Photoinitiators for Free-Radical-Initiated Photoimaging Systems

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I. Introduction and Summary

A. Definition of Terms and Scope of the Review

Polymer photoimaging systems are an important application of photochemical technology.[1] Imagewise exposure of these systems either forms a polymer or modifies the properties of a preformed polymer to form a latent image in the exposed region. These latent images can be converted into useful images by appropriate techniques. Polymer photoimaging systems have numerous important applications, primarily in the printing and electronics industries. Several excellent reviews of these topics are available.[1-11]

The terms photopolymer and polymer imaging system are often used to describe any of a number of systems in which a light-initiated change in a monomer or polymer is produced. Several types of imaging systems, each of which employs a distinctly different type of imaging reaction, are grouped together under these headings.[1-3]

An important class of polymer imaging systems employs photoinitiated polymerization. In these systems relatively low molecular weight monomers undergo light-initiated free-radical or cationic polymerization to form higher molecular weight materials. Polymerization is initiated by photoactivation of an added low molecular weight component, known as the photoinitiator. In cationic-initiated systems, irradiation of the photoinitiator produces a Lewis acid or a protonic acid that initiates polymerization. In free-radical-initiated systems, irradiation of the photoinitiator produces free radicals that initiate polymerization. Initiation of polymerization of a number of monomer molecules by the absorption of one photon is a form of chemical amplification. Imaging systems of high sensitivity can be developed.

This review emphasizes photoinitiators used in photoimaging systems. In order to present a comprehensive review of free-radical-initiated photoimaging systems, cationic-initiated photoimaging systems will not be discussed. This rapidly developing area has been reviewed.[12-14] A brief introduction to free-radical-initiated photoimaging systems has been included.

A comprehensive review of both cationic and free-radical photoinitiators, especially those used in radiation curable coatings, appeared after completion of this manuscript.[15] This review is an excellent source for those seeking more detailed information, especially about coating applications, than is presented here. Initiators for radiation-curable coating have also been discussed elsewhere.[16-25] Since many of the systems used in free-radical-initiated photoimaging systems, especially the earlier systems, were originally developed for radiation curable coatings, there is some overlap between these reviews and the material presented here.

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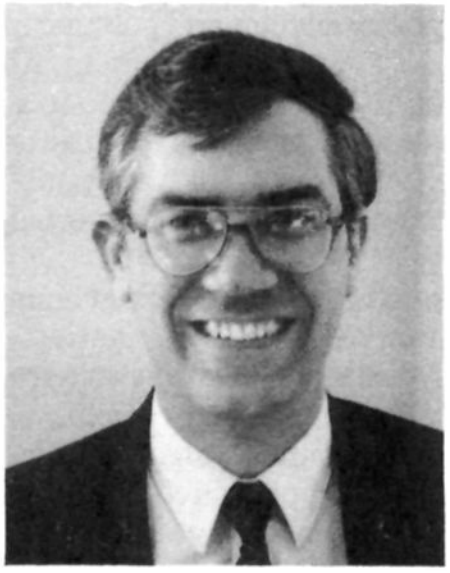


Gregory C. Weed was born in Baton Rouge, LA, in 1952. He received his B.S. degree in chemistry at Brigham Young University in 1976. At BYU he participated in undergraduate research on metal–ligand calorimetry and macrocycle-mediated cation transport across liquid membranes under the guidance of Prof. Reed M. Izatt. He received his M.A. degree in chemistry in 1979 and his Ph.D. in chemistry in 1981 with Professor Nicholas J. Turro at Columbia University. At Columbia his research was directed at magnetic field effects of photochemical reactions in organized media. He joined E. I. DuPont's Photo Products Department in 1981 and is currently a Senior Research Chemist with DuPont Electronics and a member of DuPont's Center for Imaging Applications. Over the past several years he has patented and researched in the areas of photochemistry and photoimaging. His research interests include photoinduced energy and electron-transfer mechanisms in photoinitiated systems and also radical mechanisms in photopolymers. He is a member of the American Chemical Society and Sigma Xi.

The compositions of most of the commercial photoimaging systems have not been disclosed. Thus, it can often not be stated with certainty whether a particular photoinitiator system is, or has been, used in a commercial product. We will indicate those systems whose properties make them generally suited for use in commercial products. However, systems that have not been discussed, or that we have indicated are generally unsuitable for use in photoimaging systems, may still have limited applications in commercial products.

Mechanisms will not be discussed in detail. This aspect of photoinitiator chemistry has been reviewed.[20-27] In addition, many of the commercially important photoinitiator systems have been described primarily in the patent literature. Little or no mechanistic work has been published on these systems.

We have organized this article by the type of reaction that takes place: fragmentation, electron transfer, or hydrogen abstraction. This division, however, is far from clear-cut. In some systems the mechanistic details are unknown. In others, more than one type of reaction may occur (electron transfer followed by hydrogen abstraction, electron transfer followed by fragmentation, fragmentation followed by hydrogen abstraction, etc.). The type of reaction may also vary with the conditions. For convenience, organometallic systems have been treated as a separate class.

B. Free-Radical-Initiated Photoimaging Systems

Free-radical-initiated photoimaging systems typically contain three principal components: polymerizable monomer(s), binder(s), and a photoinitiator system. Other components may be present to modify the physical properties of the composition. Such components include stabilizers, plasticizers, dyes, pigments, fillers, and other miscellaneous ingredients.[1,5]

The composition of various commercial systems varies with the application. However, to obtain a dry, dimensionally stable film, the binder normally must be greater than 25% by weight and the monomer less than 60% of the composition. If there is less than 25% binder or more than 60% monomer, the composition generally has insufficient viscosity to form a film. As discussed below, the amount of initiator system is determined by its absorption, the thickness of the film, and the desired optical density.

Free-radical-initiated photoimaging systems are versatile materials. They have been adapted for numerous applications that take advantage of their ability to produce high-quality images with short access times, convenient processing, and relatively high speed and at moderate cost. Their relative advantage over other non-silver systems appears to be due to the fact that the imaging reaction is a chain process. In addition, in systems that are developed by washout, crosslinking of the monomer entraps and insolubilizes large binder molecules so that a small amount of polymerization can cause a large change in solubility. In most other non-silver imaging systems, the imaging reaction has a maximum quantum yield of one.

Imagewise irradiation creates a latent image of polymerized material in the exposed regions. Useful applications depend on the methods used for detecting, reading out, playing back, or developing this image. Conventionally, changes in solubility, tackiness, and adhesion and cohesion have been employed. Development techniques have included washout, delamination, and toning. Recent applications have utilized changes in electrical conductivity and refractive index.

Free-radical-initiated photoimaging systems have been most extensively used in the printing and electronics industries. Photoresists are a major application for these systems.[2] Other applications include proofing and printing plates.[1,5] Holographic displays and integrated optics are under development.[11]

C. Photoinitiator Systems

The photoinitiator system generates the free-radicals that initiate radical chain polymerization of the unsaturated monomer or monomers. It may be a single compound, typically called a photoinitiator rather than a photoinitiator system, that absorbs light and undergoes unimolecular reaction to form radicals. Or it may consist of several different compounds that undergo a complex series of reactions to produce the initiating radicals. In addition to the compound that forms the free radicals, photosensitizers, activators, and coinitiators may be present.

Activators, or coinitiators, interact with photoexcited molecules to produce radicals. Chain transfer agents, or hydrogen donors, may be included as coinitiators to form secondary radicals that are better initiators of free-radical polymerization than the initially formed radicals.

A photosensitizer is strictly defined as a molecule that absorbs light energy to form an excited state that transfers the energy to a second molecule to form the excited state of the second molecule and the ground state of the sensitizer. Although irradiation of a system containing an absorbing molecule can produce changes that arise from processes other than energy transfer,[28] in these systems it is conventional to refer to any added absorber as a photosensitizer, even though it may not satisfy the strict photochemical definition.

Any compound or group of compounds that produces free radicals when struck by light and is compatible with the other components of the photoimaging system is a potential photoinitiator system. A practical photoinitiator system, however, should have a high molar absorption coefficient in the desired absorption range as well as a high quantum yield for radical production.

The photoinitiator system should have other desirable properties, such as low toxicity. Free-radical photoimaging systems generally have stringent requirements for speed, image resolution, and spectral sensitivity. Since they are often supplied as precoated dry films, shelf life, dark stability, and stability to manufacturing conditions are important. Although still a factor, cost is generally of lesser importance because these systems have a high value in use.

Certain properties that are important for radiation-curable coatings are not important in photoimaging. In applications in which the photoimaging system is a temporary coating, it is unnecessary that a clear or colorless coating remain after exposure. Photoresists, for example, are stripped from the printed circuit boards after the boards have been etched.

According to the First Law of Photochemistry: "Only the light which is absorbed by a molecule can be effective in producing photochemical change in the molecule".[29] Therefore, the photoinitiator system must have high molar absorptions for the wavelengths emitted by the radiation source.

The concentration of photoinitiator must be high enough that enough energy is absorbed to produce photopolymerization, yet not so high that all the light is absorbed near the surface. If the concentration is too low, photopolymerization will be inefficient. If the concentration is too high, the photoinitiator near the surface will act as a filter for the photoinitiator beneath it. Thus, unless the initiator fades to a nonabsorbing material during irradiation, only the monomer near the surface will be polymerized. As a result, in systems developed by washout, undercutting of the image will occur.

Using different approaches, two groups have calculated that a nonfading initiator system will produce efficient photopolymerization when the optical density is 0.43.[30,31] At this optical density, about 63% of the light is absorbed. The intensity at the bottom of the system is 37% of that at the surface. If the initiator system fades to nonabsorbing species, films with higher optical densities can be used. Experimental investigation of this relationship has shown that it does not strictly apply if multiple wavelengths are present in the exciting radiation.[32-34]

D. Summary of Recent Trends

Historically free-radical-initiated photoimaging systems have been exposed with ultraviolet light, using light sources similar to those used in the ultraviolet curing industry. Recently, however, reliable, relatively inexpensive, computer-driven visible and infrared lasers that can be used as output devices for electronic imaging systems have been introduced. Much current research is directed to the development of visible- and infrared-sensitive photoinitiator systems to match these new light sources.

Several systems with visible sensitivity have recently appeared. The dye/borate systems, for example, are potentially sensitive to any desired region of the visible spectrum. Visible sensitization of the well-known triazine and hexaarylbisimidazole initiator systems has been achieved. As these and other yet to be developed photoinitiator systems are introduced, there will be even less overlap between the initiator systems for radiation-curable coatings and for photoimaging systems since the latter are primarily clear coatings, requiring photoinitiators that are color free.

II. Fragmentation

Photofragmentation occurs when a photoexcited molecule undergoes homolytic bond cleavage to form a pair of free radicals (eq 1).[35]

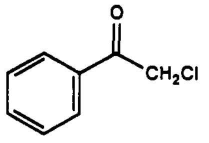
$$\text{A–B} \xrightarrow{h\nu} \text{A}^{\bullet} + \text{B}^{\bullet} \qquad (1)$$

Either one or both of the resulting radicals can initiate free-radical polymerization. Fragmentation reactions will be discussed by the type of bond broken on irradiation.

A. Halogen Compounds

1. α-Haloacetophenones

Halogen-substituted acetophenones, such as 1-chloroacetophenone (**1**), *p*-phenoxy-1,1-dichloroacetophenone (**2**), and desyl chloride (**3**), were among the earliest photoinitiators investigated.[36] Other substituted haloacetophenone photoinitiators have been subsequently described.[37-39]



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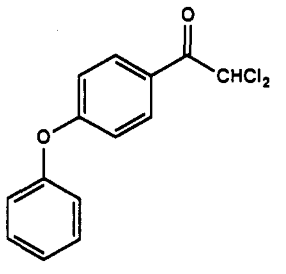

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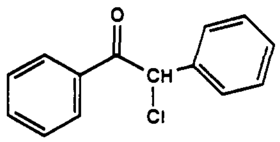

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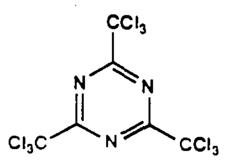
The haloacetophenones are not extensively used in photoimaging systems. They absorb at relatively short wavelengths and so can be irradiated with commonly available light sources. The carbon–halogen bond is frequently of low enough energy that the compounds are not stable to manufacturing conditions. Some of these compounds are also lacrimators which makes them inconvenient to use.

2. (Trichloromethyl)-1,3,5-triazines

(Trichloromethyl)-1,3,5-triazines are an important class of photoinitiators for free-radical initiated photoimaging systems. Although, by itself, tris(trichloromethyl)triazine (**4**) is not a practical photoinitiator, chromophore substitution and photosensitization have been used to extend its spectral response to longer wavelengths.



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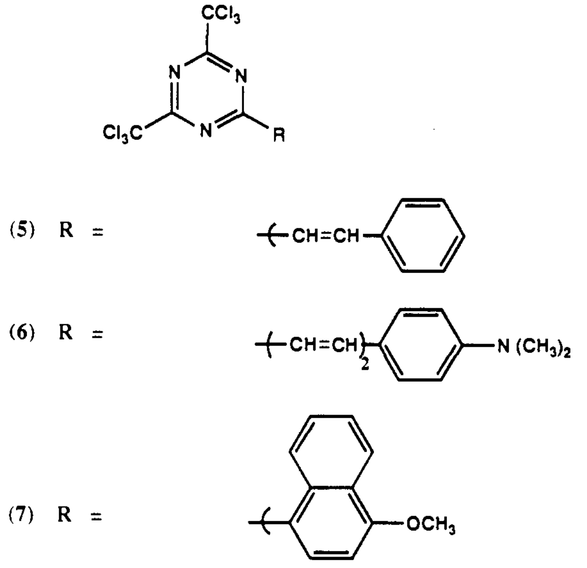
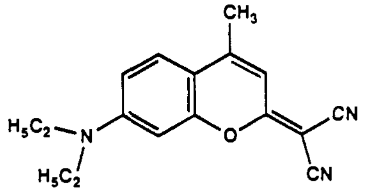
Many chromophore-substituted triazines have been reported in the patent literature, but it has not been disclosed which of these compounds have important commercial applications.[40-50] Chromophore-substituted triazines are typically bis(trichloromethyl)triazines substituted in the 2-position with a group that absorbs ultraviolet or visible radiation. Variation of the chromophore is used to vary the wavelength of response of the imaging system. Representative chromophore substituted triazines are illustrated below.



No detailed studies of triazine photochemistry have appeared, but it has been proposed that the primary process in the direct irradiation of triazine **7** is homolytic cleavage of the carbon–chlorine bond.[51]

Sensitization by a number of different photosensitizers has also been reported.[52-56] Typical sensitizers are shown below (**8–10**). Again it has not been reported which, if any, of these systems is important commercially.



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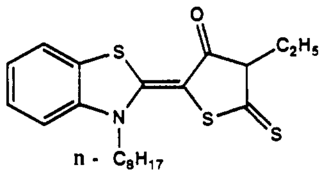

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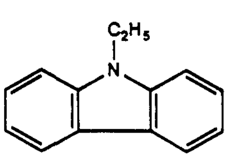

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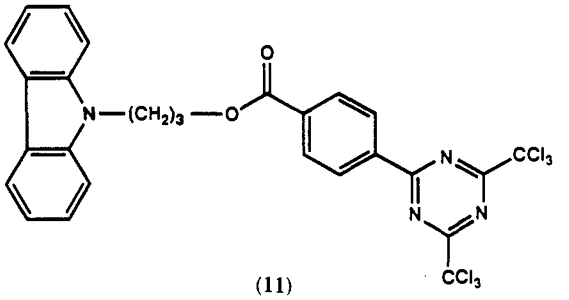
Triazines in which the sensitizer is chemically bound to the triazine moiety, such as **11** and **12**, have also been described. Electron transfer between the excited dye and the triazine has been proposed for the dye/triazine systems.[57]

A variety of polymer-bound triazines has also been prepared.[58,59] Two methods of preparation have been used. A bis(trichloromethyl)triazine intermediate with a functional group attached at the 2-position, such as **13**, was prepared. The functional group was used to attach the triazine to a preformed polymer. Alternatively, bis(trichloromethyl)triazine monomers with an



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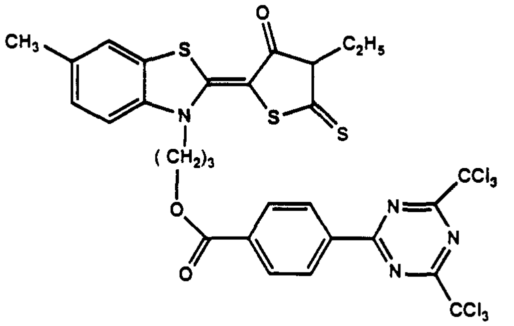

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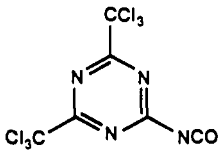
acrylate, methacrylate, or acrylamide moiety in the 2-position, such as 14, were prepared and copolymerized.



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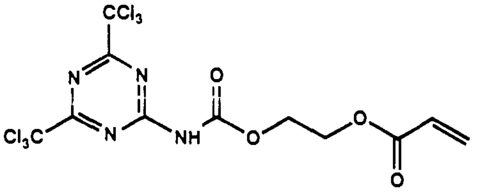

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B. Azo Compounds

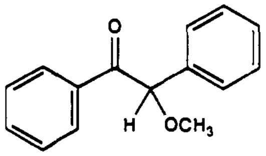
Azo compounds are widely used as initiators for thermally initiated free-radical polymerizations,[60] but are rarely, if ever, used in imaging systems. Although azo compounds can be activated photochemically,[35] they have only weak absorption at wavelengths greater than 300 nm and, thus, cannot be readily excited by commonly available light sources. They have poor thermal stability. In addition, decomposition produces nitrogen that can form bubbles and adversely affect the image.

C. Aromatic Carbonyl Compounds

1. Benzoin Ethers

Benzoin ethers, such as benzoin methyl ether (15), were one of the first classes of photoinitiators developed for the ultraviolet-curable coating industry.[13,15] Irradiation produces a benzoyl radical and an α-alkoxybenzyl radical. These radicals can either initiate polymerization or abstract a hydrogen atom from an appropriate substrate to produce a secondary radical that initiates polymerization.[13,61]

Benzoin ethers are not widely used in imaging systems since they do not have the shelf life typically required.



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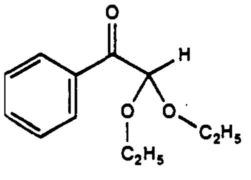
2. Ketals

Ketals are another important class of photoinitiators developed for ultraviolet-curable coatings.[62,63] Important members of this class include diethoxyacetophenone (16) and benzil dimethyl ketal (α,α-dimethoxydeoxybenzoin) (17). Ketals are also not widely used in imaging systems.



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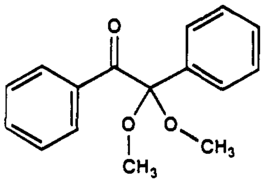

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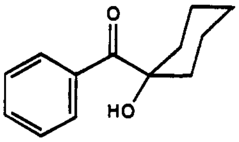
3. Acetophenones

α-Substituted acetophenones are a third important class of photoinitiators used in ultraviolet-curable coatings. 1-Benzoylcyclohexanol (18) and 2-hydroxy-2-methyl-1-phenylpropanone (19) are examples of this class.[64-67]



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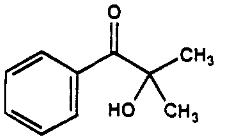

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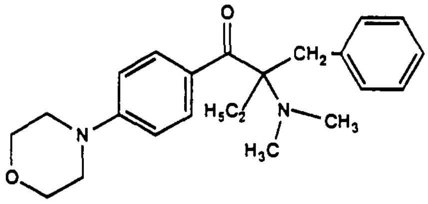

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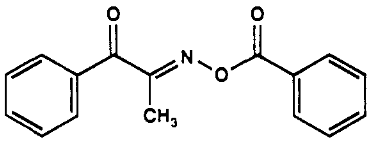
A new group of acetophenones, α-aminoacetophenones, has been developed for use in pigmented systems.[68] Aminoketone 20 is the most extensively investigated member of this group.[69-71] These compounds absorb much more strongly in the ultraviolet than the other aromatic ketone photoinitiators and appear to be quite amenable to photoimaging applications.

4. O-Acylated Oximino Ketones

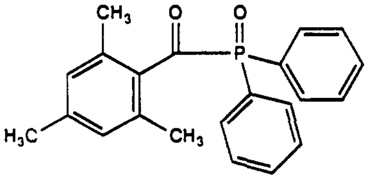
O-Acylated oximino ketones, such as 21, are reported to form radicals with high quantum efficiency[72] and have been used as photoinitiators.[73] Because of the presence of the oximino ketone chromophore, these compounds absorb more strongly in the near ultraviolet than most of the other aromatic ketone photoinitiators. However, since they have poor thermal stability,[20] they are generally unsuited for photoimaging applications.



(21)

5. Acyl Phosphine Oxides

Acyl phosphine oxides, such as **22**, have been used as photoinitiators for free-radical-initiated photopolymerization,[74,75] especially pigmented systems.[76] An application for printing plates has also been disclosed.[77] Extensive investigations on the mechanism and quantum yield of radical formation have concluded that acyl phosphine oxides undergo efficient α-scission on irradiation.[78-84]



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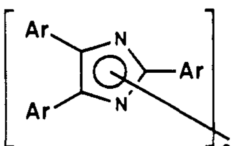
D. Hexaarylbisimidazoles

2,2′,4,4′,5,5′-Hexaarylbisimidazoles, or HABI's, have been used as photoinitiators in a number of free-radical-initiated photoimaging systems.[85-94] They have excellent shelf life and reasonably strong absorption in the ultraviolet. Sensitizers have been developed that extend the sensitivity of these systems into the visible.

These imidazole dimers, which can be prepared by oxidation of the corresponding triarylimidazoles, are conveniently represented by structure **23**, in which the Ar's are aryl groups.[95-99] Since 2,4,5-triphenylimidazole has the common name lophine, hexaarylbisimidazoles are sometimes called lophine dimers. The triarylimidazolyl radicals, derived from HABI fragmentation, are sometimes called lophyl radicals. For most dimers the location of the bond between the rings has not been determined. Mixtures of dimers, that may vary with both the dimer and the method of preparation and purification, are probably formed.



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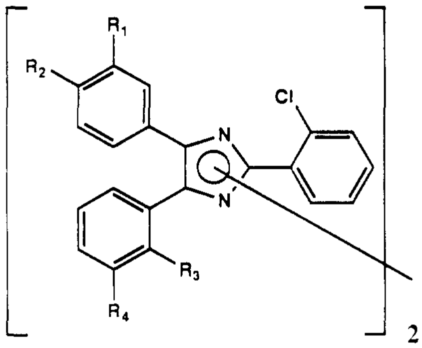
HABI's are both thermochromic and photochromic. They are readily thermally or photochemically cleaved into a pair of triarylimidazolyl radicals that recombine to reform the dimer.[100-102] However, thermal dissociation occurs at a high enough temperature that shelf life is not adversely affected.

The triarylimidazolyl radical (L$^\bullet$) is a poor initiator of free-radical polymerization, possibly because of its size. However, the radical is an excellent hydrogen abstractor.[103,104] Classical hydrogen donors and efficient chain-transfer agents serve as coinitiators (RH) to form secondary radicals (R$^\bullet$) that initiate polymerization (eq 2).[105-107]

$$L_2 \overset{h\nu}{\rightleftarrows} 2L^\bullet + RH \rightarrow LH + R^\bullet \qquad (2)$$

Radicals derived from sterically hindered dimers have the longest lifetimes.[95] Since recombination reduces initiation efficiency, dimers in which one or more of the aryl groups is ortho-substituted are the most efficient photoinitiators.[86]

The preferred dimers are 2-*o*-chlorophenyl-substituted derivatives in which the other positions on the aromatic rings are either unsubstituted or substituted with chloro, methyl, or methoxy groups.[88-90] Hexaarylbisimidazoles commonly mentioned in the literature include: *o*-Cl-HABI (**24**), CDM-HABI (**25**), and TCTM-HABI (**26**).



(24) o-Cl-HABI : $R_1 = R_2 = R_3 = R_4 = H$

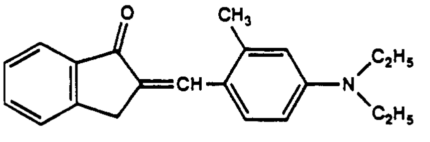
(25) CDM-HABI $R_1 = R_4 = OCH_3 : R_2 = R_3 = H$

(26) TCTM-HABI $R_1 = R_2 = OCH_3$; $R_3 = Cl$; $R_4 = H$

Hexaarylbisimidazoles absorb strongly in the 255–275-nm region of the spectrum and have lesser absorption in the 300–375-nm region. Although the absorption for some compounds extends to 430 nm, efficient initiation requires ultraviolet light. To increase sensitivity of these systems to the near-ultraviolet, Michler's ketone and other strongly absorbing *p*-aminophenyl ketones can be added as sensitizers.[108-110] Sensitization by heterocycles,[111] such as 2,5-diphenylfuran and 2,5-diphenyloxazole, and by hydroxyphthalein dyes,[112] especially halogenated compounds such as Eosin Y, Erythrosin B, and Rose Bengal, has also been described. Substituted coumarins that absorb in the near-ultraviolet also act as sensitizers.[113]

Many sensitizers have been developed to increase the photospeed and extend the sensitivity range of hexaarylbisimidazole initiator systems, first into the blue, and more recently into the green and red.[114] Sensitization by carbocyanine dyes[115] and by bis(alkylamino)acridine dyes[116] also been reported.

Derivatives of aryl ketones and *p*-(dialkylamino)aryl aldehydes are efficient hexaarylbisimidazole sensitizers.[117-118] Representative compounds, followed by their absorption maxima, are **27**, (443 nm); **28** (452 nm), and **29** (442 nm). These sensitizers have been attached to polymers to prevent migration in multilayer systems.[119] *N*-Alkylindolylidenes, such as ketone **30** (450 nm), and *N*-(alkylbenzothiazolyidene)alkanones sensitize these systems to visible light.[120] Bis[*p*-(dialkylamino)benzylidene] ketones such as **31** (477 nm) and **32** (481 nm) are also excellent sensitizers.[121] Systems containing these sensitizers can be exposed at wavelengths up to 488 nm.



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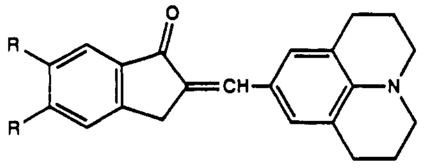
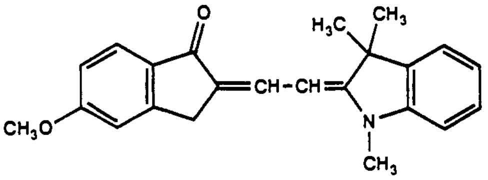


(28) R = H

(29) R = OCH_3



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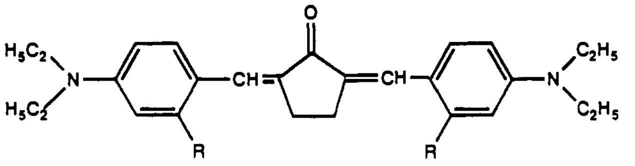
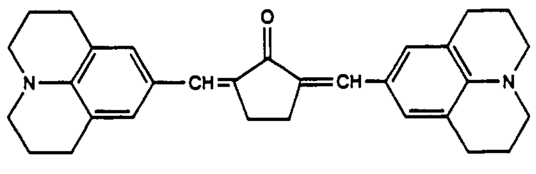


(31) R = H

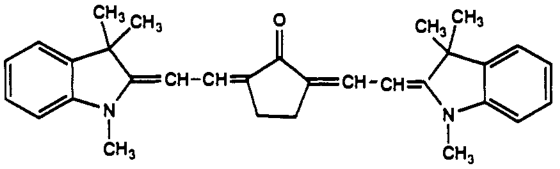
(32) R = CH_3

Sensitizers such as **27–32** extend the sensitivity of hexaarylbisimidazole initiator systems into the blue. However, few of these compounds have significant absorption beyond 550 nm. Ketone **33** (496 nm) extends sensitivity into the green so that systems with this sensitizer can be imaged with the 568-nm output of a krypton ion laser.[122]



(33)

A new class of sensitizers provides sensitivity to longer wavelength visible radiation. Typical compounds are **34** (520 nm), **35** (556 nm), and **36** (582 nm).[123] Systems sensitized by **36**, for example, can be imaged with the 632.8-nm output of the helium–neon laser. Sensitizer mixtures are useful in certain applications.[124]



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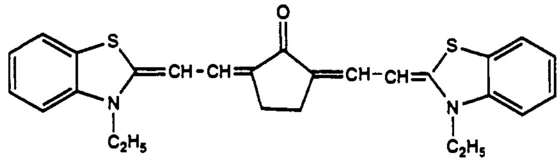

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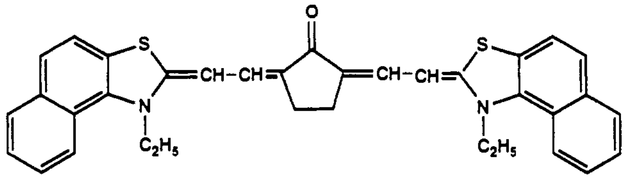


(36)

Only a few mechanistic studies of hexaarylbisimidazole photochemistry have appeared. Imidazolyl radicals are reportedly formed only from the hexaarylbisimidazole singlet state and not from the triplet state.[125] Imidazolyl radicals are believed to react with thiols[126,127] and with leucodyes[128] via electron transfer/proton loss, rather than by hydrogen abstraction. This would rationalize why the imidazolyl radical, a poor polymerization initiator by itself, becomes an excellent initiator when used in a system with the proper coinitiator.

Hexaarylbisimidazole sensitization is not well understood. For compounds of the type **27–36**, either increased planarity of the sensitizer molecule or restricted rotation of the dialkylamino group yields sensitizers with higher photospeed.[118] However, a study of the photophysics of two of these sensitizers concluded that twisting of the C–N bond is not an important excited-state relaxation process.[129] Electron transfer was proposed for sensitization by **33**.[130] Formation of an encounter complex that rapidly forms ground-state sensitizer and imidazolyl radicals was proposed for sensitization by Michler's ketone and by 2-isopropylthioxanthone.[131]

E. Peroxides and Peresters

Peroxides, such as benzoyl peroxide, are well-known thermal polymerization initiators. Although peroxides can be photochemically activated, they have relatively weak absorptions.

To improve light absorption and extend it to longer wavelengths, peresters with light absorbing chromophores have been developed. Perester derivatives of benzophenone[132-134] and of fluorenone[135,136] have been described. Sensitization of peroxides with **31** has also been reported.[137] However, their thermal instability makes peresters poor choices for photoimaging systems.

III. Hydrogen Abstraction

A. Ketones and Quinones

Many carbonyl compounds are hydrogen abstractors.[138] The excited state (**37**) of the carbonyl compound abstracts a hydrogen atom from an appropriate substrate (eq 3). A ketyl radical (**38**), derived from the carbonyl compound, and a radical (**39**), derived from the substrate, are formed. Substrate radical **39** can either initiate polymerization or abstract a hydrogen atom from a coinitiator to produce a secondary radical that initiates polymerization.

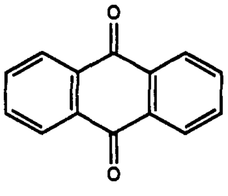
$$\underset{(37)}{[R_1COR_2]^*} + R_3H \xrightarrow{h\nu} \underset{(38)}{R_1R_2C^{\cdot}OH} + \underset{(39)}{R_3^{\cdot}} \quad (3)$$

Ketyl radical **38** typically does not initiate polymerization.[139] Instead it either disproportionates or couples with another ketyl radical to form a pinacol (eq 4). It can also terminate polymerization by reaction

$$\underset{(38)}{2R_1R_2C^{\cdot}OH} \rightarrow R_1COR_2 + R_1R_2CHOH \text{ or } [R_1R_2COH]_2 \quad (4)$$

with substrate radical **39** or with the growing radical chain, thereby reducing the photospeed of the imaging system.[139]

Quinones were among the earliest photoinitiators described.[140] Although they continue to be extensively described in photoimaging patents, except for anthraquinone (**40**) and its derivatives,[141] quinones have been largely replaced by other initiator systems. 2-Ethylanthraquinone, 2-*tert*-butylanthraquinone, or anthraquinone sulfonate may be used in place of anthraquinone to increase the solubility of the initiator in the coating solvent or to improve its compatibility with the other components of the system.[142]



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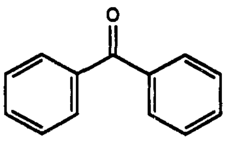
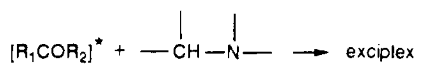
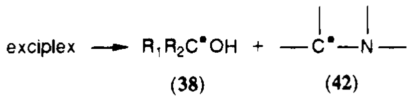


(41)

Aromatic ketones, such as benzophenone (**41**), have been extensively used in photoinitiator systems. Although these compounds are relatively inefficient initiators when used alone, efficiency increases greatly when an amine that possesses one or more hydrogen atoms on a carbon atom α to nitrogen is present in the system.[143-146] Thus, these compounds are almost always used with amine coinitiators.[147,148] The photoexcited ketone and the ground-state amine interact to form an excited-state complex known as an exciplex (eq 5).[127,149-151] A principal decay path for the exciplex is intermolecular hydrogen abstraction to form ketyl radical (**38**) and amine-derived, carbon-centered radical (**42**) (eq 6). Radical **42** is an efficient free-radical polymerization initiator.



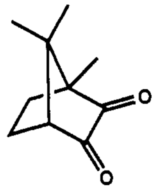
$$[R_1COR_2]^* + \text{—}\overset{|}{C}H\text{—}\overset{|}{N}\text{—} \longrightarrow \text{exciplex} \quad (5)$$



$$\text{exciplex} \longrightarrow \underset{(38)}{R_1R_2C^{\bullet}OH} + \underset{(42)}{\text{—}\overset{|}{C}^{\bullet}\text{—}\overset{|}{N}\text{—}} \quad (6)$$

Hydrogen abstraction occurs from primary and secondary amines, but tertiary amines, such as *N*-methyldiethanolamine, are better coinitiators and are generally used.[152] Amine-containing monomers, such as 2-(*N*,*N*-dimethylamino)ethyl methacrylate, have also been used with aromatic ketones.[153] An advantage of such systems is incorporation of the amine into a polymer, thus minimizing its migration following imaging.

Since aromatic ketones have little or no absorption in the visible, α-diketones, which have weak absorption in the visible,[154,155] have been used to produce systems that have blue sensitivity.[156] Camphorquinone (**43**) and benzil (**44**) are the most commonly used, generally with an amine coinitiator. Camphorquinone has also been widely used as a photoinitiator for dental applications.[157-162]



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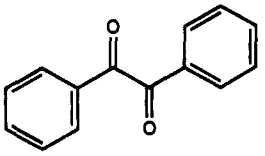
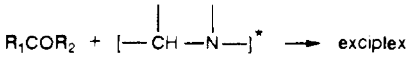


(44)

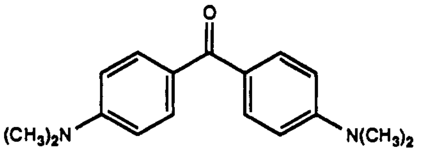
It is also possible for the amine, rather than the carbonyl compound, to absorb the light energy.[162] When a strongly absorbing amine is used, the amine absorbs the exciting radiation. An exciplex can be formed from an excited amine and a ground-state carbonyl compound (eq 7) rather than from an excited carbonyl compound and an amine (eq 5).[163]



$$R_1COR_2 + [\text{—}\overset{|}{C}H\text{—}\overset{|}{N}\text{—}]^* \longrightarrow \text{exciplex} \quad (7)$$

In this context, aromatic ketones, such as Michler's ketone (**45**), which are very strong absorbers of ultraviolet radiation, can be used in combination with more weakly absorbing ketones, such as benzophenone[164] and camphorquinone,[156] to produce efficient initiator systems. Although Michler's ketone can impart a yellow color to the final image, this does not present a problem in many imaging applications. *p*-(Dimethylamino)benzoate esters, such as methyl *p*-(dimethylamino)benzoate

(46), are reported to have many of the advantages of Michler's ketone without the yellowing problem.[165] Since *p*-(dimethylamino)benzoate esters do not absorb as strongly in the ultraviolet as Michler's ketone, they are sometimes used when systems that absorb less strongly than those containing Michler's ketone are desired.



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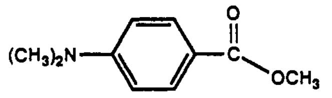
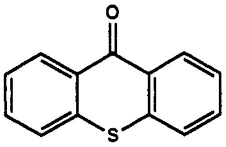


(46)

Unfortunately, the toxicity of Michler's ketone has become a serious concern. Liver tumors have been reported in rats and mice fed high levels of Michler's ketone.[166,167]

B. Thioxanthones

Thioxanthone (47) and its derivatives, especially 2-isopropylthioxanthone and 2-chlorothioxanthone, have been extensively used as photoinitiators. Thioxanthones absorb strongly in the near-ultraviolet but produce much less coloration than Michler's ketone.[168] This has made them particularly useful in thin films as well as in pigmented photoimaging systems. Thioxanes are also almost always used with amine coinitiators.[169-173]



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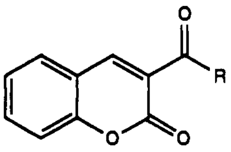
The effect of substitution on the absorption spectra, initiating efficiency, and solubility of thioxanthones has been extensively investigated.[174-183] Water-soluble thioxanthones, for example, have been developed by substituting the molecule with carboxyl and sulfonate groups.[184,185]

C. Ketocoumarins

3-Ketocoumarin (48) and its derivatives also have relatively strong absorptions in the near ultraviolet that can be modified by appropriate substitution.[186,187] Biscoumarin 49, for example, has a strong absorption maximum at 499 nm. Ketocoumarins have been used either with amine coinitiators or with acetic acid derivatives, such as (*p*-methoxythiophenoxy)acetic acid. Photoresists containing these materials have been described.[187]



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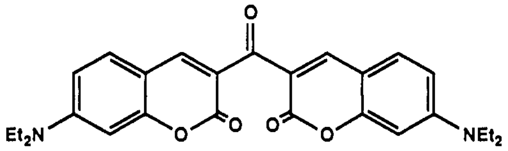
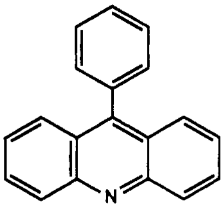


(49)

D. 9-Phenylacridine

9-Phenylacridine (50) is reported to initiate the photopolymerization of acrylate and methacrylate monomers.[188] The initial step is believed to be hydrogen abstraction by photoexcited 9-phenylacridine. Thiols have been used as coinitiators.[189] Printing plates,[188] photoresists,[190] and proofing systems[191] containing this material have been described. Substituted 9-phenylacridines that do not diffuse as readily as 9-phenylacridine have also been developed.[192]



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IV. Electron-Transfer Reactions

A. Dye-Sensitized Systems

Photoinduced electron transfer is an important route to free radicals.[127,193] Many hydrogen abstraction reactions, such as the ketone/amine system, are believed to be two-step reactions in which electron transfer is followed by proton transfer to produce the radical pair.

Numerous dye-sensitized photoinitiator systems have been described.[23] Since energy transfer is typically unfavorable in these systems, electron transfer between the photoexcited dye and an added coinitiator, or activator, can take place. Electron transfer converts the activator into a polymerization initiating free radical or a radical ion. Two types of electron transfer are possible: (1) transfer of an electron from the activator to the dye, and (2) transfer of the electron from the dye to the activator. Although both reactions are known, transfer of an electron from the activator to the photoexcited dye is the more common process. Photoreducible dyes include[194-196] xanthene dyes, such as Rose Bengal, Eosine Y, and Erythrosin B; acridinium dyes, such as acriflavine; phenazine dyes, such as methylene blue; and thiazene dyes, such as thionine. Typical activators are[23] amines, such as triethanolamine and *N*-phenylglycine; sulfinates;[197] enolates; carboxylates, such as ascorbic acid; and various organometallics, such as organotin compounds.[198]

Despite their potential to produce high photospeed and broad spectral sensitivity, dye-sensitized systems have not been extensively used in photoimaging. Dark reactions between the activator and the dye, the monomer, or other components of the system often take place. Moderately basic activators can deprotonate the dye, changing its absorption and electron-transfer characteristics. Nucleophilic activators can add to the monomers, causing loss of photospeed. These processes can reduce the useful lifetime of the system to only a few hours or, at most, a few days. Consequently, most dye-sensitized systems do not meet the storage stability requirements for photoimaging systems. Since these systems have not been widely applied in photoimaging, they will not be reviewed further. A comprehensive review by Eaton is available.[23]

B. Dye/Borate Systems

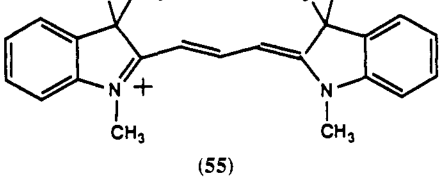
Photoinitiator systems containing cationic dyes and triaryl alkyl borate anion activators **51** have been recently described.[199-206] Unlike other dye-sensitized initiator systems, these systems are reported to be dark stable. Contrary to the behavior of other activators, the borate anion does not undergo dark reactions that reduce the life of the system.

As with other dye-sensitized systems, electron transfer from the activator to the photoexcited dye (eq 8) is believed to occur on irradiation.[207-209] Radical **52**, formed by oxidation of the borate anion activator, quickly fragments to form triphenylborane (**53**) and the butyl radical (**54**) (eq 9). The butyl radical initiates polymerization.

$$\underset{(51)}{(\mathrm{Dye})^{+}\,\mathrm{Ph_3BC_4H_9}^{-}} \xrightarrow{h\nu} (\mathrm{Dye})^{\bullet} + \underset{(52)}{\mathrm{Ph_3BC_4H_9}^{\bullet}} \qquad (8)$$

$$\underset{(52)}{\mathrm{Ph_3BC_4H_9}^{\bullet}} \rightarrow \underset{(53)}{\mathrm{Ph_3B}} + \underset{(54)}{\mathrm{C_4H_9}^{\bullet}} \qquad (9)$$

Although numerous classes of cationic dyes were mentioned in the initial work, cationic cyanine dyes, such as **55** and **56**, were reported to be especially useful.[199,200] Since numerous cyanines have been prepared for photographic applications, a complete spectrum of dyes is readily available. Proper selection of the dye allows the photosensitivity of the imaging system to be tuned to any desired region of the visible spectrum.



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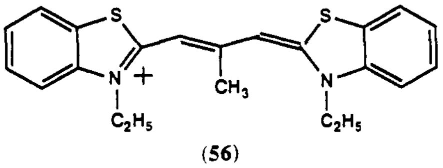


(56)

Research is continuing with additional patents appearing almost weekly. Since the initial report, initiator systems containing other cationic materials have appeared. Cationic dyes have included indolenine dyes,[210,211] azulene dyes,[212] and pyrylium and thiopyrylium dyes.[213] Initiator systems in which a cationic metal complex[214] or a metal ion[215] from group IB, IIB, IIA, or IVA replaces the cationic dye have also been described. Chain transfer agents have been used with the dye/borate system.[216] Initiator systems in which the dye/borate complex is used with other electron acceptors have also appeared.[217,218] Dye/borate initiator systems have also been combined with triazines.[219,220]

In the initial descriptions of cationic dye/borate systems, it was postulated that electron transfer was possible because in nonpolar solvents the dye/borate salts existed predominantly as ion pairs.[200,208,221,222] This suggested that only cationic materials could be used with borate anions.

More recently systems in which neutral dyes are used with triarylalkyl borate anions to initiate photopolymerization have been reported. In this work, the borate ion was sensitized by neutral merocyanine, coumarin, xanthene, and thioxanthene dyes.[223] Since the borate anion requires a cation, a quaternary ammonium or alkali metal cation was present. This indicates that it may not be necessary for the absorber and the anion to be present as an ion pair for electron transfer to occur.

Additional examples of borate anions with noncationic absorbers have appeared. Aromatic ketones, such as methyl *p*-(dimethylamino)benzoate (**46**) and biscoumarin **49**, were effective sensitizers of borate anions.[224] Systems in which the absorber was an anionic dye were also shown to initiate photopolymerization.[225]

The dye/borate initiator system was originally developed to provide the desired spectral sensitivity for a microencapsulated imaging system.[226-229] Because of its wide spectral sensitivity and good shelf life, it should find applications in other free-radical-initiated imaging systems.

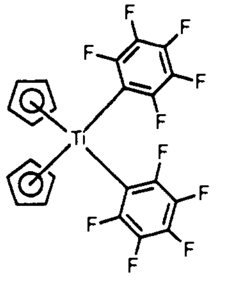
V. Organometallic Systems

Photoinitiators possessing a metal center have only recently been introduced in photoimaging systems. From the commercial standpoint, organometallics have yet to stand the test of time and experimentation. For instance, shelf life and toxicity are of concern when metals are employed.

Fragmentation, electron transfer, hydrogen abstraction, and rearrangements have all been observed or suggested in organometallic systems. For a given class of photoinitiators, the type of reaction may depend upon the nature of the attached ligands or the reactive media present. Therefore, organometallic systems will be discussed by structural type and in descending order by experience of usage and not necessarily by importance. Inorganic and organometallic photoinitiators for radiation curing have recently been reviewed.[230]

A. Titanocenes

Although dicyclopentadienyltitanocene-induced photopolymerization is well known,[231] only recently have practical systems been developed.[231-239] Bis(pentafluorophenyl)titanocene (**57**), which can be excited by visible radiation, is the most extensively investigated complex.[232,233] Fluorination of the aromatic rings provides thermal stability to the complex and prevents its oxidation in air.[233] Titanocene/*N*-phenylglycine mixtures are reported to possess a high level of photosensitivity to both the ultraviolet and visible.[240]



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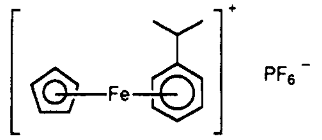
Titanocene photoinitiators have a wide spectral response, from 200–600 nm, and a high degree of sensitivity. Because they photobleach with high efficiency, titanocenes can produce images with high aspect ratios.[241] These initiators are especially useful for imaging with argon ion lasers.[233]

B. Ferrocenium Salts

Ferrocenium salts are initiators of cationic photopolymerization,[242,243] but they do not induce free-radical polymerization in the absence of other agents. Ferrocene can complex with halogenated compounds, such as RCH_2X or RSO_2X (R is typically aromatic) and, upon irradiation, generate halogen radicals to initiate polymerization.[242]

Recently the use of ferrocenium salts in free-radical-initiated photoimaging systems has been described. Initiators that photofragment exhibit enhanced reactivity and greater sensitivity to visible light in the presence of ferrocenium salts. (6-Isopropylbenzene)(5-cyclopentadienyl)iron(II) hexafluorophosphate (**58**) has been used with benzil dimethyl ketal (**17**) and other similar ketones (see section II.C).[242] Irradiation of triarylalkyl borate salts of cyclopentyldienyliron(II) arene cations produces alkyl radicals, which could be used to initiate photopolymerization.[244] Enhanced spectral response in the 500–600-nm range has been observed for photoimaging systems containing **58** and the visible dyes Nile Blue and Rhodamine B.[245] Additional coinitiators that increase the sensitivity of **58** are benzathrone and 4,4′-bis(diethylamino)benzophenone.



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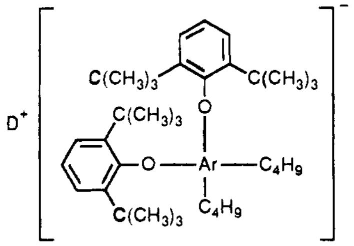
C. Aluminate Complexes

In a manner very similar to dye/borate chemistry, stable dye/aluminate complexes (**59**) that are photoinitiators have been developed. These complexes have good sensitivity in the ultraviolet and visible, but are reported to be less expensive to make than borates. The aluminate complex can be associated with either a cationic dye or a neutral dye.[246] The dye serves as a photosensitizer and bleaches upon exposure. Although no mechanism has been reported, analogy to the borate anions suggests that the aluminate anion releases an alkyl radical after photooxidation by the dye. The alkyl radical then initiates polymerization.



D^+ = a quaternary ammonium cation or a cationic dye

(59)

D. Other Systems

A few other organometallic systems or the like have been reported in the literature. Organotin compounds serve as activators of photopolymerization when used in the presence of electron-deficient sensitizers, such as anthracene derivatives, methylene blue, and Rose Bengal. Benzyltin compounds, such as tris(*n*-butylbenzyl)stannane, rapidly cleave to produce benzyl radical and tin-centered cation when oxidized through dye-sensitized electron transfer. The benzyl radical initiates polymerization. Although organotins have good shelf life, they are not as efficient as other activators, such as *N*-phenylglycine.[23,198]

Semiconductor pigments, such as titanium dioxide and cadmium sulfide, were used with a photooxidizable dye sensitizer and *p*-nitrobenzyl halides to induce photopolymerization. Dyes that adsorbed strongly to the pigment surface and sensitized photoredox reactions in the semiconductor pigment were most effective. Electron transfer from the photoreduced semiconductor reduces the nitro compound to a transient radical anion which fragments to the initiating *p*-nitrobenzyl radical.[23,127,247]

A singlet oxygen sensitizer such as zinc tetraphenyl porphyrin combined with a metal reducing agent such as vanadyl naphthenate or vanadyl acetylacetonate was used in combination with a singlet oxygen acceptor and was capable of inducing photopolymerization at high sensitivity for very thin films. Argon ion laser imaging at 514 nm was used.[248–250]

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