The use of IR techniques is widespread: the rate of consumption of the vinyl/acrylate band at 812 cm^{-1} is monitored during cure with respect to that of a reference band which does not change, i.e. the ester group at 1730 cm^{-1}. The reference band will also compensate for changes in film properties during cure, such as contraction. The reader is referred elsewhere for further reading [3,8].

3.1. Radical addition

The basic mechanism for any photocurable free radical system involves the formation of free radical species through the absorption of light by the photoinitiator. The active radicals will then add to the monomer, inducing a chain growth polymerization/crosslinking and eventually termination. Through steady state kinetic analysis, it may be shown that the rate of a typical photoinduced free radical polymerization is proportional to the square root of the light intensity, which indicates that the reaction is controlled by bimolecular terminations [5]. The photophysical and photochemical properties of the photoinitiators are therefore extremely important in controlling the reactivity and they should possess the following properties:

1. high absorptivity in the region of activation, which will depend on the application and light source used;
2. high quantum yield for free radical formation;
3. adequate solubility in the resin system used;
4. high storage stability;
5. odourless and non-yellowing;
6. non-toxic, cheap and handled easily.

There are two basic categories of photoinitiator which meet these requirements. The first group involves type I photoinitiators [1–3,6,7]. Examples of such structures are illustrated in Fig. 2, which provides a reasonable coverage of the different structures available. It is interesting to note that, apart from the azo structure [9], all are based on the acetophenone (benzoyl) functionality which is significant in their mechanism. The second group involves type II photoinitiators and examples of these structures are shown in Fig. 3 [1–3,6,7]. The nature of the substituent R group varies enormously in the literature, consisting of alkyl, aryl, alkylaryl, alkoxy, substituted alkyl [1–3,6,10,11], halogen [12], alkyl-

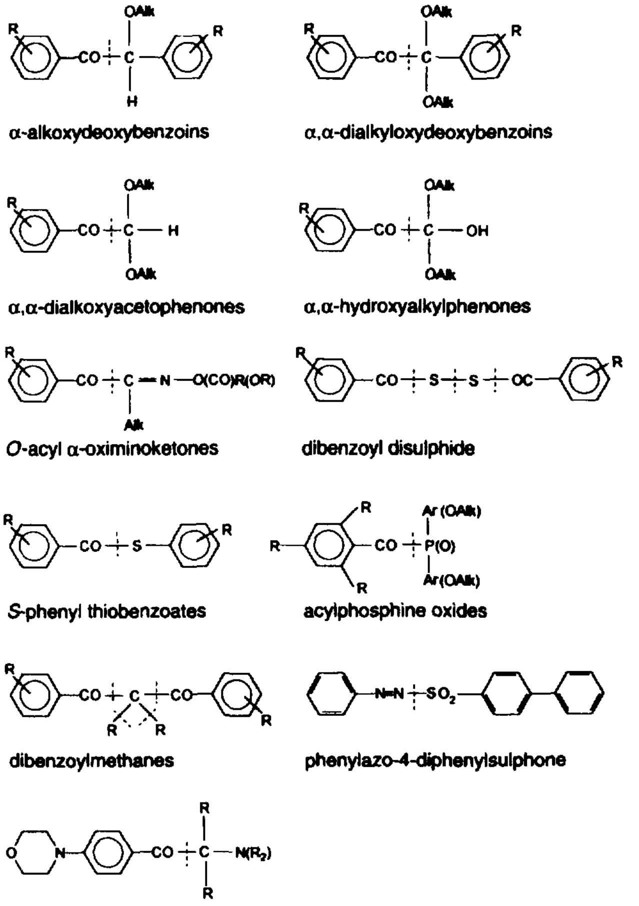

Fig. 2. Some typical photofragmenting type I photoinitiators.

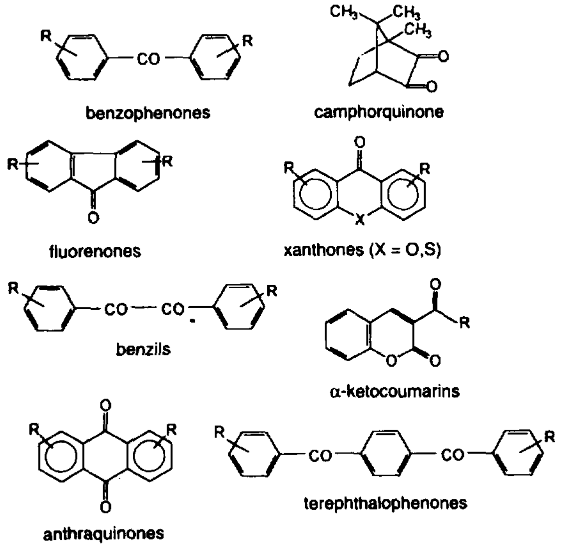

Fig. 3. Some typical type II hydrogen atom abstracting photoinitiators.

sulphonates [13] and alkylammonium sulphonates [14], acrylates [15,16], peresters [17], cinnamates [18] and tertiary amines [19] to name but a few. These usually enhance the chromophore reactivity, provide improved oil or water solubility and co-reactivity with the resin or prevent oxygen inhibition, examples of which will be discussed shortly. The absorption spectrum of the chromophore is obviously one of the most important features of a photoinitiator, which, in turn, will depend on the nature of the light source used for photocuring. Thus, whilst all of the chromophores are effective initiators in the far-UV region, visible sensitization, especially for pigmented systems, is restricted to those molecules with a longer wavelength absorption band above 380 nm, i.e. thioxanthones, fluorenones, camphorquinone and anthraquinones. Camphorquinone is widely used, for example, in dental fillings. This is where the presence of a transmission window in the coating system becomes important for the photoinitiator to be activated.

For many commercial applications, a tertiary amine co-synergist is used in conjunction with the aromatic ketone for enhanced efficiency, and these are available in a variety of structural types. These are shown in Fig. 4. A liquid tertiary amine is still commonly used but, due to migration, loss of gloss, adhesion and toxicity problems, a solid amine in the form of ethyl-4-dimethylaminobenzoate is more acceptable. Other directions involve the use of the amine diacrylate resin (shown in Fig. 1) or amine groups on the initiator chromophore itself. Michler's ketone, shown in Fig. 4, is an example of the latter type of structure, although in this case toxicity problems have eliminated its practical use. Furthermore, this approach, although effective, can be very expensive in terms of its overall cost. One commercial success is the structure shown in Fig. 2 for the 4-morpholino-α-dialkylaminoacetophenones under the Irgacure range, made by Ciba-Geigy Corporation (Switzerland).

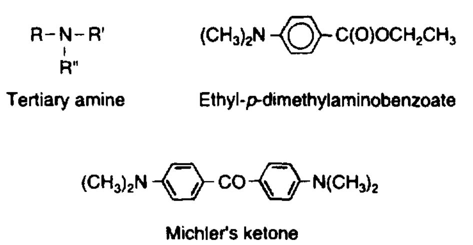

Fig. 4. Examples of amine co-synergists used with photoinitiators for UV curing formulations.

The photoinitiators in the second class (type II) (Fig. 3) undergo a primary process of hydrogen atom abstraction from the environment (R–H), which may be the resin itself or a solvent, to produce a ketyl radical [1–3], as shown in Fig. 5 for benzophenone. The reaction usually occurs from the lowest excited triplet state of the ketone or the quinone and depends on the intersystem crossing (ISC) rate, the configuration of the triplet state ($n\pi^*$ or $\pi\pi^*$) and its corresponding energy. The photoreductive ability of the environment is also an important factor and is related to the carbon–hydrogen bond strength of the species donating the hydrogen atom. However, more recent theories in this area point to the formation of a complex between the ketone (acceptor) and solvent (H donor) [2]. The ketyl radicals couple to produce pinacol as a product, while the alkyl radical or some other radical $R^\bullet$ is believed to act as the initiator of polymerization or crosslinking. In the case of quinones, a semiquinone radical is produced, which undergoes disproportionation with itself to regenerate the original quinone and a quinol [14].

The photoinitiators in the first class (type I) (Fig. 2) undergo a direct photofragmentation process in the excited state into free radicals, as shown in Fig. 6 for a benzoin aryl ether [1–3]. It is believed from experimental evidence that there is no triplet state precursor to this reaction, since the presence of oxygen or other triplet quenchers does not influence the reaction [1–5]. Depending on the structure of the molecule, scission may occur in the α or β position. The former is more important and produces benzoyl and benzyl

$$Ar_2C{=}O \xrightarrow{h\nu} Ar_2C{=}O^1 \xrightarrow{ISC} Ar_2C{=}O^3$$

$$Ar_2C{=}O^3 + R{-}H \longrightarrow Ar_2\dot{C}OH\ (\text{ketyl}) + R^\bullet$$

$$2Ar_2\dot{C}OH \longrightarrow Ar_2C(OH)C(OH)Ar_2\ (\text{Pinacol})$$

$$R^\bullet + CH_2{=}CHX \longrightarrow RCH_2CHX^\bullet \longrightarrow \text{Polymer}$$

Fig. 5. Hydrogen atom abstraction reaction and photoinduced polymerization of a monomer by benzophenone.

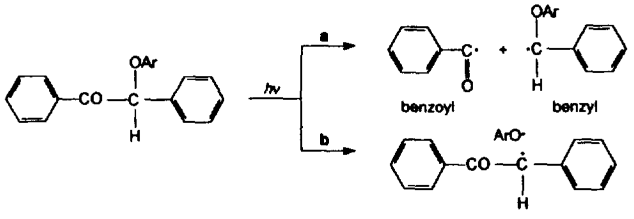

Fig. 6. A typical photofragmentation process for a type I benzoin ether photoinitiator.

radicals, both of which are considered to be important in initiating polymerization.

As mentioned previously, the efficiency of carbonyl photoinitiators may be enhanced through the use of a tertiary amine co-synergist. Here, the excited triplet state of the ketone forms an intermediate excited electron transfer complex (exciplex) with the tertiary amine as shown in Fig. 7. The exciplex is stabilized by charge transfer because of the low ionization potential of the amine donor. The efficiency of complex formation will also depend on the ionization potential of the amine and the corresponding electron affinity of the ketone [10]. Such complexes are particularly effective with thioxanthone and fluorenone where the lowest excited triplet state has low reactivity due to its $\pi\pi^*$ character. Triplet states which are $n\pi^*$ in character have a high affinity for intermolecular hydrogen atom abstraction [1–3]. The reaction scheme in Fig. 7 is applicable to thioxanthone (T), where the semiquinone radical formed is $TH^\bullet$, the radical cation is $T^{\bullet+}$ and the corresponding radical anion of the amine is $A^{\bullet-}$. The alkylamino radical is then believed to be the photoinitiator. However, in the case of the type I initiators, the alkylamino radical is not important [10] probably due to competition from the two active benzoyl/benzyl radicals.

Generally, the type II photoinitiators based on thioxanthone require a tertiary amine co-synergist for effective photocuring. Recently, however, 1-substituted chloro- and bromo-4-*n*-propoxythioxanthones have been synthesized and found to exhibit initiation activity in the absence of an amine co-synergist [20]. These photoinitiators have also been found to be synergistic with benzophenone and exhibit a high ISC quantum yield. On irradiation, they undergo a dehalogenation reaction which is enhanced in the presence of an amine as shown in Fig. 8. The reaction involves an initial step of electron transfer via a triplet exciplex. The radical anion formed can then delocalize the electronic charge with the formation of a chloride ion and a thioxanthyl radical, which may either initiate polymerization or abstract a hydrogen atom from the tertiary amine to give an alkylamino radical. The latter will then initiate polymerization. The chloride ion may then abstract a proton from the environment (i.e. the alkylamino radical cation) to give hydrogen chloride, which is trapped by the amine to give a hydrochloride salt. Decreased amounts of dehalogenated products on irradiation in the absence of an amine appear to confirm this mechanism.

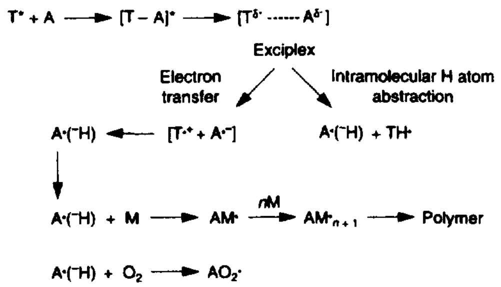

Fig. 7. Synergism between a tertiary amine (A) and an aromatic carbonyl initiator such as thioxanthone (T).

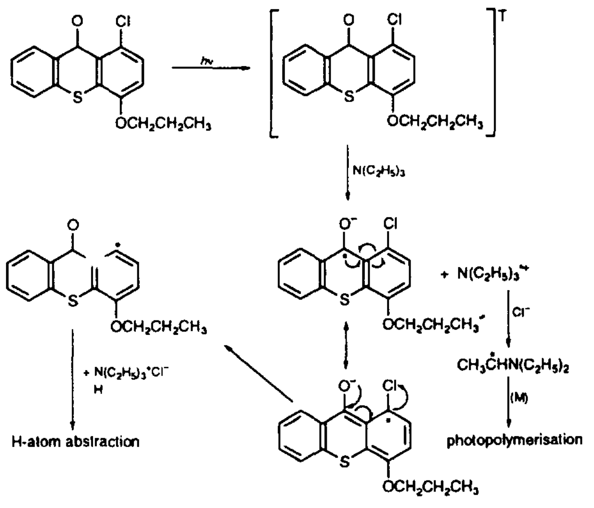

Fig. 8. Dehalogenation mechanism for 1-chloro-4-*n*-propoxythioxanthone in the presence of a tertiary amine co-synergist.

However, direct dehalogenation cannot be ruled out in the absence of an amine. In fact, recent work in the Chemistry Department, Manchester Metropolitan University has shown that direct photolysis of the aromatic halogen bond does indeed take place very efficiently. Furthermore, cationic photopolymerization can be induced very efficiently with cycloaliphatic epoxides.

Oxygen inhibition in free radical radiation curing is a particular problem which has been the subject of much activity in recent years. The main problem is twofold. Firstly, the lowest excited triplet state of many aromatic ketones is quenched by oxygen. Secondly, the free radicals arising from the initiation process may also be quenched. The exclusion of oxygen has been undertaken through nitrogen blanketing (an expensive operation) and through the use of transparent foils [19] and paraffin waxes [21]. In the latter case, the wax forms a thin oxygen barrier on the surface of the coating. The use of tertiary amine co-synergists also impairs the quenching effect of oxygen and this is believed to be due to the ability of the alkylamino radicals in Fig. 7 to react with and hence scavenge the oxygen-forming peroxy radicals [1–3]. Thiol and phosphite compounds are also effective in scavenging oxygen and are often added to commercial monomers and prepolymers to prevent oxidation. The use of oxygen-insensitive photoinitiators is another more recent method [10].

Alkanesulphonic acid esters of, for example, methylbenzoin and its ethers are claimed to be oxygen insensitive, as well as the use of type I with type II photoinitiators [22]. The former derivatives produce sulphonic acid on photolysis, which is claimed to migrate to the surface of the resin where it reacts with oxygen (Fig. 9) [23]. The latter, on the other hand, provides sacrificial free radicals for reaction with oxygen, while allowing the hydrogen atom abstraction reaction to proceed uninhibited. Surface-active photoinitiators based on a surfactant-type structure are also claimed to be particularly effective [24].

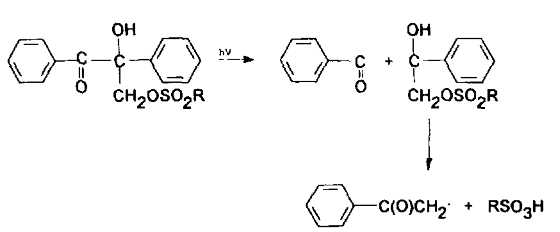

Fig. 9. Water-soluble sulphonic acid initiators undergoing type I photolysis.

3.2. Cationic initiation

In contrast with the free radical-type photoinitiators, cationic photoinitiators have been developed more recently for the polymerization of epoxy- and vinyl ether-based monomers and prepolymers [1–3]. Depending on the structure, these initiators are capable of producing either Lewis acids, such as BF_3 and PF_5, or Brönsted acids, such as $H^+BF_4^-$ or $H^+AsF_6^-$ [25]. In the early stages of development, aryldiazonium compounds were used to generate the Lewis acids. However, these were found to be unstable and produced nitrogen gas on curing which released bubbles into the resin films. To overcome these problems, more stable diaryliodonium, triarylsulphonium and selenonium salts have been developed. On photolysis, these compounds produce strong Brönsted acids (H^+X^-), where X^- is usually a tetra- or hexafluoro-substituted salt, such as PF_6^-, SbF_6^-, BF_4^- or AsF_6^-. These are shown in Fig. 10 for the sulphonium salt, where the acid readily reacts with the monomer M in order to induce polymerization. Termination usually occurs through impurities or the anion X^-. However, in their absence, living polymers may be produced for further reaction. Many other types of cationic initiator are available, e.g. mixed-ligand arene-cyclopentadienyl metal salts or complex metal halides, e.g. iron or titanium [26,27]. Some typical cationic photoinitiators are shown in Fig. 11. The mode of initiation of the iron–arene complex is shown in Fig. 12. The spectral sensitivity of the complex can be varied by changing the conjugation of the arene groups, e.g. from cumene to polynuclear aromatics, such as naphthalene, for red sensitivity. In the reaction scheme, the cumene is replaced by three epoxide groups, one of which then ring opens. The counterion is also considered to be important and, in the absence of the epoxide, hydrogen fluoride has been identified [5]. Many workers consider the cationic-type initiators to be superior to those of free radical type. In particular, they are insensitive to oxygen quenching, are readily sensitized by dyes in the visible region of the spectrum and may be post-thermally cured. It should be noted from Fig. 10 that free radicals are also produced and these have been found to induce the curing of acrylated monomers and prepolymers. Indeed, mixed acrylate–epoxy systems may be polymerized with such initiators, either alone or more preferably in conjunction with type I and II free radicals. Such mixed systems have acquired a new terminology called "hybrid initiators" [1–3]. However, many cationic initiators are expensive and toxic and, for certain monomers, such as epoxidized rubbers, curing activity is poor. In this regard, the newer halogenated aromatic ketones pose a potential threat to the cationics and in the author's view could attract interest in the future.

$$Ar_3S^+X^- + R{-}H \xrightarrow{h\nu} Ar_2S + Ar + R^{\cdot} + H^+X^-$$

$$H^+X^- + M \longrightarrow HM^+X^-$$

$$HM_n^+X^- + M \longrightarrow HM_{n+1}^+X^-$$

$$HM_n^+X^- + \text{Impurity} \longrightarrow \text{Polymer}$$

Fig. 10. Example of a triarylsulphonium salt photolysis reaction to form an acid and its involvement in the polymerization of a monomer (M).

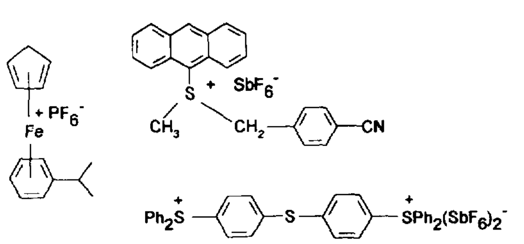

Fig. 11. Some typical cationic photoinitiators.

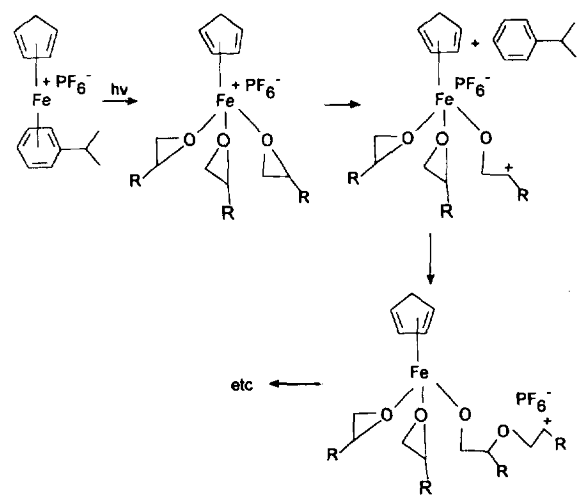

Fig. 12. Typical ring opening reaction of an epoxide by an iron–arene complex.

3.3. Visible sensitizers

One of the major limitations of conventional aromatic ketone photoinitiators is their inability to induce curing with visible light energies. Some of the structures shown in Fig. 2 and Fig. 3 have limited sensitivity up to about 450 nm, e.g. camphorquinone, ketocoumarins, thioxanthones and anthraquinones. The introduction of substituents to extend their conjugation and hence absorption range can reduce their photochemical activity due to the introduction of less active low-lying charge transfer states. This has resulted in an active search for dye sensitizers with enhanced visible sensitivity. Selective examples in this regard include the use of rose bengal derivatives [28] and cyanine [29,30] cationic dyes in conjunction with alkyltriphenylborate anions. These latter systems have excellent sensitivity for laser-induced curing (e.g. argon ion laser at 514 nm), especially for producing three-dimensional objects via stereolithography. The cyanine borates are particularly interesting for applications in cylithography where the polymerizable acrylate is encapsulated in a microcapsule. Variations in the degree of cure, depending on the image, produce capsules with varying degrees of conversion. The application of pressure on rollers will then fracture the capsules and release colour formers depending on the extent of cure. The cyanine dyes are powerful electron acceptors which are capable of oxidizing the borate anion to give a cyanine radical and fragmentation of the borate anion. The reaction shown in Fig. 13 gives an alkyl radical and triphenylboron with the former acting as the radical initiator. These systems appear to have tremendous potential for visible light sensitization and many "cocktails" have been developed [5]. More recently, the use of aromatic ketones with amines and dyes such as methylene blue and phenosafranine has been claimed to give effective through cure of thick coatings coupled with dye bleaching [31]. Here, the dye quenches the triplet excited state of the ketone generating the dye triplet, which itself reacts with the amine to produce an alkylamino radical that initiates polymerization. A number of iron–arene and titanocene complexes have also been claimed to be highly effective visible sensitizers for free radical initiation [5].

3.4. Co-reactive/polymeric initiators

One of the major directions in this field is the development of co-reactive and non-migratory initiators, especially where food contact is required. Currently, there is a dilemma with users of initiators regarding the importance and need for such molecules. Many are complex and expensive and this outweighs their additional performance. Furthermore, evidence to date indicates that even some of the more conventional types of initiator react-in with the cured resin. However, there is no doubt that, at the high levels often used in radiation curing, a substantial percentage of unreacted molecules remains. In this regard, co-reactive type I photoinitiators have been developed with functionalities based on trimethylsilyl, epoxy and azo groups [27]. The most typical direction, however, is in the development of acrylated chromophores of type I and type II initiators [4]. Such acrylated chromophores will themselves either co-react with the cured resin or are capable of homo- or co-polymerization to produce homopolymers or copolymers which are less extractable. Functionalized polystyrenes or polymethacrylates have also been prepared. Acrylated derivatives of thioxanthone [14], anthraquinone [15], benzoin ethers [32] and peresters [33] are examples of solid monomers capable of polymerization as shown in Fig. 14. Claims as to their reactivity compared with other initiators are variable. For example, the 2-acrylamido derivative of anthraquinone has been found to photocrosslink thermoplastics very efficiently to a high degree of conversion [15], while in terms of spectral sensitivity it is five or more orders of magnitude more effective than camphorquinone in terms of recent evaluations [34]. Polymers with pendant benzophenone perester groups have been made and are claimed to be more effective than their monomeric counterparts [35]. Here, the perester group undergoes photolysis via a type I mechanism to give arylcarboxy and tertbutoxy radicals (Fig. 15). The carboxy radical will then fragment to release carbon dioxide and produce a phenyl radical. In the presence of oxygen, peroxy radicals develop [2,8]. Whilst polymeric photoinitiators appear to be attractive, their activity is open to question. The structures of the polymer and the chromophore determine very much the overall activity and, to date, no predictability can be made in this regard. Energy transfer processes and intermolecular and intramolecular interactions play an important role in controlling the polymer photoactivity. In some cases, they can be made cheaply, but obviously

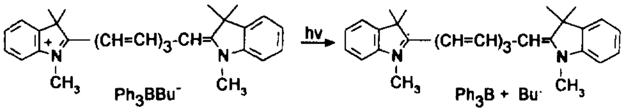

Fig. 13. Photolysis of a cyanine borate complex.

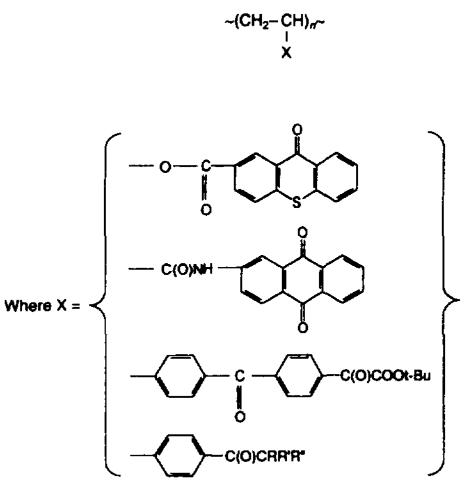

Fig. 14. Examples of some polymeric initiators, where X can be any of the illustrated chromophores.

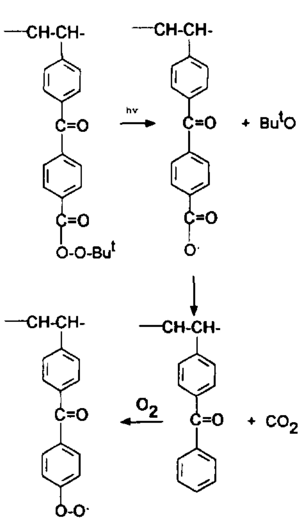

Fig. 15. Photolysis of a polymeric benzophenone perester initiator.

further studies are needed on structure–activity relationships before any empirical deductions can be made.

3.5. Future developments

Photoinitiator chemistry is an exciting and rapidly expanding field with many new developments being undertaken. Future directives include the following:

1. the development of cheap co-reactive initiators with no toxicity, low migration and good solubility;
2. improved water-soluble photoinitiators;
3. improved cost-effective visible sensitizers which bleach;
4. less toxic and cheap cationic initiators;
5. more durable UV-curable packages;
6. more effective initiators for epoxidized rubbers;
7. more effective initiators for crosslinking thermoplastics for improved property requirements such as flammability and physical properties.

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