Nr 7—8 (447—570) CZERWIEC 1999 Tom XLIV

POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

Od Redakcji

Niniejszy, podwójny zeszyt naszego czasopisma w znacznej części poświęcamy tematyce polimerowej na Zjeździe PTChem "Wrocław '98", 14—18 września 1998 r. Dotyczące tych zagadnień artykuły, oparte na wygłoszonych na Zjeździe referatach, stanowią zwarty blok pierwszych ośmiu publikacji i zostały opatrzone odpowiednimi przypisami.

JULITA JAKUBIAK*), JAN F. RABEK**)

Photoinitiators for visible light polymerization***)

Summary — A review with 178 references covering metal-based photoinitiators (ferrocenium salts, ferrocene/polyhalogen systems, titanocene photoinitiators, metal carbonyl/onium salts systems, benzene/chromium tricarbonyl/polyhalogen systems, cationic metal coordination complexes/borate systems), camphorquinone systems, dye/co-initiator systems (dye/amine, methylene blue/benzyltrimethylstannane, dyes/peroxide, xanthene dyes/borate, cyanine dyes/triazine/mercaptan, triarylmethane dyes/diphenyliodonium salts, lophine/julolidine/mercaptobenzoxazole, ketocoumarin/co-initiator systems) and applications of visible light photoinitiator systems in reprography, holographic recording, nano-scale micromechanics and in clinical photocuring of polymeric restorative resins used in dentistry.

Key words: photoinitiators for visible light polymerization.

This paper sets out to provide an overview of photoinitiators for visible light polymerization. These photoinitiators are discussed in the following order: metal based systems, camphorquinone/amine systems, and dyes/co-initiator systems. In each section, mechanisms of photoinitiation of a given photoinitiation system are presented to some extent. In the last section applications of visible light photoinitiators systems are discussed. It is assumed that the reader of this chapter has a basic understanding of photochemistry.

METAL-BASED PHOTOINITIATORS

Fine reviews of this subject have been published elsewhere [1—4]. Potential advantages of organo-metallic complexes as photoinitiators have become evident. Two of them, ferrocenes and titanocenes, have found practical industrial application.

---

*) Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland.

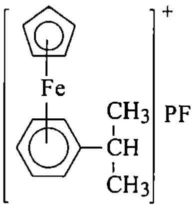
**) Polymer Research Group, Department of Dental Biomaterial Science, Karolinska Institute (Royal Academy of Medicine), Box 4064, 141 04 Huddinge (Stockholm), Sweden.

***) Paper presented at the PTChem Congress "Wroclaw 98", Wroclaw (Poland), 14—18 September 1998.

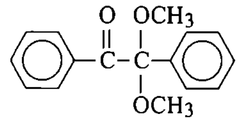
Ferrocenium salts

Ferrocenium salts are initiators of cationic photopolymerization. Photolysis of these compounds led to pure arene and a Lewis acid, which later initiated a cationic polymerization of epoxides [1]. Two of them (η^5-2,4-cyclopentadien-1-yl)(1,2,3,4,5-η)-(1-methyl) benzene-iron (1+) hexafluorophosphonate (Irgacure 264, Ciba-Geigy) and (η^5-2,4-cyclopentadien-1-yl)(1,2,3,4,5-η)-naphthalene-iron (1+) hexafluorophosphonate (Complex KM 1144, Ciba-Geigy) have found industrial applications.

Ferrocenium salts do not induce free-radical polymerization in the absence of other agents. A photoinitiating system based on (η^5-2,4-cyclopentadien-1-yl)-6-isopropylbenzene-iron (1+) hexafluorophosphate (Irgacure 261, Ciba-Geigy) (1)/benzyl dimethyl ketal (2) (or other similar ketones) exhibits enhanced reactivity and greater sensitivity to visible light [5].



(1)



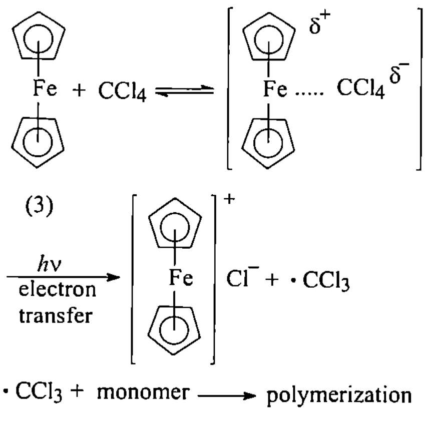
(2)

Irradiation of triaryakryl borate salts of cyclopentyldienyliron (1+) arene cations produces alkyl radicals, which could be used to initiate polymerization [6]. Enhanced spectral response in the 500—600 nm range has been observed for photoimaging systems containing (1) and the visible dyes Nile Blue and Rhodamine B [7]. Additional co-initiators that increase the sensitivity of (1) are benzanthrone and 4,4'-bis(diethylamino)benzophenone.

Ferrocene/polyhalogen systems

Ferrocenes (3) form ground-state complexes with polyhalogenated compounds like carbon tetrachloride. On irradiation of these complexes, an electron is transferred from the iron to a chloride atom to form a ferrocenium cation and a trichloromethyl radical [8—10]. The latter radical may initiate polymerization of methyl methacrylate, acrylonitrile, and vinyl acetate and exhibits enhanced reactivity and greater sensitivity to visible light, but is ineffective in the polymerization of styrene [11—13] (Scheme I).

Scheme I



Imaging systems based on ferrocene derivatives/BBr_4 have also been developed [14].

Titanocene photoinitiators

Various titanium complexes are known to be photoreactive for a long time [15].

Titanocenes are orange to red solids or liquids that absorb up to 560 nm with two pronounced absorption bands around 405 and 480 nm (Fig. 1) [16]. Upon irradiation, they photobleach with high efficiency (Fig.1).

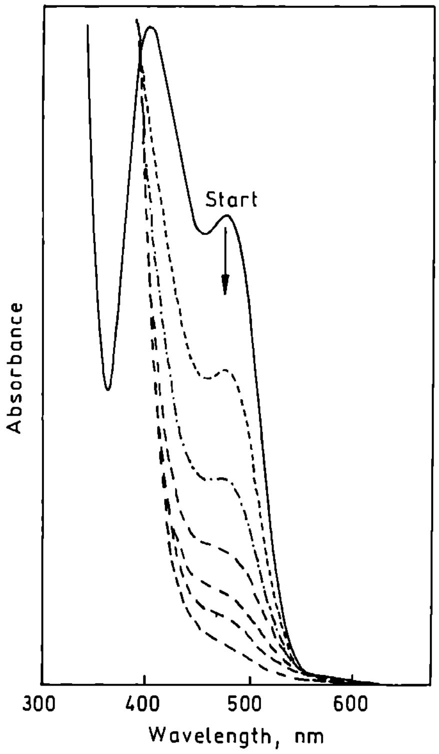
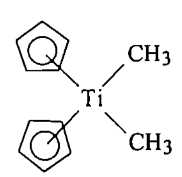


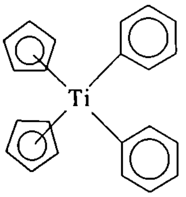
Fig. 1. Absorption spectrum of bis(pentafluorophenyl) titanocene and bleaching upon irradiation [16]

Dimethyl titanocene [bis(η^5-cyclopentadien-1-yl)-bis(methyl)titanium] (4) and diaryltitanocene [bis(η^5-cyclopentadien-1-yl)-bis(phenyl)titanium] (5) are highly oxygen sensitive and decompose in air by oxidative routes. Fluorination of the aromatic rings [bis(η^5-cyclopentadien-1-yl)-bis(2,3,4,5,6-pentafluorophenyl titanium] (6) provides thermal stability to the complex and prevents its oxidation in air [16, 17]. Variation of the substitution pattern of the ligands enables modifications of the secondary properties to be obtained without significantly affecting their photochemical reactivity [15, 16].

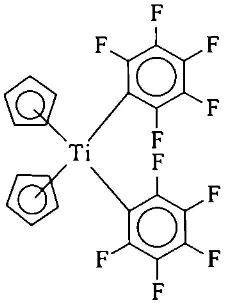
Titanocene (7) [bis(η^5-2,4-cyclopentadien-1-yl)-bis-



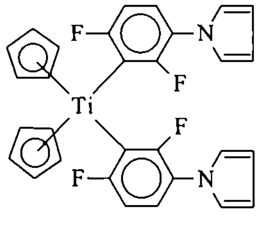
(4)



(5)



(6)

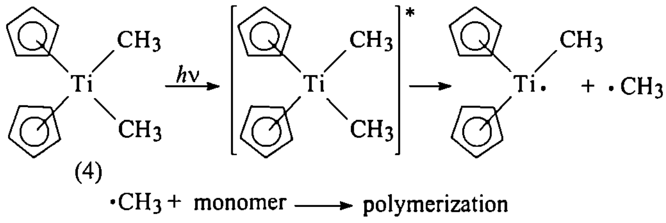


(7)

[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium], Irgacure 784 (CGI 784, Ciba Geigy) is the compound most recently developed [17—26]. It can be used alone or in combination with co-initiators (such as α-hydroxyketones, α-aminoketones, thioxanthones, amines, benzophenone and its derivatives, ketocoumarins, *etc.*). CGI 784 is a highly efficient visible light curing photoinitiator for photopolymerization of acrylates in combination with mono- or multi-functional vinyl monomers as reactive thinners.

Titanocenes such as dimethyl titanocene (4) [27—30], diaryl titanocene (5) [29, 31] and fluorinated diaryl titanocene (6) [32, 33] undergo homolytic cleavage of the methyl (aryl)-metal bond upon irradiation in the solution to give a metal compound at a low oxidation state and a methyl (aryl) radical (Scheme II).

Scheme II



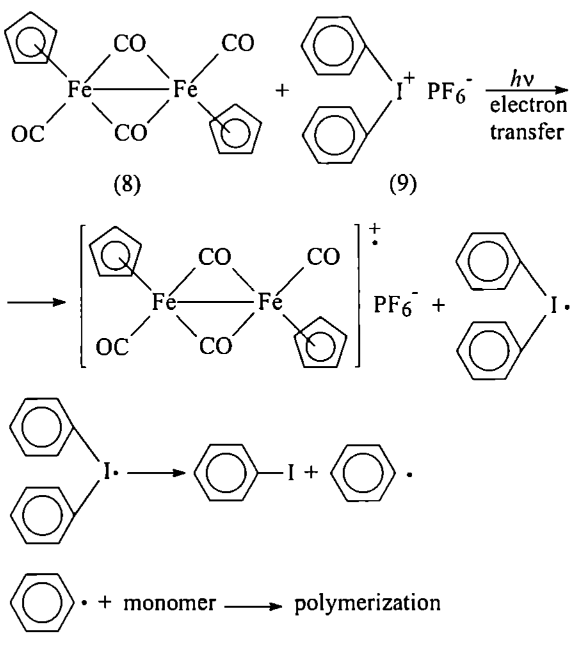
Titanocene/*N*-phenylglycine systems are reported to possess a high level of photosensitivity to both ultraviolet and visible irradiation [34].

Titanocenes initiate photopolymerization of methyl methacrylate and styrene [35]. The inefficient polymerization of styrene photoinitiated by diphenyltitanocene (5) has also been reported [36]. Titanocenes are especially useful for imaging with argon ion lasers [16].

Metal carbonyls/onium salts systems

Various metal carbonyls $[CpFe(CO)_2]_2$ (where $C_p = \eta^5$ cyclopentadienyl) (8) in the presence of onium salts such as diaryliodonium hexafluorophosphate $(Ar_2I^+PF_6^-)$ (9) under irradiation produce aryl radicals which can initiate polymerization [37, 38] (Scheme III).

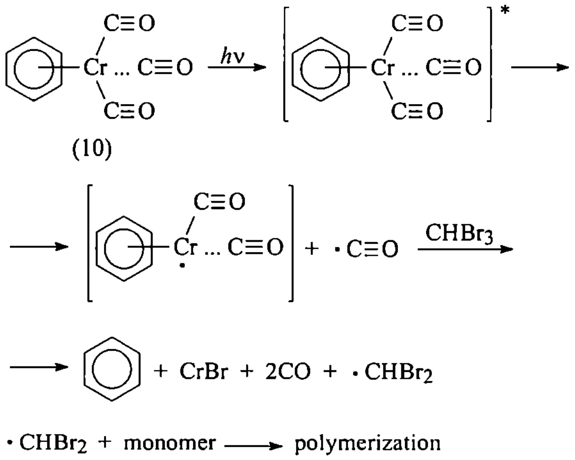
Scheme III



Benzene chromium tricarbonyl/polyhalogen systems

On irradiation in tribromomethane, benzene chromium tricarbonyl (10) loses one carbonyl ligand and the reactive intermediate undergoes an electron transfer reaction with the halogen compound. The resulting dibromomethane radical can initiate a polymerization reaction [39] (Scheme IV).

Scheme IV

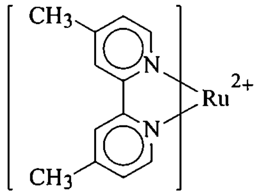


The halide activity in all these systems is governed by the ability of the compound to accept electrons. Thus, as the degree of substitution with electron attracting groups is increased, the activity increases (CH_3Cl < CH_2Cl_2 < $CHCl_3$ < CCl_4). Bromine derivatives are much more reactive than the corresponding chlorine derivatives.

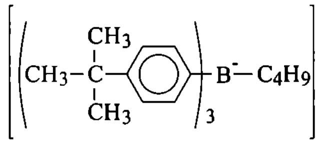
None of these photoinitiating systems has found a widespread practical use, because of their inadequate thermal and/or oxidative stability which fails to meet the industrial requirements. Another reason is the toxicity of many organic compounds (like metal carbonyl compounds) which precludes their practical use.

Cationic metal coordination complexes/borate systems

Cationic transition metal complexes containing a metal atom with d^6-configuration like Ru(II), Co(II), Fe(II) or Ir(III), used with triarylalkylborate, give very effective photoinitiating systems [40]. These metal cations are coordinated to bidentate or tridentate ligands like bipyridyls or tripyridyls, which possess low lying unoccupied π orbitals capable of accepting electrons. An example, *viz.* tris(4,4'-dimethylbipyridyl)ruthenium (II) (11)/triarylalkyl borate (12), is shown below.



(11)



(12)

CAMPHORQUINONE/AMINE SYSTEMS

Camphorquinone [bornanedione, 1,7,7-trimethylbicyclo(2,2,1)heptane-2,3-dione] (CQ) (13) absorbs UV radiation in the region 200—300 nm due to the π, π* transition and the visible light in the region 400—500 nm (responsible for its yellow color) due to the *n*, π* transition of dicarbonyl group (Fig. 2) [41—43]. There is a significant difference between ε_{max} for the two transitions, with ε_{max} amounting to about 10, 000 for the *n*, π* transition, compared to 40 for the *n*, π* transition. This reflects the fact that the *n*, π* transition is symmetry forbidden, whilst *n*, π* transition is freely allowed.

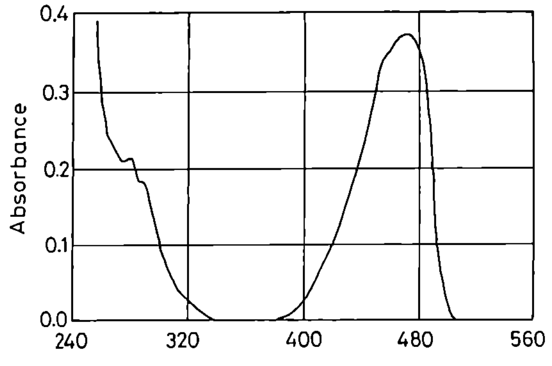
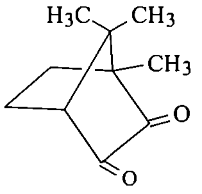


Fig. 2. Absorption spectrum of camphorquinone [55]

The CQ has a rigid structure and coplanar dione chromophores. Visible light irradiation leads to the formation of the excited singlet $^1CQ^*$ state and, by intersystem crossing (ISC), the triplet $^3CQ^*$ state [44].



(13)

$$CQ(S_0) \xrightarrow{h\nu} {}^1CQ^*$$

$$^1CQ \xrightarrow{(ISC)} {}^3CQ^*$$

The triplet energy of CQ is E_T = 51.6 kcal mol^{-1}, whereas the quantum yield is Φ_{ISC} = 1 [41, 45].

The reactivity of the excited $^3CQ^*$ can be assigned to two pathways involving different reductants as shown below:

1. Radical type — a direct hydrogen atom abstraction by the $^3CQ^*$ from a hydrogen atom donor monomer (MH).

$$^3CQ^* + MH \longrightarrow CQH\cdot + M\cdot$$

$$M\cdot + nMH \longrightarrow polymer$$

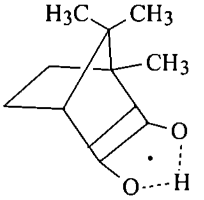
2. Electron/proton transfer (charge-transfer type) occurring in the presence of amines (AMH).

$$^3CQ^* + AMH \longrightarrow CQH\cdot + AM\cdot$$

$$AM\cdot + MH \longrightarrow AMH + M\cdot$$

$$M\cdot + nMH \longrightarrow polymer$$

The formation of camphorquinone ketyl radical (CQH·) (14) has been well established by ESR spectroscopy [46—52]. However, (CQH·) cannot initiate polymerization reaction itself.

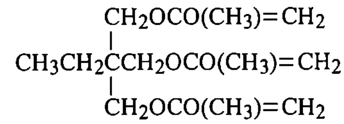


(14)

Hydrogen atom donor abstraction by $^3CQ^*$ from different monomers depends highly on their chemical structure. The monomers having repeatable oxyethylene units (CH_2-O) in their ester group, like tri(ethylene glycol)dimethacrylate (TEGDMA) (15), are much better hydrogen-atom donors for $^3CQ^*$ than are monomers with no ether links such as decane-1,10-diol dimethacrylate (DDMA) (16) or trimethylpropane trimethacrylate (TMPTMA) (17) [53]. Replacement of the hydrogen atom by the sulfur atom results in increased ability of the CH_2 group attached to the hetero atom to donate a hydrogen atom. Thus, the CH_2S unit is the better hy-

$$CH_2{=}C(CH_3)COO[CH_2CH_2O]_3COC(CH_3){=}CH_2 \quad (15)$$

$$CH_2{=}C(CH_3)COO[CH_2]_{10}OCOC(CH){=}CH_2 \quad (16)$$



$$\begin{array}{c} CH_2OCO(CH_3){=}CH_2 \\ | \\ CH_3CH_2CCH_2OCO(CH_3){=}CH_2 \\ | \\ CH_2OCO(CH_3){=}CH_2 \end{array} \quad (17)$$

$$CH_2{=}C(CH_3)COOCH_2CH_2SCH_2CH_2OCO(CH_3){=}CH_2 \quad (18)$$

drogen atom donor than the CH_2O unit [54]. Therefore, the photopolymerization of 2,2′-thiodiethyl dimethacrylate (TDMA) (18) induced by benzophenone occurs faster than that of its oxygen analog [54]. However, when CQ is used as the photoinitiator, the polymerization is markedly retarded.

The $^3CQ^*$ can also abstract a hydrogen atom from the propagating radical as well as from polymer molecules. In this case, branched structures can be formed. Polymerization of di-, tri- and multifunctional monomers yields high-crosslinked networks [55—63].

The $^3CQ^*$ can also initiate polymerization in the presence of oxygen (air) [56—59]. However, all radicals formed are immediately oxidized by oxygen to peroxy and oxy radicals and to hydroperoxide groups. The peroxy radicals are 2000 times less reactive in the initiation of polymerization than alkyl radicals [55]; however, they can easily abstract a hydrogen atom from the monomer. Oxygen causes an inhibition effect which retards polymerization, especially at the surface open to the air environment resulting in a wet or tacky layer.

Photoreaction of $^3CQ^*$ with amines (AMH) occurs *via* a short-lived excited charge-transfer complex (CTC) called also the exciplex [45—47, 56]. The nature of an exciplex depends significantly on the structure of the reacting partners, especially on the AMH structures and polarity of monomers. In nonpolar monomers leads to a contact ion pair (CIP) in which is formed of a planar amine radical cation ($^+\cdot$AMH) and camphorquinone radical anion ($CQ\cdot^-$), whereas, in polar monomers, leads to monomer-separated ion pair (MSIP) [64—69].

$$^3CQ^* + AMH \longrightarrow \underset{(CTC)}{CQ...AMH^*}$$

$$CTC \longrightarrow \underset{(MSIP)}{[CQ\cdot^- \,||\, ^+\cdot AMH}$$

$$CTC \longrightarrow \underset{(CIP)}{[CQ\cdot^- ... ^+\cdot AMH}$$

Back electron transfer and/or free-ion formation arise from the MSIP pair, whereas proton transfer with the formation of ketyl radical (CQH·) and amine radical (AM·) can occur in the CIP pair but also from the free ions [70].

$$CIP \longrightarrow CQH\cdot + AM\cdot$$

It is generally accepted that only AM · radicals initiate polymerization reaction, whereas CQH · radicals are inactive. One of the most effective amine co-initiators is *N*-phenylglycine [53]. The kinetics of photopolymerization of multifunctional monomers with CQ/amine systems has been reported [53, 55—63, 71—82]. The main application of CQ/AMH photoinitiators is in commercially available dental restorative resins. The photopolymerization occurs in a complicate formulation that, besides a mixture of different mono-, di- and trifunctional monomers and CQ/AMH (even up to 3—5 wt. %), contains different additives such as stabilizers, pigments, reinforcing fillers (even up to 70 wt. %), and coupling agents.

DYE/CO-INITIATOR SYSTEMS

Visible light photopolymerization initiated by dyes has been widely reviewed elsewhere [65, 83—92].

Pure dye systems

Only few (photoreducible) dyes (dye $^+X^-$) such as xanthene and acridine dyes (Table 1) can directly photoinitiate polymerization of methyl methacrylate, styrene and acrylonitrile, with low efficiency [93]. Photoinitiation occurs by electron transfer between the singlet excited dye molecule and monomer.

$$dye^+X^- \xrightarrow{h\nu} {}^1(dye^+X^-)^*$$

$$^1(dye^+X^-)^* + R-CH=CH_2 \longrightarrow$$

$$\longrightarrow dye\cdot + [R-CH-CH_2{}^+X^-]$$

$$dye\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

$$[R-CH-CH_2{}^+X^-] + \text{monomer} \longrightarrow \text{polymerization}$$

Electron deficient monomers (like acrylates) react preferentially as electron acceptors, whereas polymerization of electron rich monomers occurs by monomer oxidation [65].

Dyes/co-initiator systems

Usually photoinitiation of polymerization does not occur upon interaction of the excited (singlet or triplet) state of dye; it occurs in the presence of a co-initiator (electron/proton transfer mechanism). Two mechanisms are involved:

1. Photoreduction of a dye (dye $^+X^-$, electron acceptor) in the presence of co-initiator (electron donor, DH)

$$dye^+X^- \xrightarrow{h\nu} {}^1(dye^+X^-)^* \longrightarrow {}^3(dye^+X^-)^*$$

$$\underset{\text{electron transfer}}{^3(dye^+X^-)^* + DH \longrightarrow (dye^+X^-)\cdot^- + DH\cdot^+}$$

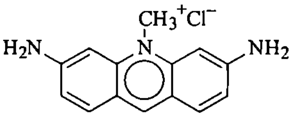
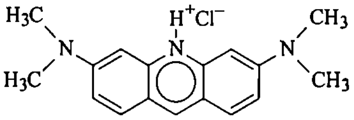
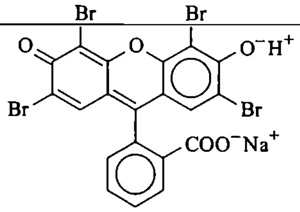
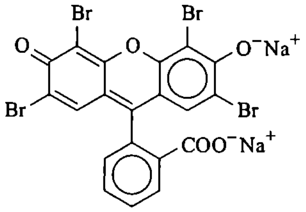
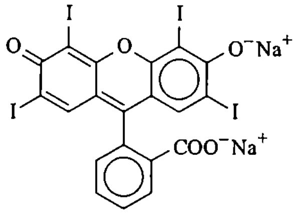
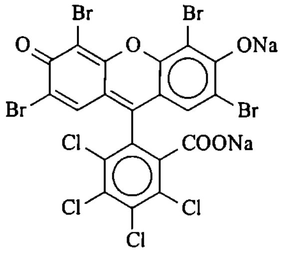
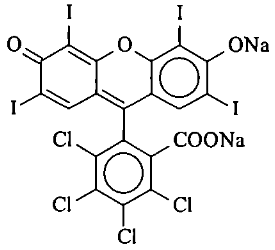
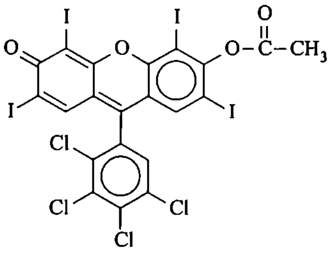
$$DH\cdot^+ \longrightarrow D\cdot + H^+$$

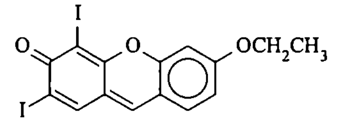
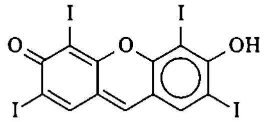
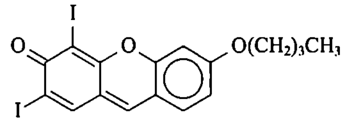
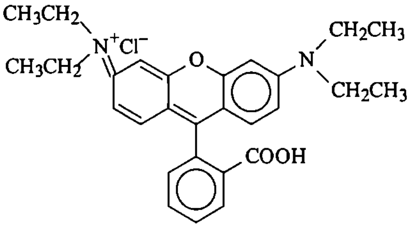
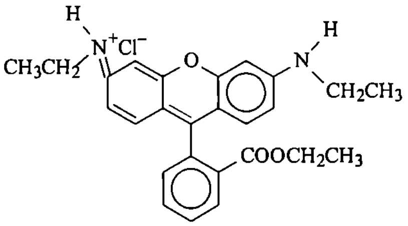
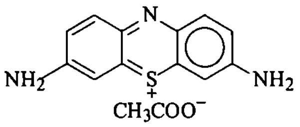
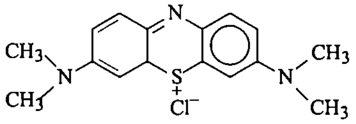
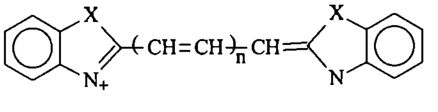
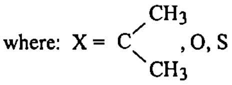
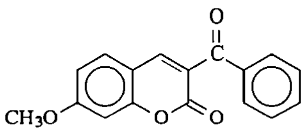
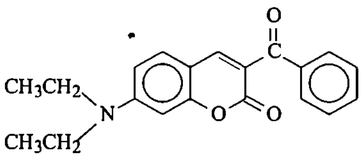
$$\underset{\text{proton transfer}}{(dye^+X^-)\cdot^- + H^+ \longrightarrow (dye^+X^-)H\cdot}$$

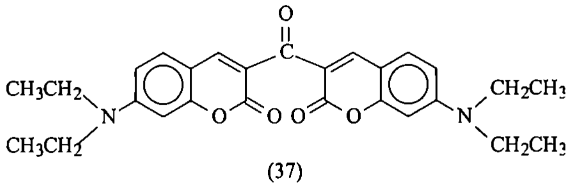
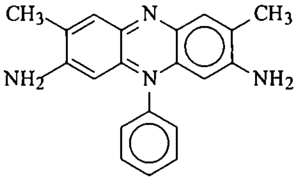
$$D\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

$$(dye^+X^-)H\cdot + \text{momer} \longrightarrow \text{polymerization (if any?)}$$

Table 1. Photoreducible dyes

Dye type	Name	Structure	Absorption, λmax, nm
1	2	3	4
Acridine dyes	Acriflavine	 (19)	460
	Acridine Orange	 (20)	490
Xanthene dyes	Eosin	 (21)	510
	Eosin B	 (22)	514
	Erythrosin B	 (23)	525
	Fluorescein	 (24)	565
	Rose Bengal	 (25)	548
	RBAX	 (26)	492

1	2	3	4
	Fluorone dyes DIEF	 (27)	470
	TIHF	 (28)	538
	DIBF	 (29)	470
	Rhodamine B	 (30)	556
	Rhodamine 6G	 (31)	420
Thiazine dyes	Thionin	 (32)	
	Methylene Blue	 (33)	668
Polymethine dyes	Cyanine dyes	 (34)  where: X = $C\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$, O, S	n = 0 ~ 400—480 n = 1 ~ 480—570 n = 2 ~ 580—650 n = 3 ~ 690—750
Coumarin dyes		 (35)	343
		 (36)	415

1	2	3	4
		 (37)	449
Safranine dyes	Safranine T	 (38)	420—430

2. Photooxidation of a dye (dye $^+X^-$, electron donor) in the presence of co-initiator (electron acceptor, A).

$$\mathrm{dye^+X^-} \xrightarrow{h\nu} {}^1(\mathrm{dye^+X^-})^* \longrightarrow {}^3(\mathrm{dye^+X^-})^*$$

$${}^3(\mathrm{dye^+X^-})^* + \mathrm{A} \xrightarrow[\text{electron transfer}]{} (\mathrm{dye^+X^-})^{\cdot +} + \mathrm{A}^{\cdot -}$$

$$(\mathrm{D^+X^-})^{\cdot +} + \text{monomer} \longrightarrow \text{polymerization (if any?)}$$

$$\mathrm{A}^{\cdot -} + \text{monomer} \longrightarrow \text{polymerization}$$

Initiation of polymerization by photoreducible dyes (Table 1) in the presence of different co-initiators (electron donors) is very common, whereas polymerization initiated by photooxidation of dye in the presence of an electron acceptor is very rare. For example, thiazine dyes such as methylene blue can react both as electron acceptors in the presence of *N*-phenylglycine [94, 95] as a co-initiator, or as electron donor in the presence of benzyltrimethylstannane as a co-initiator (see below) [96].

All photoreducible dyes have maximum absorption in the visible light spectrum (Table 1). A suitable dye/co-initiator system must first exhibit a high absorption in the wavelength delivered by visible light sources (lasers) (Fig. 3) and, secondly, efficiently generate the reactive initiating radicals [97]. During photopolymerization most of the dyes bleach, permitting substantial depth of cure [98].

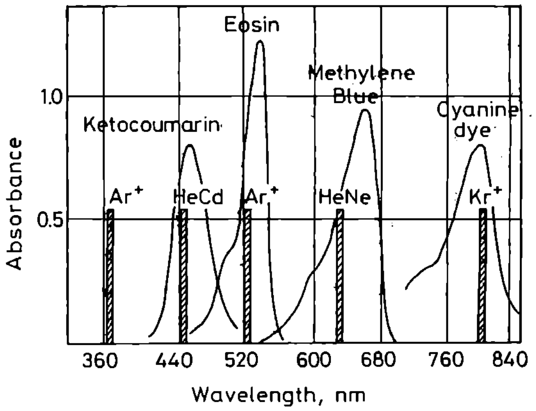


Fig. 3. Matching between the absorption spectra of typical dye photoinitiators and lines of some lasers [97]

Dyes/amine systems

Tertiary amines (AMH) are one of the very important classes of electron donors (reductants) used in combination with photoreducible dyes [65, 99]. Photoreduction, abstraction of hydrogen by an excited dye from amine, was proposed as the initial process in the oxidation by oxygen of tertiary aliphatic amines, sensitized by thiazine dyes and xanthene dyes [100—102]. Secondary and primary aliphatic amines show low reactivity, whereas aniline, dialkylanilines, and DABCO (1,4-diazabicyclo[2,2,2]octane) are unreactive. Flash photolysis of solution of the dyes and tertiary amines in methanol has led to spectra of transients attributable to the radical ions of the dyes. Irradiation of the dye (dye $^+X^-$)/amine (AMH) systems caused formation of a reactive amine radical (AM·) by the electron/proton transfer mechanism. The amine radical is, first of all, responsible for the initiation of polymerization.

$$\mathrm{dye^+X^-} \xrightarrow{h\nu} {}^1(\mathrm{dye^+X^-})^* \longrightarrow {}^3(\mathrm{dye^+X^-})^*$$

$${}^3(\mathrm{dye^+X^-})^* + \mathrm{AMH} \xrightarrow[\text{electron transfer}]{} (\mathrm{dye^+X^-})^{\cdot -} + \mathrm{AMH}^{\cdot +}$$

$$\mathrm{AMH}^{\cdot +} \xrightarrow[\text{proton transfer}]{} \mathrm{H^+} + \mathrm{AM}\cdot$$

$$\mathrm{AM}\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

A wide variety of photoreducible dyes (Table 1) when used in conjuction with tertiary amines act as initiators of polymerization in the visible region [103—107].

N-phenylglycine is the most efficient amine type co-initiator acting by unimolecular fragmentation [84, 96, 108].

$${}^3(\mathrm{dye^+X^-})^* + \mathrm{C_6H_5-NH-CH_2-COOH} \longrightarrow$$
$$\longrightarrow (\mathrm{dye^+X^-})^{\cdot -} + \mathrm{C_6H_5-NH-CH_2-COOH}$$

$$C_6H_5-NH-CH_2-COOH \longrightarrow$$
$$\longrightarrow C_6H_5-NH-CH_2 + CO_2 + H^+$$

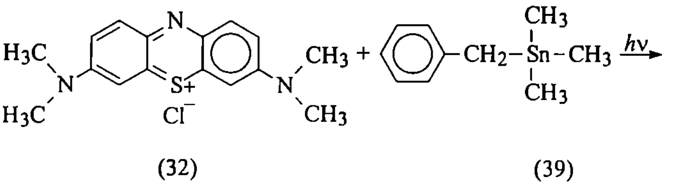
$$C_6H_5-NH-CH_2\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

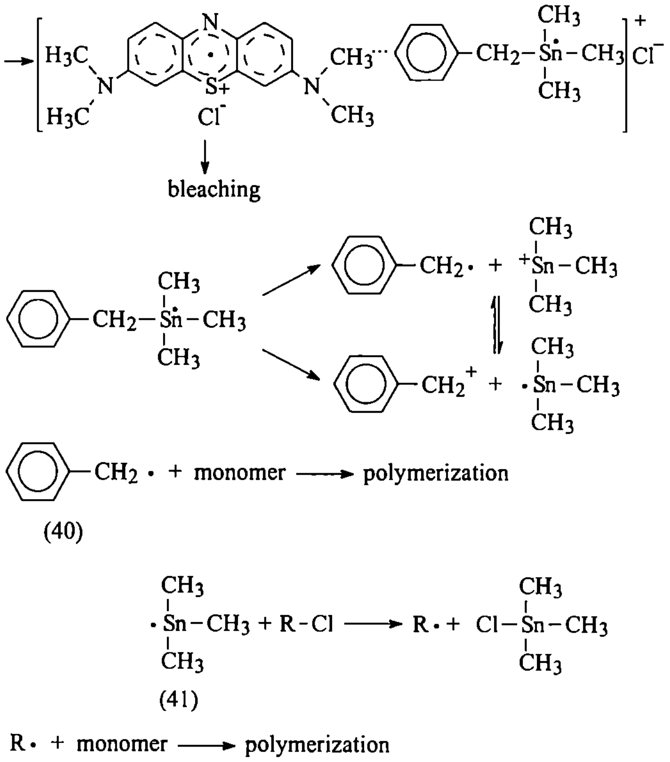
The role of dye/*N*-phenylglycine systems in the photoinitiation of polymerization has been amply discussed [94, 95, 102, 109—115]. Systems of three components, *viz.*, dye/amine/onium salts, are excellent photoinitiators for polymerization of acrylates [116—118].

Methylene blue/benzyltrimethylstannane system

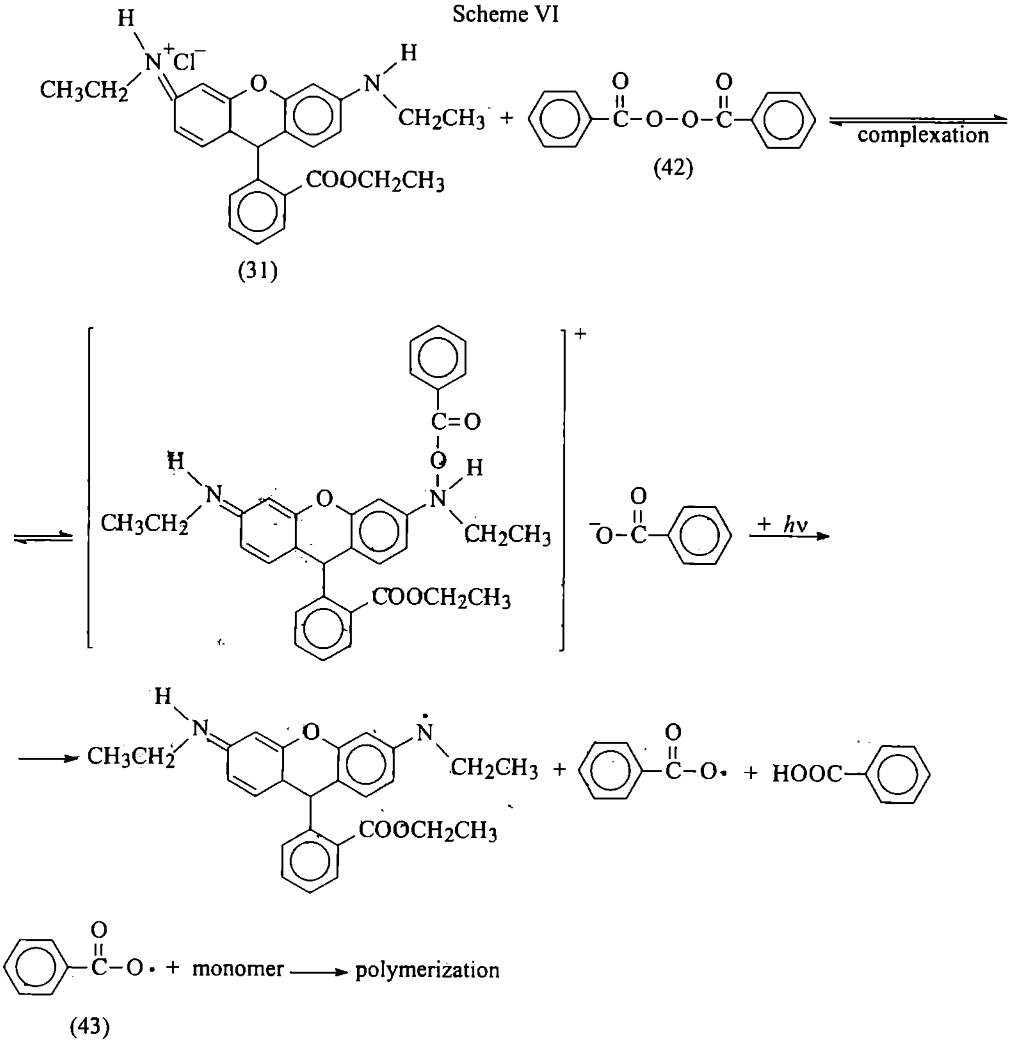
Methylene blue (33) can react as an electron donor in the presence of benzyltrimethylstannane (39) as a co-initiator [96] (Scheme V).

Scheme V

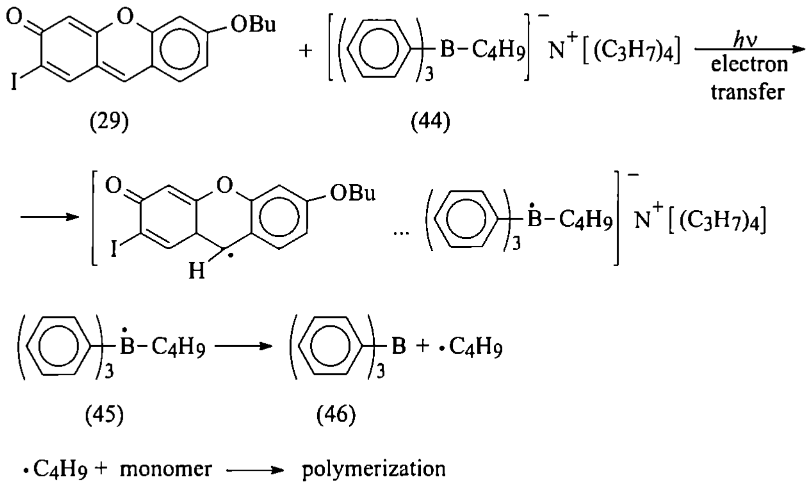




Scheme VI



Scheme VII



This reaction yields a benzyl radical (40) and a trimethylstannane radical (41) which can initiate polymerization. However, the radical (41) is reactive only in the presence of chlorocarbon compounds.

Dyes/peroxide systems

Several dyes like thioxanthenes [119, 120], thiazines [120—122], coumarins [123] and ketocoumarins [120] accelerate photodecomposition of peroxides such as benzoyl peroxide or *tert*-butylbenzoate. Rhodamine 6G (31) gives a salt with benzoyl peroxide (42), which upon excitation by visible light, decomposes to give initiating benzoyl radicals (43) [124] (Scheme VI).

Xanthene dyes/borate systems

Several xanthene dyes (electron acceptors) such as decarboxylated and further acetylated Rose Bengal (RBAX) (26) [125], and 2,4-diiodo-6-butoxy-3-fluorene (DIBF) (29) [97, 126—130] form with tetrabutylammonium triarylalkyl borate (electron donor) (44) very efficient photoinitiating systems based on the electron transfer mechanism. The boranyl radical (45) formed undergoes a fragmentation reaction to give a stable triaryl borane (46) and an alkyl radical. The latter initiate polymerization reaction (Scheme VII).

Fluorone dyes/onium salt/amine systems

Fluorone dyes (such as 2,4-diiodo-6-ethoxyfluorone) (DIEF) (27) 2,3,5,7-tetraiodo-6-hydroxyfluorone (TIHF) (28) combined with onium salts (diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroantimonate, *etc.*) and amines (*e.g.*, *N*,*N*-dimethyl-2,6-diisopropylaniline) as co-initiators greatly improve photocuring of acrylate resins [97, 131]. The following mechanisms are involved in this three-component dye, onium salt ($\text{ArI}^+\text{ArSbF}_6^-$) (46) and amine (AMH) system [97, 98, 131].

$$^3(\text{dye}^+X^-)^* + \text{ArI}^+\text{ArSbF}_6^- \longrightarrow (\text{dye}^+X^-)^\bullet + \text{Ar}_2\text{I}^\bullet + \text{SbF}_6$$

$$\text{Ar}_2\text{I}^\bullet \longrightarrow \text{ArI} + \text{Ar}^\bullet$$

$$\text{Ar}^\bullet + \text{AMH} \longrightarrow \text{ArH} + \text{AM}^\bullet$$

$$\text{AM}^\bullet + \text{monomer} \longrightarrow \text{polymerization}$$

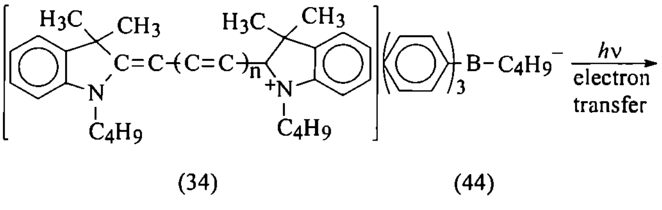
In this hybrid donor/acceptor mechanism, the excited dye both donates an electron to the onium salt and accepts an electron from the amine. The dye/amine system results in a significant opportunity for the back electron transfer diminishing the effectiveness of this process. The dye/onium salt system, however, results in immediate decomposition of the onium salt with no possibility for back electron transfer. Aryl radical (Ar$^\bullet$) can initiate polymerization, but with a low efficiency. The preferred reaction is a hydrogen atom abstraction by Ar$^\bullet$ radicals from the amine forming the amine radical which is a very effective polymerization initiator. Optimized molar ratios of the dye, onium salt and amine result in a synergetic effect more efficient than dye and either onium or amine alone.

Cyanine dyes/borate systems

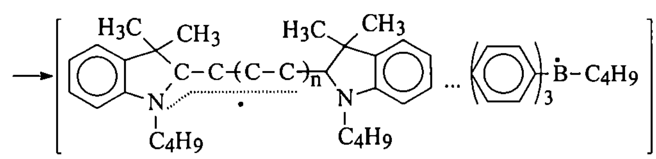
Cationic cyanine dyes (34) have sharp absorption maxima in the visible light spectrum (400—800 nm), possessing a high molar absorption coefficient (ε = 50,000—250,000), which depends on the chain length of the ethylene bridge (each additional double bond fragment induces a red-shift of about 100 nm) and the type of heterocycles (Table 1) [93].

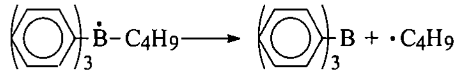
Cyanine dyes (34) in the presence of triarylalkylborates (44) are very efficient photoinitiators of polymerization; however, this reaction is very sensitive to air (oxygen) [132—134]. Electron transfer occurs from the borate [135] to the excited state of cyanine dye [125—142].

Scheme VIII



(34) (44)





(45) (46)

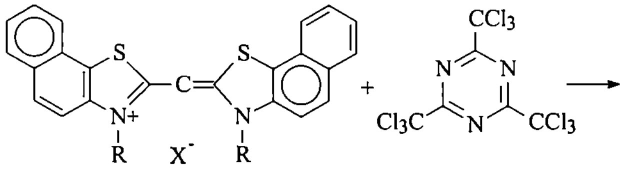
$\cdot C_4H_9$ + monomer ⟶ polymerization

The boranyl radical (45) formed undergoes a fragmentation reaction to give a stable triaryl borane (46) and an alkyl radical. The latter initiate polymerization reaction (Scheme VIII).

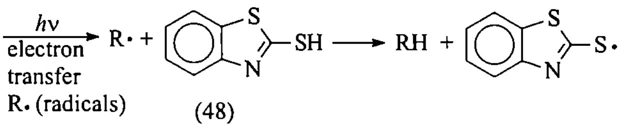
Cyanine dyes/triazine/mercaptan systems

Cyanine (or merocyanine) (34) or coumarin dyes (35—37) in the presence of 2,4,6-tris(trichloromethyl)-1,3,5-triazine (47) and mercaptans [like 2-mercaptobenzimidazole or 2-mercapto-benzthiazole (48), acting as chain transfer agent] are very efficient polymerizing systems [143, 144]. Polymerization is initiated by the mercaptan sulfur centered radical (49) (Scheme IX).

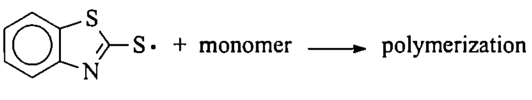
Scheme IX



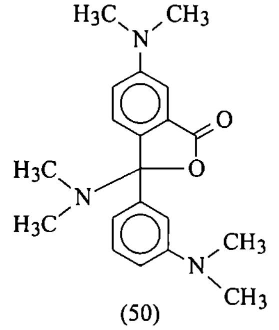
(34) (47)



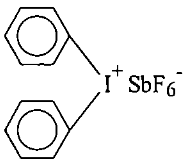
(48)



(49)



(50)



(51)

Triarylmethane dyes/diphenyliodonium salts systems

Visible light irradiated Crystal Violet Lactone (CVL) (50) in the presence of diphenyliodonium salts (51) produces free radicals which can initiate polymerization [145, 146].

$$\mathrm{CVL} \xrightarrow{h\nu} {}^1\mathrm{CVL}^* \longrightarrow {}^3\mathrm{CVL}^*$$

$$^3\mathrm{CVL}^* + \mathrm{RH} \longrightarrow \mathrm{CVLH}\cdot + \mathrm{R}\cdot$$

$$\mathrm{CVLH}\cdot + \mathrm{ArI^+ArSbF_6^-} \longrightarrow \mathrm{CVLH^+} + \mathrm{Ar_2I}\cdot + \mathrm{SbF_6^-}$$

$$\mathrm{Ar_2I}\cdot \longrightarrow \mathrm{ArI} + \mathrm{Ar}\cdot$$

$$\mathrm{R}\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

$$\mathrm{Ar}\cdot + \text{monomer} \longrightarrow \text{polymerization}$$

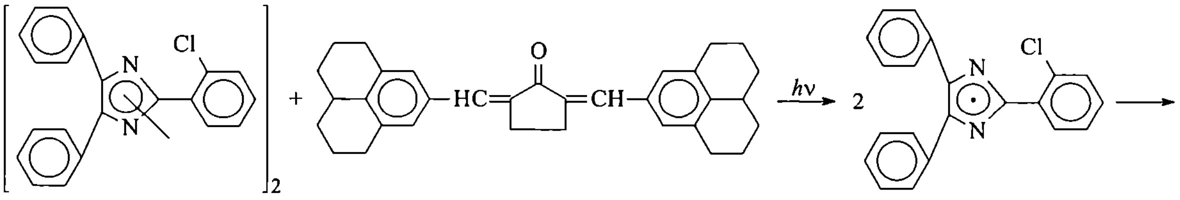
The reaction can be sensitized by triplet sensitizers [147], and ketocoumarins [148, 149].

Lophine/julolidine/mercaptobenzoxazole system

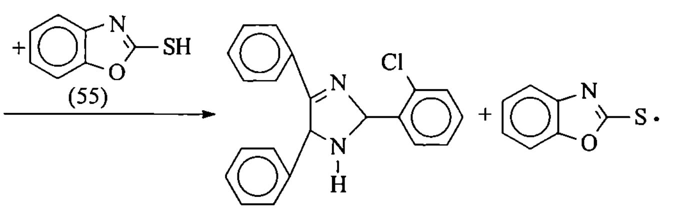
Lophine (2,4,5-triphenylimidazole) (52) can be readily photocleaved (at 532 nm from a pulsed Nd:YAG laser) in the presence of photosensitizer julolidine (2,5-bis[(1H,5H-benzo[i,j]quinolizin-1-yl)methylene]cyclopentanone (53) to lophyl radical (54), which abstracts a hydrogen atom from mercaptobenzoxazole (55) (chain transfer agent) to give a sulfur centered radical (56) [150—152] (Scheme X).

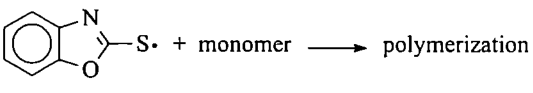
Reaction between lophine and julolidine only involves the singlet excited, since the lophyl radicals are formed mostly through singlet state dissociation

Scheme X



(52) (53) (54)





(56)

[153—155]. The lophyl radical alone is a poor initiator of free radical polymerization, because of both high stability and steric factors. However, the radical is an excellent hydrogen atom abstractor and this can be exploited in initiation by using co-initiator compounds such as a chain transfer agent to form secondary radicals that can initiate polymerization [152, 156—159]. Suitable sensitizers include also xanthene or acridine dyes [88].

Ketocoumarin/co-initiator systems

3-Ketocoumarins (35—37) have absorption maxima between 330 nm and 450 nm with triplet energies ranging from 48 to 60 kcal mol^{-1} [160]. Usually initiation of polymerization does not occur upon interaction of the triplet state of coumarin and the monomer. The proper combination of 3-coumarins with a suitable co-initiator capable of undergoing electron transfer, provides highly reactive photoinitiating system in the visible part of the spectrum [161, 162]. The substitution pattern of the 3-ketocoumarins (37) determines if the excited compound will act as an electron acceptor or as an electron donor (7-dialkylamino-substituted ketocoumarins). Accordingly, an electron donor (such as ethyl para-dimethylaminobenzoate) or electron acceptor (such as alkoxypyridinium salts) (57) has to be chosen as co-initiator (Scheme XI).

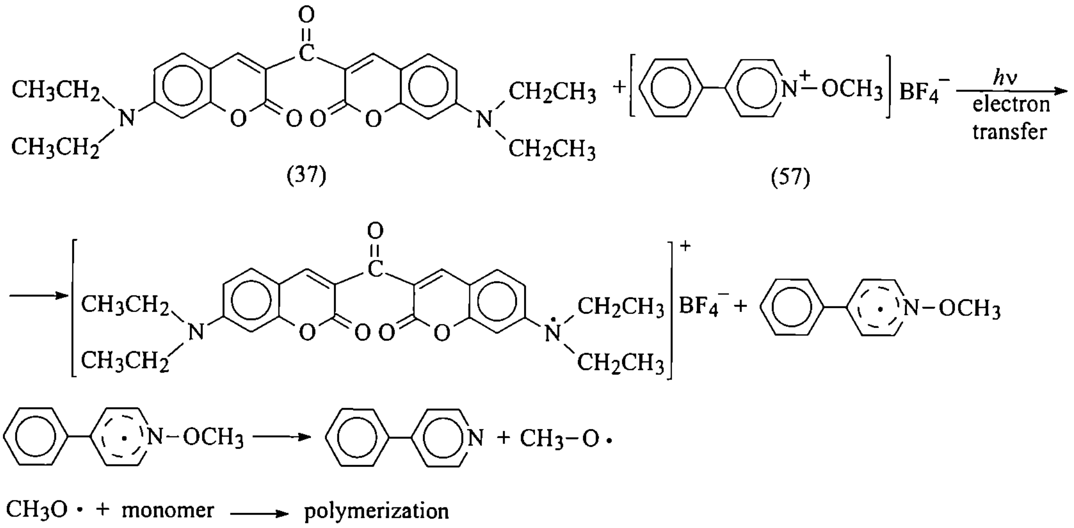
However, 7-dialkylamino-substituted ketocoumarins (36) in the presence of *N*-phenylglycine (53) [163] or substituted acetic acid derivatives [164] can also react as electron acceptors (Scheme XII).

In the presence of *N*-phenylglycine and diphenyl iodonium salt ketocoumarin dyes have a higher reactivity than in the presence of amine only [90, 165].

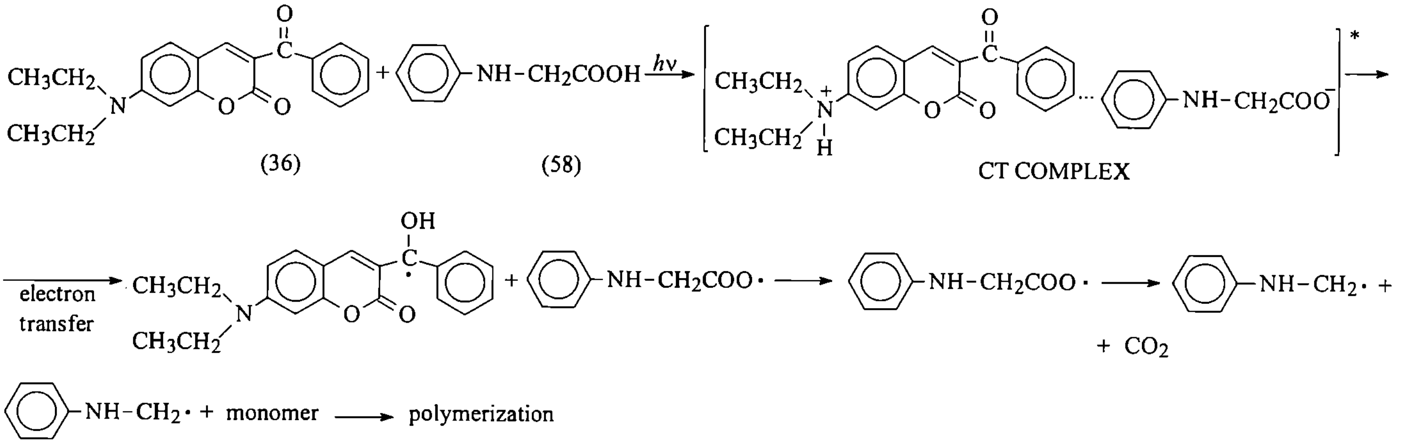
APPLICATIONS OF VISIBLE LIGHT PHOTOINITIATORS SYSTEMS

Visible radiation curing has become an integral part of the technology used in the application of surface coatings including printing inks. Visible radiation curing employ common visible light sources [166, 167] or lasers [168, 169] in inducing polymerization and rapid conversion of reactive liquids to solids. Photoinitiator/co-initiator systems absorb radiation energy and the free radicals formed begin polymerization that al-

Scheme XI



Scheme XII



most immediately converts the liquid into a solid cured film. Visible radiation curing becomes a new future technology and will be a rapidly growing sector of the coating industry.

Visible light radiation curings have also found applications in reprography (printing plates, integrated circuits, photoresists, solder masks). More recently, laser induced 3D (three dimensional) curing, holographic recording and nano-scale micromechanics have been developed. Photopolymers used in electronic and printing industries usually consist of a plasticized polymer matrix, photoinitiator/co-initiator system, photosensitizer monomer, and a variety of chain transfer agents [65, 85, 170—175].

Visible light radiation curing is widely used in the clinical photocuring of polymeric resins in dentistry [76, 77, 80]. The photocuring is carried out under special conditions, which differ from any type of industrially applied photocuring. The whole procedure is performed *in vivo* and is restricted by biophysiological demands such as the oral temperature (which should not exceed 50°C); visible light over 400 nm has to be used to avoid photocancerogenic and photoallergic effects caused by UV radiation and to eliminate the risk of tissue burning [176]. Photocuring is always made in the presence of air, water and saliva (the last can be technically limited to some extent). There are also very strict toxic, neurotoxic, cancerogenic, mutagenic, and allergic restrictions for the use of dental formulation components, *e.g.*, photoinitiator systems. Only visible light photoinitiator systems can be used for the photocuring of dental materials. The most common photoinitiator used is the camphorquinone/amine system. However, the employed amines belong to hepatoxins, which can cause activation of toxic substances in the liver and which can act as hepatocarcinogens [177]. An amine such as *N,N*-dimethyl-*p*-toluidine used as co-initiator is cancerogenic and mutagenic [178], but in spite of this it is widely used in commercially available dental compositions to accelerate the polymerization process.

ACKNOWLEDGMENTS

The Authors gratefully acknowledge the support of the Swedish Institute, who generously provided a post-doc Stipend for Dr. J. Jakubiak enabling this project to be continued.

REFERENCES

[1] Lohse F., Zweifel H.: *Adv. Polym. Sci.* 1986, **78**, 61. [2] Klingert B., Riediker M., Rollof A.: *Comments Inorg. Chem.* 1988, **7**,109. [3] Dietliker K.K.: in "Chemistry & Technology of UV/EB Formulation for Coatings", Inks & Paints, Vol. III, "Photoinitiators for Free Radical and Cationic Polymerization" (ed. Oldring P. K. T.), SITA Technology Ltd., London 1991, p. 228. [4] Cunningham A. F. Desorby A.: in "Radiation Curing in Polymer Science and Technology", Vol. II, Photoinitiating Systems (eds. Fouassier J. P., Rabek J. F.), Elsevier Applied Science, London 1993, p. 323. [5] Gatechair L. R., Blurnenstain G. M., Schirmann P. J.: *U. S. Patent* 4 707 432. [6] Chrisope D. R., Schuster G. B.: *Organometallics* 1989, **8**, 2737. [7] Kitamura K.: *Japanese Patent* 1-152109. [8] Koerner von Gustorf., Grewels F. W.: *Fortsch. Chem. Forsch.* 1969, **13**, 366. [9] Rabek J. F.: *Proc. Rad. Tech. Europe 91*, p.618. [10] Giannotii G., Gaspard S., Kraus P.: in "Photoinduced Electron Transfer, Part D, Photoinduced Electron Transfer Reactions: Inorganic Substrates and Applications" (eds. Fox M. A., Chanon M.), Elsevier.

[11] Tsubakiyama K., Fjiusaki S. J.: *J. Polym Sci.* 1972, **B10**, 341. [12] Tsubakiyama K., Fjiusaki S. J, Tabata E., Nakahara S.: *J. Macromol. Sci. Chem.* 1991, **A28**, 557. [13] Tsunooka M., Tanaka M.: *J. Polym. Chem.* 1978, **B16**, 119. [14] Nesmeyanov A. N., Vannikov A. V., Zverkov V. A. Balabanova L. V., Shverkhgeimer M. A., Kochetkova N. S.: *Dokl. Akad. Nauk SSSR* 1978, **A28**, 557. [15] Pouerrau D. B., Geoffrey G.: *Adv. Organomet. Chem.* 1985, **24**, 249. [16] Finter J., Riediker M., Rohde O., Rotzinger B.: *Makromol. Chem. Macromol. Symp.* 1989, **24**,177. [17] Riediker M., Roth M., Buehier N., Berger J.: *Eur. Patent Appl.* 12 223 (1983). [18] Riediker M., Meier K., Zweifel H.: *Eur. Patent Appl.* 186 626 (1984). [19] Riediker M., Steiner E., Beyeler H., Rembold M., Sitek F.: *Eur. Patent Appl.* 255 486 (1986). [20] Klingert B., Rembold M., Sitek, F.: *Eur. Patent Appl.* 256 981 (1986).

[21] Riediker M., Steiner E., Beyeler H., Sitek F., Huesler R.: *Eur. Patent Appl.* 318 893 (1987). [22] Klingert B., Steiner E., Rembold M., Huesler R., Roloff A.: *Eur. Patent Appl.* 318 894 (1987). [23] Angerer H., Desobry V., Riediker M., Spahni H., Rembold M.: Proc. Conf. Radiat. Curing Asia, Tokyo, Japan, 1988, paper nr 3M06, p. 461. [24] Steiner E., Beyeler H., Riediker M., Desobry V., Dietliker K., Huesler R.: *Eur. Patent Appl.* 401 165 (1989). [25] Steiner E., Beyeler H., Huesler R.: *Eur. Patent Appl.* 401 166 (1989). [26] Rutsch W., Angerer H., Desobry V., Dietliker H., Huesler R.: Proc. 16th Intern. Conf. in Organic Coatings Science and Technology, July 9—13, 1990, Athens, Greece, p. 423. [27] Alt H., Rausch M. D.: *J. Am. Chem. Soc.* 1974, **96**, 5936. [28] Rausch M. D., Boon W. H., Alt H.: *J. Organomet. Chem.* 1977, **141**,299. [29] Van Leuwen P. W. N. M., Van der Heijden H., Roobeek C.F., Frijns J. H. G. J.: *Organomet. Chem.* 1981, **209**, 169. [30] Rausch M. D., Boon W. H., Mintz E. A.: *J. Organomet. Chem.* 1978, **159**,81.

[31] Roloff A., Meier K., Riediker M.: *Pure Appl. Chem.* 1986, **58**, 1267. [32] Finter J., Riediker M., Rohde O., Rotzinger B.: Proc. 1st Meeting Eur. Polym., Fed., Eur. Symp. Polym. Mat., Lyon, France, 1987, paper ED03. [33] Klingert B., Roloff A., Urwyler B., Wirtz J.: *Helv. Chim. Acta* 1988, **71**, 1858. [34] Doha T., Watanabe B.: *Eur. Patent Appl.* 497 552 (1992). [35] Bamford C. H., Puddwphatt R. J., Slater D. M.: *J. Organomet. Chem.* 1978, **150**, C31. [36] Tung H. S., Brubaker Jr. C. H.: *Inorg. Chim. Acta* 1981, **52**, 197. [37] Brown-Wensley K. A., De Voe R. J., Palazzotto M. C.: *Europ. Patent Appl.* 306 161

(1987). [38] Palazzotto M. C., Brown-Wensley K. A., De Voe R. J.: *Europ. Patent Appl.* 306 162 (1987). [39] Wagner H. M., Purbrick M. D.: *J. Photogr. Sci.* 1981, **29**, 230. [40] Adair P. C., Gottschalk P.: *US Patent* 4954414 (1988).

[41] Evans T. R., Leermakers P. A.: *J. Am. Chem. Soc.* 1967, **89**, 4380. [42] Charney E., Tsai L.: *J. Am. Chem. Soc.* 1971, **93**, 7123. [43] Luk C. K., Richardson F. S.: *J. Am. Chem. Soc.* 1974, **96**, 2006. [44] Singh A., Scott A. R., Sopchyshyn F.: *J. Phys. Chem.* 1969, **75**, 2633. [45] Eloy D., Escaffre P., Gautron R., Jardon P.: *J. Chim. Phys. Biol.* 1992, **89**, 897. [46] Depew M. C., Wan J. K. S.: *J. Phys. Chem.* 1986, **90**, 6597. [47] Monroe B. M., Weiner S. A.: *J. Am. Chem. Soc.* 1969, **91**, 450. [48] Russell G. A., Chang K. Y.: *J. Am. Chem. Soc.* 1965, **87**,4381. [49] Russell G. A., Chang K. Y., Jefford C. W.: *J. Am. Chem. Soc.* 1965, **87**, 4383. [50] Sur P., Colpa J. P., Wan J. K. S.: *Chem. Phys.* 1986, **108**, 133.

[51] Fujimori Y., Kaneko T., Kaku T., Yoshiko N., Nishide H Tscuchida E.: *Polym. Adv. Technol.* 1992, **3**, 37. [52] Andrzejewska E., Andrzejewski M.: *J. Polym. Sci. A1* 1998, **36**, 665. [53] Andrzejewska E., Andrzejewski M.: *J. Polym. Sci. A1.* 1993, **31**, 2365. [54] Anseth K. S., Newmans S. M., Bowman C. M.: *Adv. Polym. Sci.* 1995, **122**, 177. [55] Nie J., Lindén L- Å., Rabek J. F., Fouassier J. P., Morlet-Savary F., Ścigalski F., Wrzyszczynski A., Andrzejewska A.: *Acta Polym.* 1998, **49**, 145. [56] Andrzejewska E., Andrzejewski M., Lindén L- Å., Rabek J. F.: *Polimery* 1998, **43**, 427. [57] Andrzejewska E., Lindén L- Å., Rabek J. F.: *Macromol. Chem. Phys.* 1998, **199**, 441. [58] Nie J., Andrzejewska A., Lindén L- Å., Rabek J. F., Fouassier J. P., Ścigalski F., Wrzyszczynski A.: *Macromol. Chem. Phys.* (in print). [59] Nie J., Lindén L- Å., Rabek J. F., Ekstrand J.: *Angew. Makromol. Chem.* 1998, **257**, 47. [60] Nie J., Lindén L- Å., Rabek J. F., Ekstrand J.: *Europ. Polm. J.* (in print).

[61] Nie J., Lindén L- Å., Rabek J. F., Ekstrand J.: *Acta Odontol., Scand.* 1999, **57**, 1. [62] Nie J., Lindén L- Å., Rabek J. F.: *Polym. Intern.* 1999, **48**, 129. [63] Cook W. D.: *Polymer* 1992, **33**, 600. [64] Davidson R. S.: in "Radiation Curing in Polymer Science and Technology", vol. III (eds. Fouassier J. P., Rabek J. F.), Elsevier Applied Science, London 1993, p. 153. [65] Fouassier J. P.: " Photonitiation, Photopolymerization and Photocuring; Fundamentals and Applications", Hanser Publ., Munich 1995. [66] Mattay J., Vandenhoff M.: *Topics Curr. Chem.* 1991, **159**, 219. [67] Mizuno K., Ueda H., Otsuji Y.: *Chem. Lett.* 1981, 1237. [68] Masuhara H., Mataga M.: *Acc. Chem. Res.* 1981, **14**, 2684. [69] Lewis F. D.: *Acc. Chem. Res.* 1986, **19**, 401. [70] Devadoss C., Fessendem R. W., Richard W.: *J. Phys.* 1996, **95**, 7253.

[71] Kucybala Z., Pietrzak M., Paczkowski J., Lindén L- Å., Rabek J. F.: *Polymer* 1996, **37**, 4585. [72] Peutzfeld A., Asmussen E.: *Acta Odontol. Scand.* 1989, 229. [73] Cook W. D.: *J. Polym. Sci.* 1933, Al, **31**, 1053. [74] Cook W. D.: *Polymer* 1992, **33**, 2152. [75] Lindén L- Å.: *Proc. Rad. Tech Europe 93* 1993, 557. [76] Lindén L-Å.: in "Radiation Curing in Polymer Science and Technology" (eds. Fouassier J. P., Rabek J. F.), Vol. IV, Ch. 8, Elsevier Science Publisher, London 1993, p. 466. [77] Lindén L-Å.: *Proc. Indian Acad. Sci.* 1993, **105**, 405. [78] Adamczak E., Lindén L- Å., Rabek J. F., Wrzyszczynski A.: Proc. RadTech Asia, 1995, p. 196. [79] Wrzyszczynski A., Adamczak E., Lindén L- Å., Morge S., Rabek J. F.: Proc. RadTech Europe 95, 107. [80] Lindén L- Å.: *Plast. Rubber Compl. Proc. Appl.* 1997, **26**,91.

[81] Rabek J. F., Lindén L- Å., Andrzejewska E.: Proc. RadTech Europe, 1997, p. 135. [82] Rabek J. F., Fouassier J. P., Lindén L- Å., Nie J., Andrzejewska E., Jakubiak J., Paczkowski J., Wrzyszczynski A., Sionkowska A.: in "Photosensitive Systems for Photopolymerization Reactions" (ed. Fouassier J. P.), Research Trends, 1999 (in print). [83] Ketley A. D.: *J. Radiat. Curing* 1982, **(3)**, 35. [84] Eaton D. F.: *Adv. Photochem.* 1986, **13**, 427. [85] Timpe H. J., Baumann H.: Photopolymere; Principen und Anwedungen, VEB Deutscher Verlag für Grund-stoffindustrie, Leipzig 1985. [86] Fouassier J. P.: *J. Radiat. Curing* 1990, **(2)**, 28. [87] Dietliker K. K.: "Chemistry & Technology of UV & EB Formulation for Coating, Inks & Paints" (ed. Oldring P. K. T.), Vol.3., Sita Technology Ltd., London 1991, p. 239. [88] Monroe B. M., Weed G. C.: *Chem. Rev.* 1993, **93**, 435. [89] Timpe H. J., Jockusch S., Korner K.: in "Radiation Curing in Polymer Science and Technology", Vol. II, Photoinitiating Systems (eds. Fouassier J. P., Rabek J. F.), Elsevier Applied Science, London 1993, p. 575. [90] Morlet-Savary F., Fouassier J. P., Parret S., Erddalane A.: *Polimery* 1994, **39**, 434.

[91] Lindén L- Å., Paczkowski J., Rabek J. F., Wrzyszczynski A.: *Polimery* 1999, **44**, 161. [92] Paczkowski J., Kucybala Z., Scigalski F., Wrzyszczynski A.: in "Photosensitive Systems for Photopolymerization Reactions" (ed. Fouassier J. P.), Research Trends, 1999 (in print). [93] Takemura F.: *Bull. Chem. Soc. Jpn.* 1962, **35**, 1073. [94] Matsumoto S.: *Bull. Chem. Soc. Jpn.* 1962, **35**, 1860 and 1866. [95] Matsumoto S.: *Bull. Chem. Soc. Jpn.* 1964, **37**, 491 and 499. [96] Eaton D. F.: *Photogr. Sci. Eng.* 1979, **23**, 150. [97] Fouassier J. P., Carre C., Lougnot D. J.: SPIE Photopolymer Device *Phys. Chem. Appl.* 1990, **121**, 201. [98] Marino T., Long O. Y., Neckers D. C.: "I&EC Research" 1955, **34**, 4549. [99] Rabek J. F.: "Mechanisms of Photophysical Processes and Photochemical Reactions in Polmers; Theory and Practice, Wiley, Chichester, 1987. [100] Bartholomew R. F., Davidson R. S.: *Chem. Commun.* 1971,1174.

[101] Bartholomew R. F., Davidson R. S.: *J. Chem. Soc. C* 1971, 2347. [102] Davidson R. S.: *J. Photochem. Photobiol., A. Chem.* 1993, **73**, 81. [103] Chesneau E., Fouassier J. P.: *Angw. Macromol. Chem.* 1985, **135**, 41. [104] Fouassier J. P., Wu S. K.: *J. Appl. Polym. Sci.* 1992, **44**,1779. [105] Paczkowski J., Neckers D. C.: *Chemtracts Macromol. Chem.* 1992, **3**, 75. [106] Paczkowska B., Paczkowski J., Neckers D. C.: *Polimery* 1994, **39**, 527. [107] Previtali C. M., Bertolotti S. G., Neumann M. G., Pastre I. A., Rufs A. M., Encinas M. V.: *Macromolecules* 1994, **27**, 7454. [108] Yamaoka T., Zhang Y. C., Koseki K.: *J. Appl. Polym. Sci.* 1989, **38**, 1271. [109] Paczkowski J., Neckers

D. C.: *Macromolecules* 1992, **25**, 548. [110] Torres-Filho A., Neckers D. C.: *J. Appl. Polym. Sci.* 1994, **51**, 931.

[111] Tanabe T., Torres-Filho A., Neckers D. C.: *J. Polym. Sci.* 1995, **Al 33**, 1691. [112] Paczkowski J., Kucybala Z.: *Macromolecules* 1995, **28**, 269. [113] Paczkowski J., Pietrzak M., Kucybala Z.: *Macromolecules* 1996, **29**, 5057. [114] Kucybala Z., Pietrzak M., Paczkowski J.: *J. Mater. Sci.* 1988, **10**, 3555. [115] Kabatc J., Kucybala Z., Pietrzak M., Scigalski F., Paczkowski J.: *Polymer* 1999, **40**, 735. [116] Kawabata M., Takimoto Y.: *Photopolym. Sci.* 1990, **2**, 147. [117] Fouassier J. P., Chesneau E.: *Makromol. Chem.* 1991, **192**, 1307. [118] Fouassier J. P., Wu S. K.: *J. Appl. Polym. Sci.* 1992, **44**, 1779. [119] Restaino A. J., Lu R. T. Y.: *Ger. Patent* 2410218 (1973). [120] Yamaoka T., Nakamura Y., Koseki K., Shirosaki T.: *Polym. for Adv. Technol.* 1990, **1**, 287.

[121] Yamaoka T., Koseki K., Goto Y.: *Belg. Patent* 89-7694 (1983). [122] Kawabata M., Kimoto K., Takimoto Y.: *Eur. Patent Appl.* 211615 (1986). [123] Yamaoka T., Koseki K., Shirosaki T.: *Jpn. Patent* 6,323,901 (1988). [124] Goh P., Biswas P., Niyogi U.: *J. Polym. Sci.* 1986, **A24**, 1053. [125] Valdez-Aquilera O., Pathak C. P., Shi J., Watson D. C.: *Macromolecules* 1992, **25**, 541. [126] Shi J., Zhang X., Neckers C.: *J. Org. Chem.* 1992, **57**, 4418. [127] Klimtchuk E., Rodgers M. A. J., Neckers D. C.: *J. Phys. Chem.* 1992, **96**, 9817. [128] Shi J., Zhang X., Neckers D. C.: *Tetrahedron Lett.* 1993, **34**, 6013. [129] Polykarpov A. Y., Hassoon S., Neckers D. C.: *Macromolecules* 1996, **29**, 8274. [130] Sarker A. M., Polykarpov A. Y., Neckers D. C., de Raaff A. M., Marino T.: *J. Polym. Sci.* 1996, **Al 34**, 2817.

[131] Hassoon S., Neckers D. C.: *J. Phys. Chem.* 1995, **99**, 9416. [132] Weed G. D.: *Eur. Patent Appl.* 383,648 (1992). [133] Kondo K., Murofushi K., Gan G., Hododa K.: *Jap. Patent* 04,261,406 (1992). [134] Hipps S. J., Shanklin M. S., Davis. P.: *US Patent* 5,176,984 (1993). [135] Sarker A. M., Kaneko Y., Nikolaitschik V., Neckers D. C.: *J. Phys. Chem. A* 1998, **102**, 5375. [136] Schuster G. B.: *Pure Appl. Chem.* 1990, **62**, 1565. [137] Chatterjee D., Davis P. D., Gottschalk P., Kurtz M. E. Sauerwein B., Yang X., Schuster G. B.: *J. Am. Chem. Soc.* 1990, **112**, 6329. [138] Yang X., Zaitsev A., Sauerwein B., Murphy S., Schuster G.B.: *J. Am. Chem. Soc.* 1992, **114**, 793. [139] Tatikolov A. S., Dzhulibekov K. S., Svedova L. A., Kuzmin V. A., Ishchenko A. A.: *J. Phys. Chem.* 1995, **99**, 6525. [140] Murphy S., Yang X., Schuster G. B.: *J. Org. Chem.* 1995, **60**, 2411.

[141] Owen D. J., Schuster G. B.: *J. Am. Chem. Soc.* 1996, **118**, 259. [142] Kabatc J., Pietrzak M., Paczkowski J.: *Macromolecules* 1998, **31**, 4651. [143] Ishikawa S. I., Iwasaki M., Tamoto K., Umehara A.: *Eur. Patent* 10929 (1982). [144] Shimizu S., Fumaya S., Urano T.: *Jap Patent* 6,344,651 (1988). [145] Ren Y., Jager W. F., Neckers D. C.: *Macromolecules* 1996, **29**, 3751. [146] Kaneko Y., Neckers D. C.: *J. Phys. Chem. A* 1998, **102**, 5356. [147] Manivannan G., Wu S. K., Fouassier J. P.: *Bull. Soc. Chim. Belg.* 1990, **99**, 969. [148] Timpe H. J., Kronfeld K. P., Lannel Y., Fouassier J. P. Lougnot D. J.: *J. Photochem. Photobiol., A. Chem.* 1991, **52**, 111. [149] Timpe H. J., Kronfeld K. P., Mahlow R.: *Eur. Polym. J.* 1991, **27**, 69. [150] Coract G. R., Maclachlan A., Riem R. H., Urban E. J.: *J. Org. Chem.* 1971, **36**, 2272.

[151] Lin Y., Eiu A., Trifunac A. D., Krongauz V. V.: *Chem. Phys. Lett.* 1992, **198**, 200. [152] Zammit M. D., Davis T. P., Willett G. D., 153. Qin X. Z., Liu A., Trifunac A. D.: *J. Phys. Chem.* 1991, **95**, 5822. [154] Liu A., Trifunac A. D., Krongaus V. V.: *J. Phys. Chem.* 1992, **96**, 207. [155] Barnabas M., Trifunac A. D., Krongauz V. V.: *J. Phys. Chem.* 1992, **96**, 212. [156] Delzenne G. A.: *Adv. Photochem.* 1979, **11**, 1. [157] Dueber T. E.: *US Patent* 162,162 (1979). [158] Dueber T. E.: *US Patent* 4,454,218 (1979). [159] Dueber T. E.: *US Patent* 4,535,052 (1989). [160] Yamaoka T., Naamura Y., Koseki K., Shirosaki T.: *Polym. for Adv. Technol.* 1990, **1**, 287.

[161] Specht D. P., Matric P. A., Farid S.: *Tetrahedron* 1982, **38**, 1203. [162] Williams J. L. R., Specht D. P., Farid S.: *Polym. Eng. Sci.* 1983, **38**, 1203. [163] Specht D. P., Farid S., Payne K. L., Houle C. G.: *Eur. Patent Appl.* 22188 (1979). [164] Specht D. P., Houle G. H., Farid S.: *US Patent* 4289844 (1981). [165] Fouassier J. P., Ruhlmann D., Graff B., Takimoto Y., Harada M., Kawabata M.: *J. Imaging Sci. Tech.* (in print). [166] Rabek J. F.: in "Radiation Curing in Polymer Science and Techology", Vol. I, "Fundamentals and Methods" (eds. Fouassier J. P., Rabek J. F.), Elsevier Applied Science, London 1993, p. 453. [167] Mehnert R., Pinius A., Janovsky I., Stove R.: in "Chemistry & Technology of UV & EB Formulation for Coating, Inks & Paints" (ed. Oldring P. K. T.), Vol.1., "Curing Equipment", Sita Technology Ltd., London 1991. [168] Fouassier J. P., Rabek J. F. (eds.): "Lasers in Polymer Science and Technology", Vol. I—IV, CRC Press, Boca Raton 1990. [169] Decker C., Elzahouk B.: in "Current Trends in Polymer Photochemistry" (eds. Allen N. S., Edge M., Bellobono I. R., Selli E.), Ellis Harwood, N.Y. 1995, p. 130. [170] Reiser A.: "Photoreactive Polymers: The Science and Technology of Resists", Wiley 1989.

[171] Bottcher H., Bendig J., Fox M. A., Hopf G., Timpe H. J.: "Technical Applications of Photochemistry", Deutscher Verlag für Grundstoffindustrie, Leipzig, 1991. [172] Thompson L. F., Wilson C. G., Tagawa S. (eds.): "Polymers for Microelectronics", ACS Symp. Series No. 537, ACS Washington DC. 1994. [173] lto H., Tagawa S., Horie K. (eds.): "Polymeric Materials for Microelectronic Applications", ACS Symp. Series No. 579, ACS Washington DC. 1994. [174] Reichmanis E., Ober C. K., MacDonald S. A., lwayanagi T., Nishikubo T. (eds.): "Microelectronic Technology", ACS Symp. Series No. 614, ACS Washington DC. 1995. [175] Jenkhe S. A., Wynne K. J. (eds.): "Photo and Optoelectronic Polymers", ACS Symp. Series No. 672, ACS Washington DC. 1995. [176] Cook W. D.: *J. Dent. Res.* 1982, **61**, 1436. [177] Mehendale H. M.: in "Handook of Toxicology" (eds. Haley T. J., Berndt O.) Hemisphere, N.Y. 1987, p. 74. [178] Albrecht W. N., Stephenson R. L., Scand.: *J. Work Environ. Health* 1988, **14**, 209.