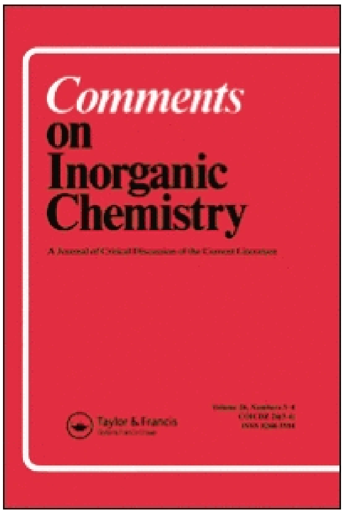

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# Light Sensitive Organometallic Compounds in Photopolymerization

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# Light Sensitive Organometallic Compounds in Photopolymerization

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Polymerization methods to manufacture printed and integrated circuits have been studied in great detail. Recently organometallics have been evaluated as photoinitiators for these processes. We discuss the use of organometallic compounds in cationic and radical polymerization initiation.

**Key Words:** *organometallic compound, photoinitiator, photopolymerization*

## 1. INTRODUCTION

Photopolymerization processes today play an important role in polymer chemistry. Surface coating, lithographic processes and the manufacture of integrated circuits rely on such techniques.[1] Photopolymerization can be achieved by two basically different processes. One of these requires the absorption of one photon for each propagation step and is termed "direct photopolymerization." The second and more efficient process, termed "photoinitiated polymerization," requires the absorption of just one photon for the activation step. Systems working on the basis of the second process therefore contain at least two components: a photoinitiator and a polymerizable material.[2] Once the photoinitiator has started the

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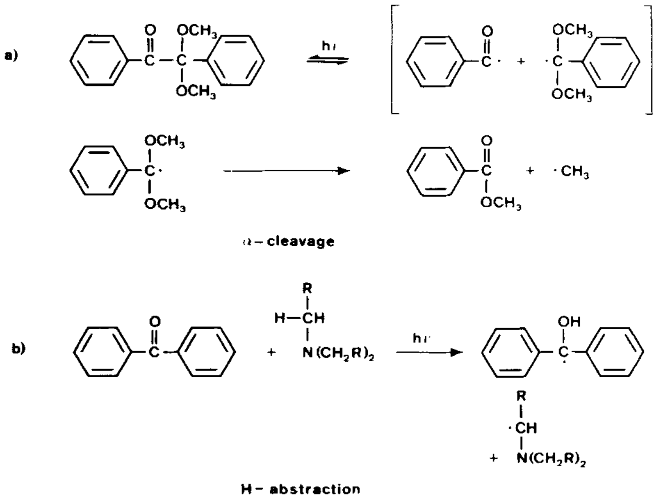
chain the polymer formation occurs by nonphotochemical propagation reactions of free radicals, cations or anions. The choice of a photoinitiator used for a certain system depends on a number of criteria, above all, however, on the nature of the polymerizable material and especially on the kind of propagation, whether that is a radical, cationic, or anionic process.

Organometallics are known to undergo light induced processes in which radicals or cations are formed.[3] If they absorb light of the desired wavelength they can be suitable photoinitiators. However, a few basic requirements have to be met:

(1) The complexes themselves and their mixtures with the polymerizable materials must be thermally stable.
(2) They must absorb strongly in the UV/visible region of the spectrum.
(3) Upon irradiation they should undergo efficient processes yielding an anion, a radical or cation capable of starting polymerization.

To date the vast majority of polymerization processes is achieved by free radical polymerization. Typical initiators start the chain via radical formation brought about by α-cleavage or hydrogen abstraction (Scheme 1).



SCHEME 1 Radical formation by (a) α-cleavage and (b) hydrogen abstraction.

An effort has been made over the last ten years to find initiators for cationic polymerization. The so formed polymers generally have a number of advantages over radically initiated systems.[4] Up until now there is no system known in which anionic polymerization can be brought about by light.

Since there are already reviews available on specific aspects of radical initiation including organometallic compounds[5] and one short review on the use of organometallics in polymerization processes,[2] we will present an overview of the organometallics in radical and cationic photopolymerization processes. Image forming systems which are based on photoredox processes of organometallics in silver free photography as they are described, e.g., by Baumann and Schlunke[6a] and other groups[6b,c] are not treated.

## 2. CATIONIC PHOTOPOLYMERIZATION

### 2.1. Introduction

Cationic photoinitiated polymerization is an area of intense current interest. The properties of photocured materials based on cationic polymerization are generally superior to those of products based on free radical polymerization. This is particularly true for their increased electrical resistance, stability to heat, chemicals, adhesion, and mechanical strength.[1,7]

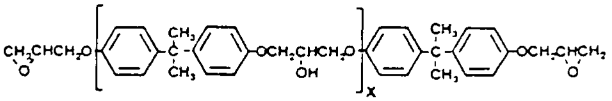
In contrast to free radical systems, only a relatively small number of alkenes, such as methyl-vinylether and heterocyclic compounds, such as epoxides and oxethanes as well as THF are susceptible to cationic polymerization. Of all the monomers mentioned epoxies are by far the most widely used substrates for cationic polymerization.

The most suitable resins for cationic polymerization are those shown in Table I, e.g., technical grade bis-phenol-A-diglycidyl ether of formula I ($n = 0.15$) and its oligomers ($n = 2.14$; 5.1; 11.8), cycloaliphatic epoxies based on derivatives of cyclohexene oxide shown in formulas II–IV, hexahydrophthalic diglycidyl ester V, or multifunctional novolacs such as VI.

The mechanism of cationic polymerization with Lewis or Brønsted acids (Scheme 2) has been examined only in a few cases.[8,9] Investigations are based on the polymerization of mono-epoxides

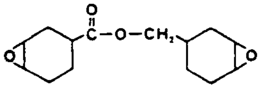
TABLE I

Most suitable epoxy resins for cationic polymerization[7]

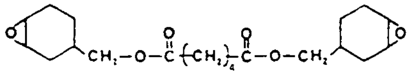


X = 0.15; 2.14; 5.1 or 11.8

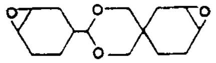
I



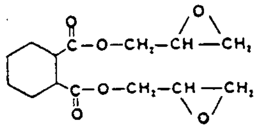
II



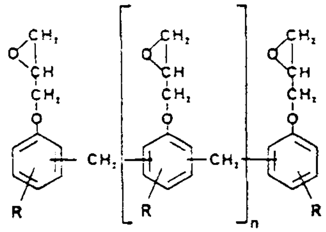
III



IV



V

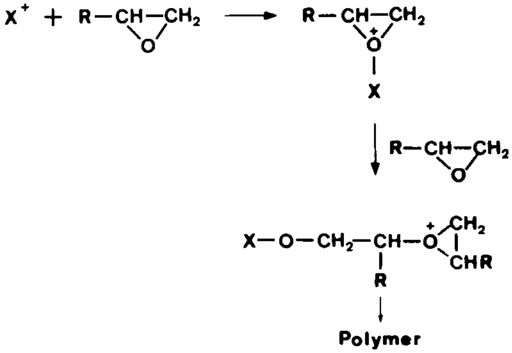


R = H or CH$_3$

VI

and on the analysis of intermediates and final reaction products. Epoxides are Lewis bases, and therefore their ring-opening by cationic species is easy. Propagation then continues via tertiary oxonium ions as shown in Scheme 2.

Unlike radical polymerization of vinyl monomers such as acrylates, cationic polymerizations are not affected by molecular oxy-



SCHEME 2 The polymerization of an epoxide.

gen. However, the presence of any strong nucleophiles such as amines does inhibit polymerization. Therefore in any initiator of salt like structure the anions must be of low nucleophilicity in order not to terminate the growing polymer chain prematurely.

Many different types of photoinitiator systems for the polymerization of epoxy resins have been described.[7,10] However, the majority of these are either too slow in their curing rate to be of much practical use or require thermal cure after irradiation. The first significant photocatalysts for the crosslinking of epoxy resins were aromatic diazonium salts (Scheme 3a) with anions of low nucleophilicity.[11] On irradiation these salts generate Lewis acids, which initiate the polymerization of the epoxy resin (Scheme 3a). Major disadvantages of these systems are the liberation of nitrogen gas

*a* Diazonium salts:

$$ArN_2^{\oplus}\quad MX_n^{\ominus} \xrightarrow{h\nu} Ar-X + MX_{(n-1)} + N_2$$

*b* Diaryliodonium salts:

$$Ar_2I^{\oplus}\quad MX_n^{\ominus} \xrightarrow[\text{H-donor (YH)}]{h\nu} ArI + Ar^{\cdot} + Y^{\cdot} + HMX_n$$

*c* Triarylsulphonium salts:

$$Ar_3S^{\oplus}\quad MX_n^{\ominus} \xrightarrow[\text{H-donor (YH)}]{h\nu} Ar_2S + Ar^{\cdot} + Y^{\cdot} + HMX_n$$

$$(MX_n^{\ominus} = BF_4^{\ominus},\ PF_6^{\ominus},\ AsF_6^{\ominus},\ SbF_6^{\ominus}\ \textit{etc})$$

SCHEME 3 Classical photoactive catalysts for the crosslinking of epoxy resins (Ref. 1).

and their limited thermal stability. These problems have recently been largely overcome with the discovery of the photoactivity of certain "onium salts" and in particular the diaryliodonium[12] and triaryl sulphonium[13] salts that are illustrated in Schemes 3b and 3c. On irradiation such salts generate Brønsted acids which are very effective catalysts for the polymerization of epoxides or the crosslinking of di- or polyepoxides.

## 2.2. Transition Metal Carbonyl Complexes

The earliest organometallics used as photoinitiators were carbonyl complexes. Strohmeier *et al.*[14] showed that by irradiation of a solution of dimanganese decacarbonyl $Mn_2(CO)_{10}$ in propylene oxide, all CO-ligands can be removed from the complex. The precipitating product is then able to polymerize the propylene oxide upon heat treatment. Subsequently $Mn_2(CO)_{10}$ has been tested as initiator for a number of other monoepoxides.[15] Besides $Mn_2(CO)_{10}$ some other transition metal carbonyls have been claimed to be photoinitiators for epoxide polymerization. Dirhenium decacarbonyl $Re_2(CO)_{10}$ proved to be an efficient initiator for propylene oxide, while $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ showed only poor conversion.[16]

Cyclopentadienyl manganese tricarbonyl compounds were found to be effective initiators for bis-epoxides such as bis-phenol-A-diglycidyl ether in the presence of acid anhydrides or poly-mercaptane curing agents.[17]

Stark and co-workers showed that $[\pi\text{-}C_5H_5Fe(CO)_2R]$ with R = $CH_3$, $CH_2C_6H_5$ and $[\pi\text{-}C_5H_5Mo(CO)_2CH_3]$ were also suitable photosensitizers for this process.[18] Thus a commercially available bis-phenol-A-derivative (Araldite 6200) could be polymerized in the presence of methyl bicyclo[2,2,1]-hept-5-ene dicarboxylic acid anhydride and one of the above mentioned photosensitizers.

## 2.3. Main Group Photoinitiator Systems

Chelate ligands derived from 1,2- or 1,3-diketones form complexes with boron, silicon, phosphorous, and germanium. With non-nucleophilic anions such as $ClO_4^-$, $PF_6^-$, $BF_4^-$, and in the presence of an organic halogen compound, such as chloroform, bis-phenol-A-diglycidyl ether can be cured upon irradiation.[19] In addition to organohalogen compounds such as $CHI_3$ bismuth trialkyls can enhance the photopolymerization of epoxides.[20]

### 2.4. Photoinitiators Derived from Transition Metals in Higher Oxidation States

Kaeriyama reports the use of ferrocene,[21] zirconocene dichloride[22] and titanocene dichloride[23] as photoinitiators for epichloro hydrin and phenyl glycidyl ether.

Titanium tetrachloride and titanium tetrabromide have been shown to catalyze the polymerization of isobutylene.[24] Their polymerization mechanism is subject to different interpretations.[25–28]

Vanadium tetrachloride has proven to be superior to the titanium halides for photocatalytic polymerization of isobutylene and isobutylene copolymers.[24–27,29–30] At low temperatures −40 and −60°C, respectively, molecular weights for polyisobutylene of one or two million[25c] could be achieved.

Irradiation of dilute solutions of salts of Ag(I), Cu(II), Cu(I) and Tl(I) having suitable noncoordinating anions in tetrahydrofuran results in the formation of polytetrahydrofuran in yields comparable to those for acid-catalyzed (dark) polymerization.[31]

### 2.5. Photodecomposable Cyclohexadienyl-Tricarbonyl Iron Complexes

Among the earliest complexes that have been looked at intensively are the tricarbonyl iron complexes with non-nucleophilic anions[32] such as $PF_6^-$ and $AsF_6^-$ (Fig. 1). Experiments have shown that these complexes are capable of photopolymerizing epoxide systems. As little as 2–3% of the cyclohexadienyl iron salt is sufficient to cure epoxides effectively upon UV irradiation at room temperature. A wide variety of these complexes can be synthesized according to known methods (Fig. 1).[33–40]

Three mechanistic pathways (Scheme 4),[2] have been proposed

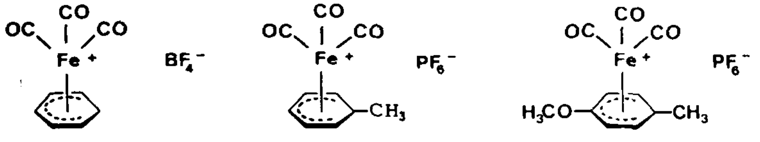
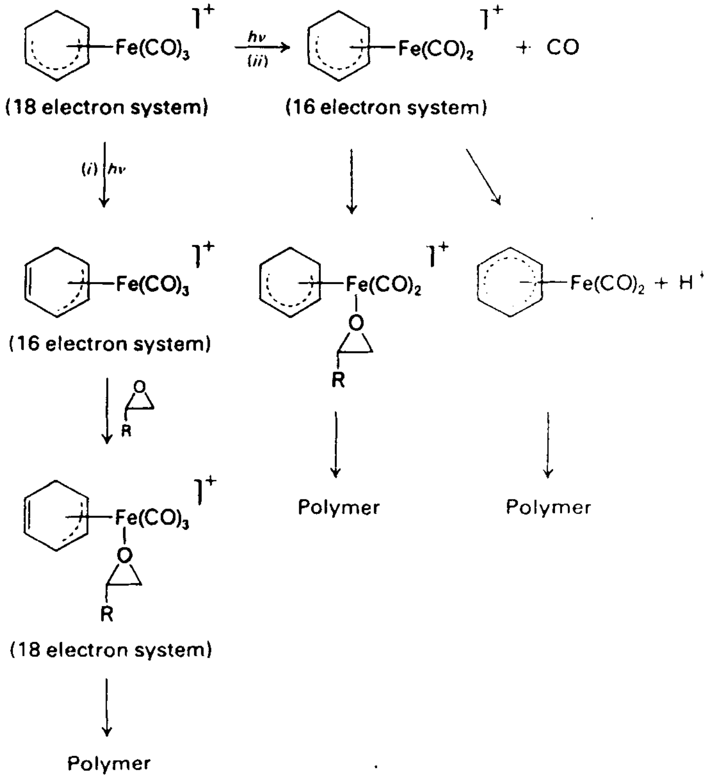


FIGURE 1 Cyclohexadienyltricarbonyl iron complexes as photoactive catalysts for the crosslinking of epoxy resins.



SCHEME 4 Possible mechanistic pathways for the photopolymerization of epoxides with cyclohexadienyltricarbonyl iron cations (Ref. 2).

as being responsible for the photoinitiated epoxide polymerization.

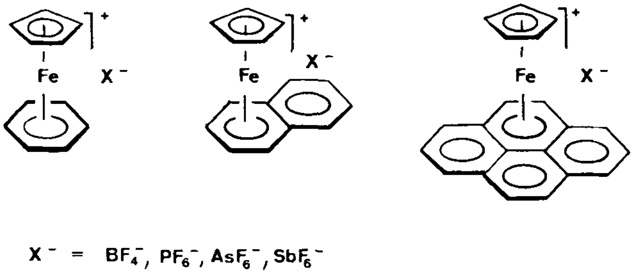
The mechanistic route (i) assumes that a free coordination site is generated through partial dislocation of the cyclohexadienyl ligand without loss of CO.

Route (ii) proposes an initial loss of CO to produce an unsaturated intermediate. This can coordinate an epoxide ligand either directly to produce an initiating species, or form by proton transfer to an epoxide unit an arene dicarbonyl iron. The photochemistry of these complexes is not very well studied, but there is evidence supporting an initial CO loss[2] as the more probable alternative.

## 2.6. Photodecomposable (Arene)cyclopentadienyl Iron Complexes

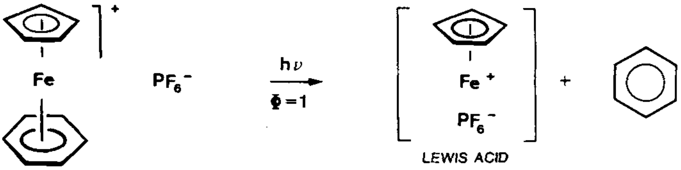
Recently, Meier and Zweifel described iron arene salts having anions with low nucleophilicity as highly efficient photoinitiators for the epoxide polymerization.[7,41–47] A similar result has also been reported by Palazzotto and Hendrickson.[48,49]

These iron arene salt photoinitiators seem to be the most promising of all the cationic organometallic initiators investigated so far. Iron arene salts can be prepared from ferrocene according to the method reported by Nesmeyanov.[50] A variety of complexes such as shown in Scheme 5 are described in the literature.[51]



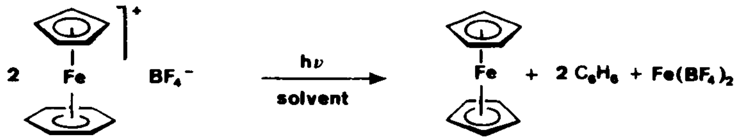
SCHEME 5 Iron-arene salt photoinitiators with anions of low nucleophilicity.

Photolysis of these compounds removes the uncharged aromatic ligand producing a coordinatively unsaturated iron cation (Scheme 6).



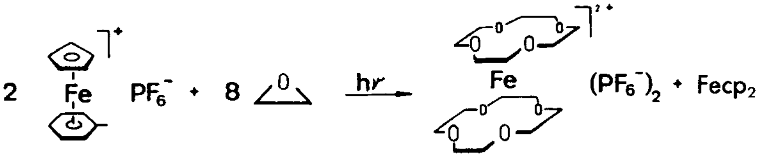
SCHEME 6 Formation of a Lewis acid by irradiation of ($\eta^6$-benzene)($\eta^5$-cyclopentadienyl)iron(II)-hexafluorophosphate.

Irradiation of the arene complexes in the presence of coordinating monodentate ligands, i.e., carbon monoxide, leads to complexes of the type $cpFe(L)_3^+$,[52] whereas photolysis in the absence of suitable ligands in aprotic solvents leads to ferrocene and iron(II) salts[53] (Scheme 7).



SCHEME 7 Photolysis of iron arene complexes in absence of suitable ligands.

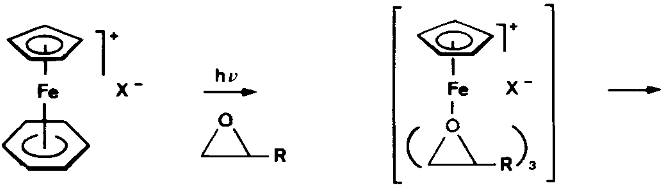
Meier and Rihs showed that photolysis in the presence of ethylene oxide in $CH_2Cl_2$ solution also yielded ferrocene and an iron(II)-salt complex. The main product was a white crystalline crown ether complex, whose structure was determined by X-ray analysis[54] (Scheme 8). Besides the [12]crown-4-complex, a minor amount of [15]crown-5-complex was formed.



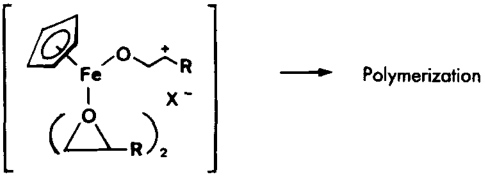
SCHEME 8 Formation of [Fe(1,4,7,10-tetraoxacyclododecane)$_2$](PF$_6$)$_2$ by irradiation of ethylene oxide in the presence of cpFe(Toluene)(PF$_6$); cp = cyclopentadienyl.

Photolysis of iron-arene complexes in solutions of epoxides which are more reactive than ethylene oxide or in epoxide solutions of high viscosity (which disfavor bimolecular reactions of the photogenerated iron species) also gave colorless iron polyether complexes but only traces of ferrocene.[54]

In view of these results, it appears likely that with technical epoxy resins upon irradiation a ligand-exchange reaction takes place leading to iron complexes with three coordinated epoxide ligands. Ring opening and polymerization could then start within the ligand sphere of the iron cation leading to polyethers (Scheme 9).

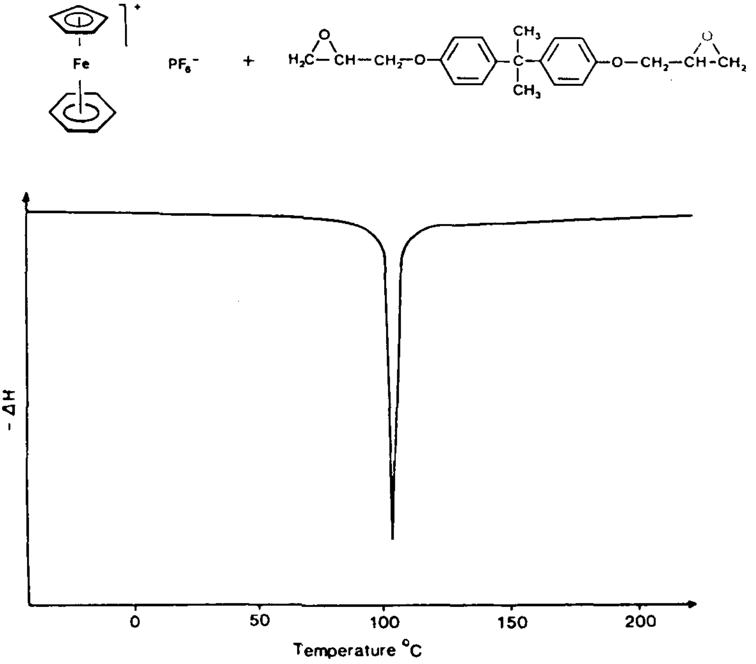


SCHEME 9 General principle of epoxide polymerization with iron-arene complexes.



SCHEME 9 Continued.

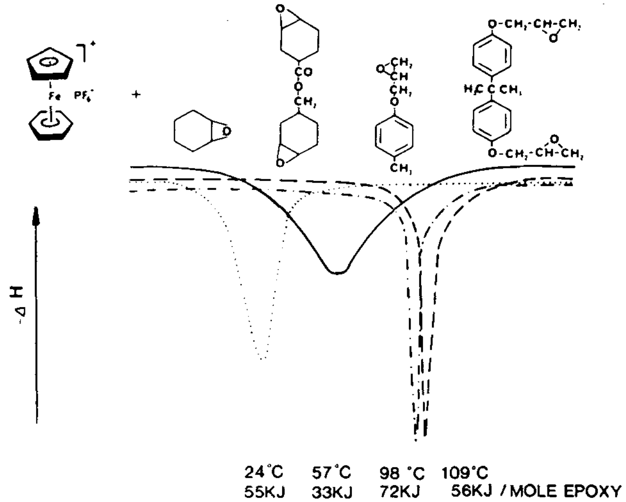
DSC experiments show that the iron cation is less reactive in epoxide polymerization than Brønsted acids obtained from, e.g., sulfonium salts (Scheme 3). Therefore, heat treatment after the irradiation step is necessary. The narrow enthalpy peak observed in DSC measurements could refer to a very uniform reaction pathway (Scheme 10).



SCHEME 10 DSC-diagram of the polymerization of bis-phenol-A-diglycidyl ether with ($\eta^6$-benzene) ($\eta^5$-cyclopentadienyl)iron(II)-hexafluorophosphate, 2.5% (w/w), after irradiation at −88°C. Heat rate: 20°C/min.

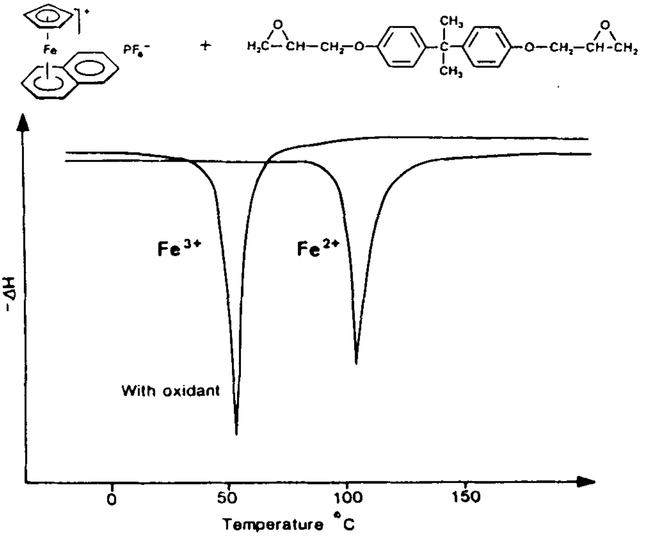
The reaction rate of the iron-catalyzed polymerization depends upon the nucleophilicity of the anion employed. The polymerization rate decreases in the order $SbF_6^-$ > $AsF_6^-$ > $PF_6^-$ > $BF_4^-$.

DSC experiments show the influence of the structure of the epoxide used. Cycloaliphatic epoxides are cured at lower temperatures than the glycidyl ethers, as shown in Scheme 11. The oxidation state of the complexed iron in these photoinitiators is +2 before and after exposure to actinic radiation. Oxidation of the iron complex to the +3 oxidation state leads to a more reactive Lewis acid with increased activity for epoxide polymerization (Scheme 12).

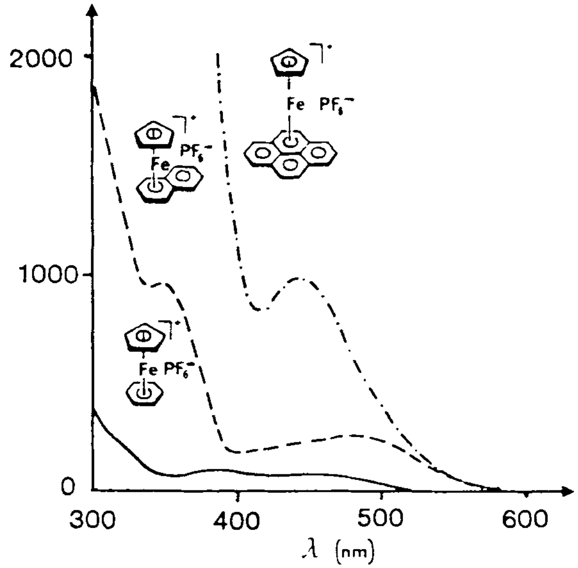


SCHEME 11 DSC-diagram of the polymerization of different epoxy derivatives with ($\eta^6$-benzene) ($\eta^5$-cyclopentadienyl)iron(II)-hexafluorophosphate, 2.5% (w/w), after irradiation at −88°C. Heating rate: 20°C/min. (Ref. 47).

In the presence of an oxidant, the polymerization reaction already occurs at about 50°C. With such compositions, tack-free coatings can be obtained in a one step process without subsequent thermal treatment.[42] Iron-arene photoinitiators have excellent light absorption properties in the ultraviolet and visible region of the spectrum. As shown in Scheme 13, absorption can be varied over a wide range by structural changes in the arene ligands. If desirable,



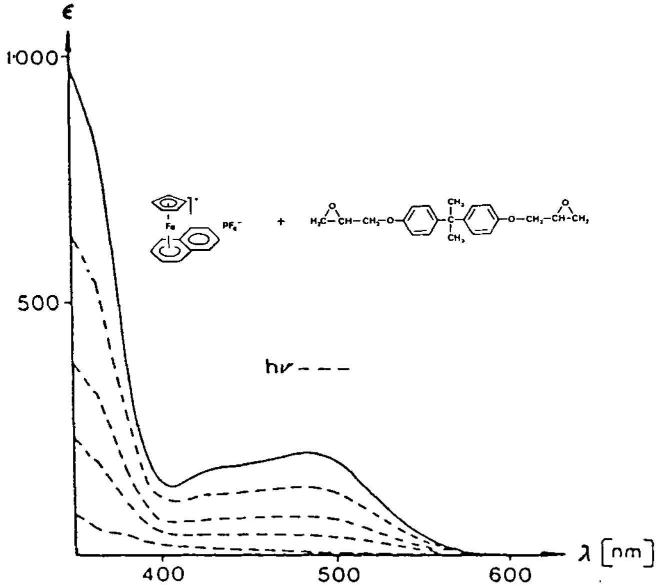
SCHEME 12 DSC-diagram of epoxide polymerization with 2.5% (w/w) photoinitiator in the presence and absence of the oxidant cumene hydroperoxide.



SCHEME 13 UV/VIS-Spectra of iron-arene complexes ($CH_2Cl_2$).

the photolysis of these iron salts can be sensitized, e.g., with anthracene derivatives.[55]

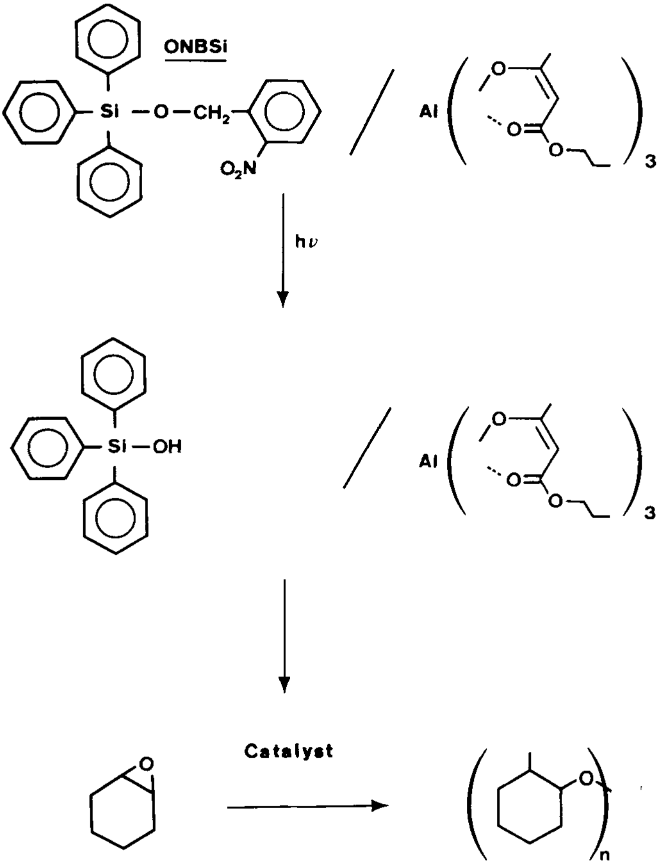
The absorption spectrum of the organometallic photoinitiator changes with prolonged exposure time (Scheme 14). A solution of the naphthalene complex in bis-phenol-A-diglycidyl ether was irradiated and the resulting spectral changes were registered after standard time intervals. As can be seen, the optical density in the near UV and visible region of the spectrum decreases with time. This states that the system is photobleachable, which permits light penetration into thick layers as photolysis proceeds.



SCHEME 14 Changes in the UV/VIS-spectrum of ($\eta^6$-naphthalene) ($\eta^5$-cyclopentadienyl)iron(II)-hexafluorophosphate ($c = 10^{-2}$ mol/l, $d = 10^{-3}$ m) in bis-phenol-A-diglycidyl ether by irradiation.

## 2.7. Photodecomposable Organosilanes

Hayase describes a new photoinitiation catalyst system consisting of an aluminium compound and o-nitrobenzyl triphenylsilyl ether (ONBSi) that initiates polymerization cationically.[56] The photopolymerization mechanism is said to take place in two steps (Scheme 15). The first step is the photogeneration of silanol from the ONBSi.

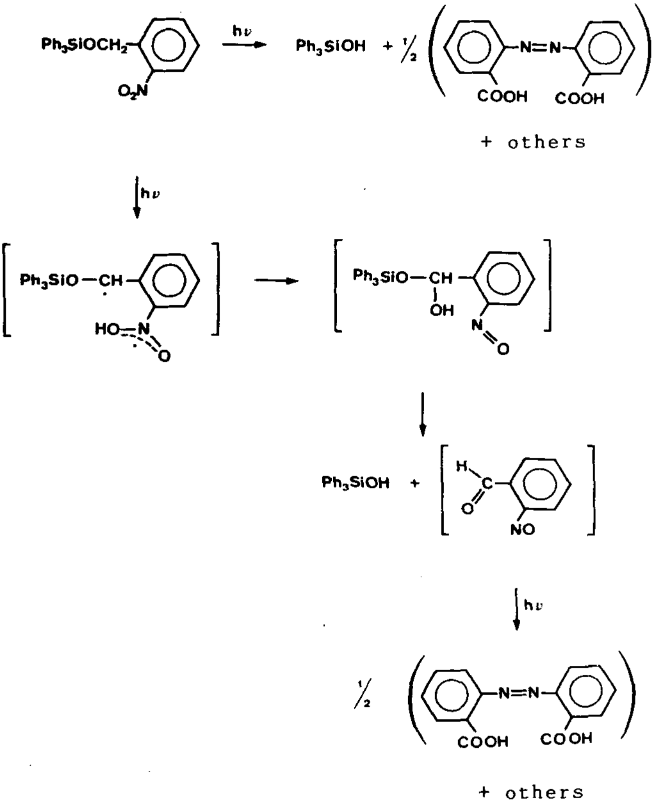


SCHEME 15 Catalyst formation from a mixture of ONBSi and an aluminium compound.

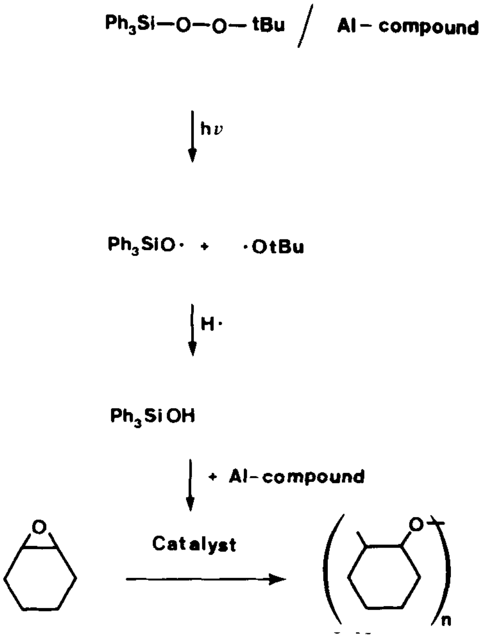
This in a second non-photolytic step forms a complex with the aluminium compound. The so formed catalyst initiates the polymerization of epoxides cationically.[57–59]

Photodecomposition pathways of ONBSi were reported by Hayase[56] as shown in Scheme 16. In this type of catalyst, any organosilane can be used that is photodecomposed to form organosilanol; however, the organosilane has to be very stable at room temperature and photodecomposes swiftly to form aryl silanol in high yield. A new system, based on aryl silyl peroxide, photogenerates silanol even more effectively (Scheme 17).[60]

The dependence of the catalyst activity on the structure of the silyl peroxide was also investigated by Hayase.[60] The catalyst with the highest activity is tris(ethyl-3-oxobutanato)aluminium and tri-2-naphthylsilyl tert.-butyl peroxide.



SCHEME 16 Proposed reaction mechanism of ONBSi photodecomposition.



SCHEME 17 Catalyst formation in a silyl peroxide/Al-compound system.

A similar system based on α-ketosilyl compounds was patented by Hayase in 1981[61]; no details on the reaction mechanism are available.

# 3. RADICAL PHOTOPOLYMERIZATION

## 3.1. Introduction

A wide variety of organometallic compounds, different with respect to the metal, the oxidation state of the metal or the structure, has already been used for photoinitiation of radical polymerization. A classification depending on the mechanism of radical formation or the mechanism of the initiation step proves to be difficult, because the precise primary physical processes occurring upon irradiation are often not fully known.

We shall discuss here organometallic photoinitiators that are used both with and without coinitiators and further subdivide each class into different types with regard to the ligands commonly involved in the photochemical steps.

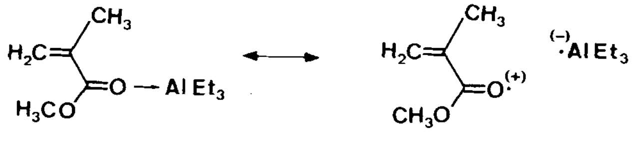
By far the most widely used monomer in free radical photopolymerization is methyl methacrylate (MMA). Other olefinic substrates used in the experiments described below comprise, e.g., styrene, ethylene, propylene, acrylamide, acrylonitrile, vinylchloride or derivatives thereof.

## 3.2. Organometallic Compound/Coinitiator Systems

A number of organometallic compounds exhibit photoinitiating properties only in the presence of a coinitiator. With regard to the mechanism of initiation, the latter may function in two different ways: (1) It may form, in a dark reaction, a charge-transfer complex with the metal containing component, which then absorbs light to produce the polymerization initiating radicals. (2) The more commonly encountered process, however, is that photolysis of a light sensitive organometallic compound leads to a coordinatively unsaturated species which upon subsequent reaction with the coinitiator yields radicals.

*3.2.1. $Et_3Al$/MMA System* An example of a non-transition metal organometallic compound used as photoinitiator for polymerization has been reported by Allen and Casey.[62] $Et_3Al$ was shown to polymerize MMA upon irradiation by a radical mechanism, as confirmed by ESR measurements. On the basis of NMR data it was concluded that mixing MMA with $Et_3Al$ yields a strong 1:1 MMA → $AlEt_3$ complex (Scheme 18, left). The broad absorption of this complex in the UV-spectrum was assigned to a CT-band in which the non-polar ground state is photoexcited to an upper state of partially charge-separated structure (Scheme 18, right). Initiation is thought to occur by the bimolecular reaction of a photoexcited state of this complex with a molecule of the complex in its ground state to form a species which then decays to radicals.[62b]

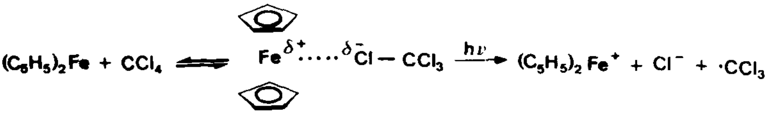
The fact that mixtures of styrene and MMA in the presence of $AlEt_3$ underwent photo-co-polymerization whereas homopolymerization of styrene failed also indicates that the formation of the MMA → $AlEt_3$ complex is a prerequisite for polymerization.



1a 1b

SCHEME 18 Proposed structures for the ground state and photoexcited state of an MMA → $AlEt_3$ complex.

*3.2.2. Metallocenes with Organic Halides as Coinitiators* Ferrocene is usually believed to be a light-stable compound. However, in organic halide solvents it decomposes upon exposure to light.[63] It has been suggested that in $CCl_4$ solution a charge-transfer complex is formed which upon absorption of UV-light dissociates liberating trichloromethyl radicals (Scheme 19).[64] This effect has been used for photosensitized initiation of vinyl polymerization.[65] Kinetic investigations as well as polymerization reactions in the presence of diphenylpicrylhydrazyl as a radical scavenger confirmed that the polymerization proceeds via a radical mechanism.



SCHEME 19 Photodecomposition of ferrocene in the presence of $CCl_4$.

In related work Nesmeyanov *et al.*[66] have used mixtures of ferrocenes with $CBr_4$ as light sensitive systems for photoimaging processes. Photopolymerization catalysts comprising a ferrocene and an active halogen-containing compound like an acid chloride or a halosulfonyl compound are claimed in a patent by McGinnis.[67] Ferrocene in that case is said to synergistically affect the organohalogens (that can act as photoinitiators on their own) in presence of light, thereby enhancing their effectiveness as catalysts for the polymerization of vinyl monomers.

In extension of the work done with ferrocene and activated halogens a wide variety of transition metal π-olefin complexes have been shown to work as well.[68]

Representative examples of the most commonly used compounds are both of the sandwich-type like dicyclopentadienyl cobalt, bis-benzene chromium or cyclopentadienyl benzene vanadium and of the half-sandwich carbonyl-type like toluene chromium tricarbonyl or cyclopentadienyl manganese tricarbonyl.

Furthermore, in a patent the dinuclear complex $[cpFe(CO)_2]_2$ is said to be superior to mononuclear species because of its strong absorption in the visible region of the spectrum.[69]

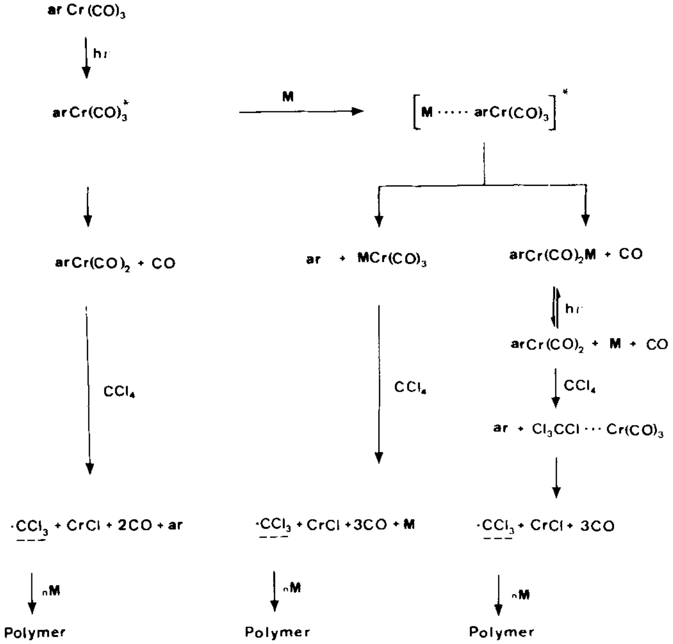
Systems containing arene chromium tricarbonyl in combination with $CCl_4$ as active photoinitiators for radical polymerization have been studied in great detail by Bamford *et al.*[70] Kinetic and quantum yield measurements have been carried out with different arene derivatives (arene = benzene, fluorobenzene, chlorobenzene, toluene, anisole). For both MMA and styrene the photochemical and polymerization data obtained support a free radical initiation process.

In MMA solution the predominant process to take place is direct interaction of the photoexcited species $ArCr(CO)_3^*$ with MMA probably involving exciplex formation. Decomposition of the exciplex subsequently may lead to unstable intermediates, which upon reaction with $CCl_4$ generate $\cdot CCl_3$ radicals. These have been shown by spin-trapping experiments to be the initiating species (Scheme 20).[70b]

In styrene solution photoinitiation seems to follow a different course. To account for the experimental results obtained, two intermediate photolysis-products have been proposed. Both contain a styrene molecule coordinated to chromium through the vinyl group (Fig. 2). It was concluded that a major portion of the radical generation arises from both photochemical and thermal reactions of these intermediates with $CCl_4$.[70c]

The use of these arene transition metal carbonyls with a halogen compound as co-reactant in the manufacture of photoresists and lithographic plates has been described by Wagner and Purbrick.[71]

*3.2.3. Transition Metal Carbonyls with Organic Halides as Coinitiators* Transition metal carbonyls, used in combination with chlorinated or brominated organic compounds, represent one of the best studied classes of organometallic photoinitiator systems for radical polymerization. Under suitable conditions the quantum yield of radical generation often approaches unity; however, the toxicity of both the starting materials and the photolysis products precludes the practical use of these compounds.[2]

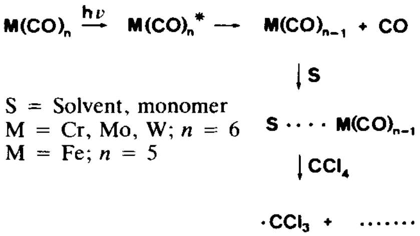


SCHEME 20 Simplified reaction scheme for the arCr(CO)$_3$/CCl$_4$ system (M = monomer).

The mechanism of the photoreaction of mononuclear carbonyls in the presence of CCl$_4$ is shown in Scheme 21. UV irradiation leads to dissociation of a carbon monoxide and formation of a coordinatively unsaturated species. The latter may undergo recombination with CO or addition of a monomer (or solvent) molecule to form a complex which reacts with suitable halides to generate the initiating free radicals.

Strohmeier *et al.*[72] have reported photosensitization of the po-

FIGURE 2 Proposed intermediates in styrene polymerization (Ref. 70c).



SCHEME 21 Simplified mechanism of the formation of $CCl_3$-radicals in the photoreaction with mononuclear carbonyl complexes.

lymerization of ethylacrylate or vinyl chloride by a number of metal carbonyls and related derivatives in the presence of $CCl_4$.

The photochemical reactions of $Fe(CO)_5$ in the presence of several olefinic monomers as well as the formation of the initiating species of this complex with organic halides have been reported in a series of papers.[73]

The role of molybdenum- and tungsten hexacarbonyl/$CCl_4$ systems in the photopolymerization of phenylacetylenes has been studied by Masuda and co-workers.[74]

Irradiation of solutions of $CH_3Mn(CO)_5$ and $CH_3COMn(CO)_5$ in MMA has been shown to start free radical polymerization of the monomer, with rates of polymerization being enhanced in the presence of $CCl_4$ as a coinitiator.[75] Analysis of polymers shows that initiation probably arises from both $\cdot CCl_3$ and $\cdot CH_3$ radicals.

Polymerization of MMA photosensitized by dinuclear carbonyls $M_2(CO)_{10}$ (M = Mn,Re) in the presence of $CCl_4$ was studied by Bamford *et al.*[5a] The manganese complex was of particular interest, since its absorption spectrum extends to about 460 nm and visible light can be used to initiate polymerization. Upon photolysis, scission of the metal–metal bond occurs and subsequent reaction of the fragments with $CCl_4$ produces $\cdot CCl_3$ as the initiating radical.

As shown above the most frequently encountered initiation process with carbonyls involves electron transfer to an organic halide with consequent rupture of a carbon–halogen bond. A different mechanism of initiation, called "non-halide" mechanism, has been found by investigating the photoinitiating properties of $M_2(CO)_{10}$ (M = Mn,Re) in association with fluoroolefins.[76] In these systems initiation appears to be the result of electron transfer from a product of $M_2(CO)_{10}$ photolysis to the olefin, producing in the first place a radical anion and resulting ultimately in a species containing a metal-carbon bond.

$$M^0 + CF_2{=}CF_2 \longrightarrow [M^+ \ldots {}^-CF_2\text{-}CF_2] \longrightarrow M\text{-}CF_2CF_2.$$

In a more detailed study[76d] it has been shown that depending on the substituents of the olefinic coinitiators, photoinitiation occurs either by "halide-abstraction"—or the "non-halide"—mechanism.

### 3.3. Organometallics without Coinitiators

Irradiation of the complexes described below usually causes intramolecular photoredox reactions, i.e., reduction of the metal atom with concomitant formation of a ligand radical. Metal chelates will be included in the discussion although they do not match exactly the definition of an "organometallic" compound.

*3.3.1. Transition Metal Chelates* Manganese acetylacetonate $Mn^{III}$ (acac)$_3$ and 1,1,1-trifluoroacetyl-acetonate $Mn^{III}$ (facac)$_3$ are reported to photosensitize the polymerization of MMA and styrene with low quantum yields. Initiation occurs as a result of the formation of an ·acac or ·facac radical with formation of a $Mn^{II}$ chelate.[5a]

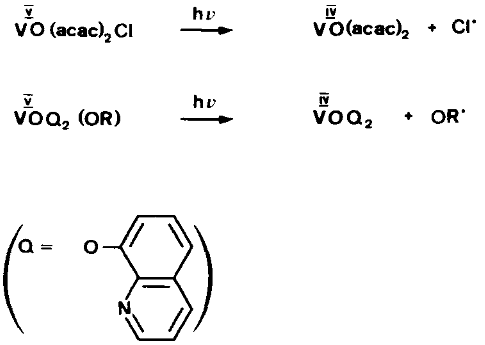
$$Mn^{III}\,(acac)_3 + h\nu \rightleftharpoons Mn\,(acac)_3^* \rightarrow Mn^{II}\,(acac)_2 + {}^{\cdot}acac$$

Irradiation of vanadium(V) chelates also results in photoreduction of the metal (from V to IV), but in these systems the metal-chelate bonds remain intact. The primary process is rupture of the V-Cl resp. V-OR bond leading to ·Cl resp. ·OR radicals as the polymerization initiating species (Scheme 22).[77]

In the photochemically initiated polymerization of acrylamide using $K_3[Fe^{III}(C_2O_4)_3]$, light absorption causes electron-transfer from the oxalate ligand to the $Fe^{3+}$ in the primary step. Decomposition of the reduced complex leads to $C_2O_4^{\overline{\cdot}}$ radicals as the initiating species.[78]

$$[Fe^{III}(C_2O_4^{2-})_3]^{3-} \overset{h\nu}{\rightleftharpoons} [Fe^{II}(C_2O_4^{2-})_2\,(C_2O_4^{\overline{\cdot}})]^{3-}\ {}^*$$

$$\longrightarrow [Fe^{II}(C_2O_4^{2-})_2]^{2-} + C_2O_4^{\overline{\cdot}}$$



$$\overset{V}{V}O(acac)_2Cl \xrightarrow{h\nu} \overset{IV}{V}O(acac)_2 + Cl^{\cdot}$$

$$\overset{V}{V}OQ_2(OR) \xrightarrow{h\nu} \overset{IV}{V}OQ_2 + OR^{\cdot}$$

SCHEME 22 Initiation via photoreduction and radical formation.

The blue tris-o-phenanthrolineiron(III)complex $Fe(phen)_3^{3+}$ [79] as well as iron(III) complexes with multidentate N-donor chelates such as tetraphenylporphyrine or trimethylenetetramine[80] (the latter in the presence of $CCl_4$) have also been reported to be photoinitiators for vinylpolymerization.

$K_3[Co^{III}(C_2O_4)_3]$ has been used for photoinitiation of MMA,[81] acrylamide[82] and acrylonitrile.[83] The mechanism of initiation is identical to that described for the analogous iron complex. Photopolymerization initiated by copper(II) amino acid chelates has recently been reported.[84]

*3.3.2. Transition Metal Tetraalkyl Complexes* Homoleptic transition-metal σ-hydrocarbyls $MR_4$ as photoinitiators for free radical polymerization have been reported for M = Ti, Zr, Hf and Cr.[85a–e]

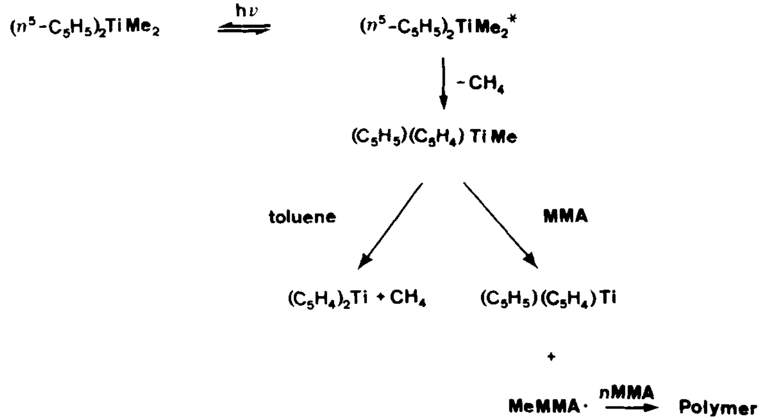
The first photolytic step seems to be scission of a metal–carbon bond. Initiation of polymerization may occur through both alkyl radicals and $M^{III}$ species (Scheme 23).

$$R_4M^{IV} \xrightarrow{hv} [\,R_4M^{IV}\,]^* \longrightarrow R_3M^{III\cdot} + R^{\cdot}$$

M = Cr , R = Alkyl [85a,b]; M = Ti , R = Neopentyl [85c];

M = Ti, Zr, Hf , R = Benzyl [85d,e]

SCHEME 23 Photoreaction leading to $M^{III}$ species and alkyl radicals.

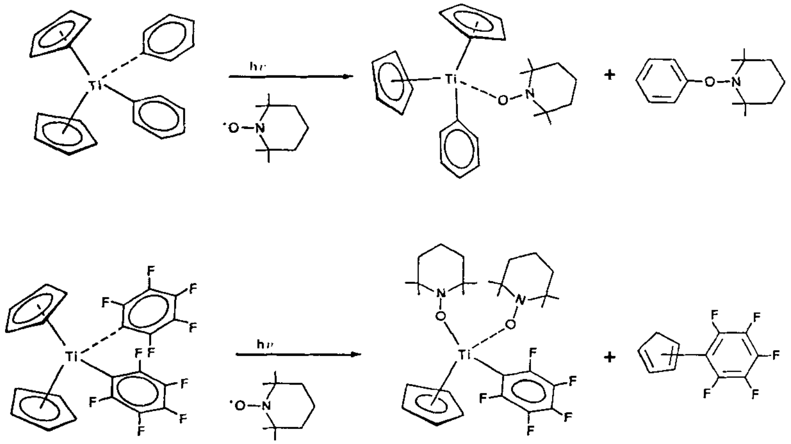


SCHEME 24 Mechanism of initiation of MMA by $cp_2TiMe_2$ (Ref. 87).

*3.3.3. Bis(cyclopentadienyl)titanium Complexes* Titanocenedichloride sensitizes photopolymerization by both a radical and a cationic mechanism depending on the type of monomer used.[86] A mechanism for the photopolymerization of MMA by $cp_2Ti(CH_3)_2$ was proposed by Bamford *et al.* (Scheme 24).[87]

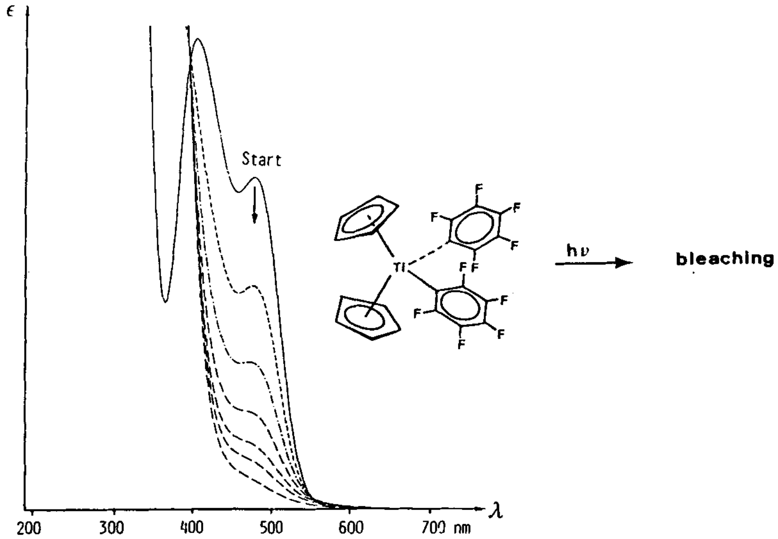
The photochemistry of the analogous titanocene-bis-aryl compounds $cp_2TiPh_2$ and $(C_5Me_5)_2TiPh_2$ has been studied in detail by various groups.[88] Photolysis of a toluene solution of $cp_2TiPh_2$ in the presence of styrene produced a small amount of polystyrene.[88a] For practical purposes, however, the complex proved to be too unstable thermally. The same is true for $cp_2TiMe_2$. During our work with titanium complexes we found enhanced thermal and oxidative stability when a fluorinated aryl ligand is introduced into the complex.[89a] To determine the nature of the initiating species in photopolymerization, photolysis has been performed in the presence of TMPNO as a radical trap with both $cp_2TiPh_2$ and $(Mecp)_2Ti(C_6F_5)_2$.[89b] The results obtained are summarized in Scheme 25.

Whereas in the case of $cp_2TiPh_2$ phenyl radicals—the potential initiating species—can be trapped, no adduct of the scavenger with $\cdot C_6F_5$ could be found in the experiment with the fluorinated compound. From these results it is currently unclear what in the latter case actually initiates the polymerization.



SCHEME 25 Radical scavenger experiments.

Applied for vinyl polymerization, the titanium based photoinitiators show a very high curing speed.[89c,d] Due to their bleaching, as shown in Scheme 26, they are suitable initiators for thick film applications.



SCHEME 26 Photobleaching of $cp_2Ti(C_6F_5)_2$.

## 4. CONCLUSION

Research activities in the field of organometallic photoinitiators have lead to industrially applicable products for both cationic[41] and radical[89] photopolymerization.[90] Suitable initiators for anionic polymerization are currently not known. However, recently the investigation on a cobalt amine system, which had been looked at by Delzenne,[91] has been taken up again by Kutal.[92] It may offer possibilities to polymerize various monomers by different initiation mechanisms. The use of organometallic compounds for photopolymerization initation is a rather recent development which in the future is sure to bear more fruit.

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