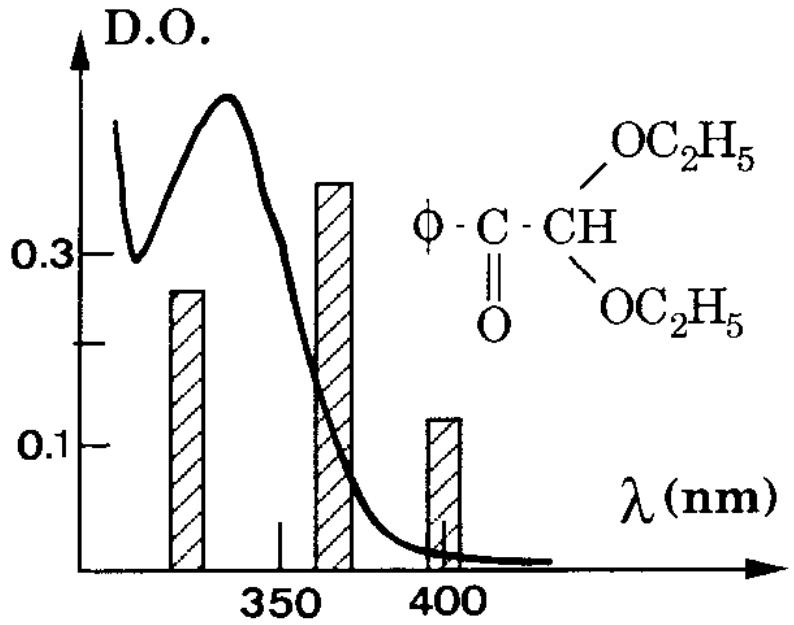
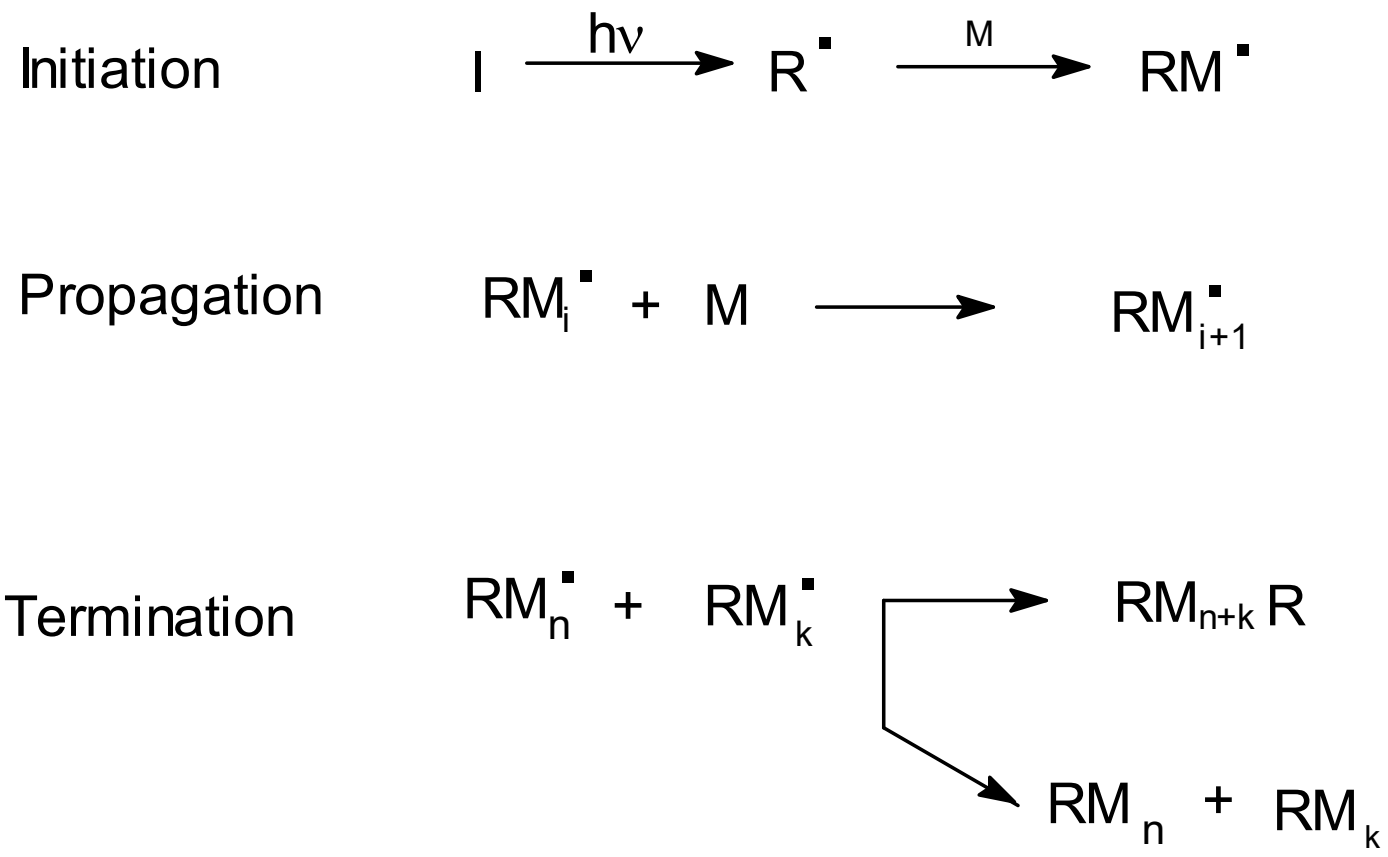
PHOTOINITIATORS



The spectral absorption range of photoinitiators is important to fit the spectral range of the light source

RADICAL PHOTOINITIATORS

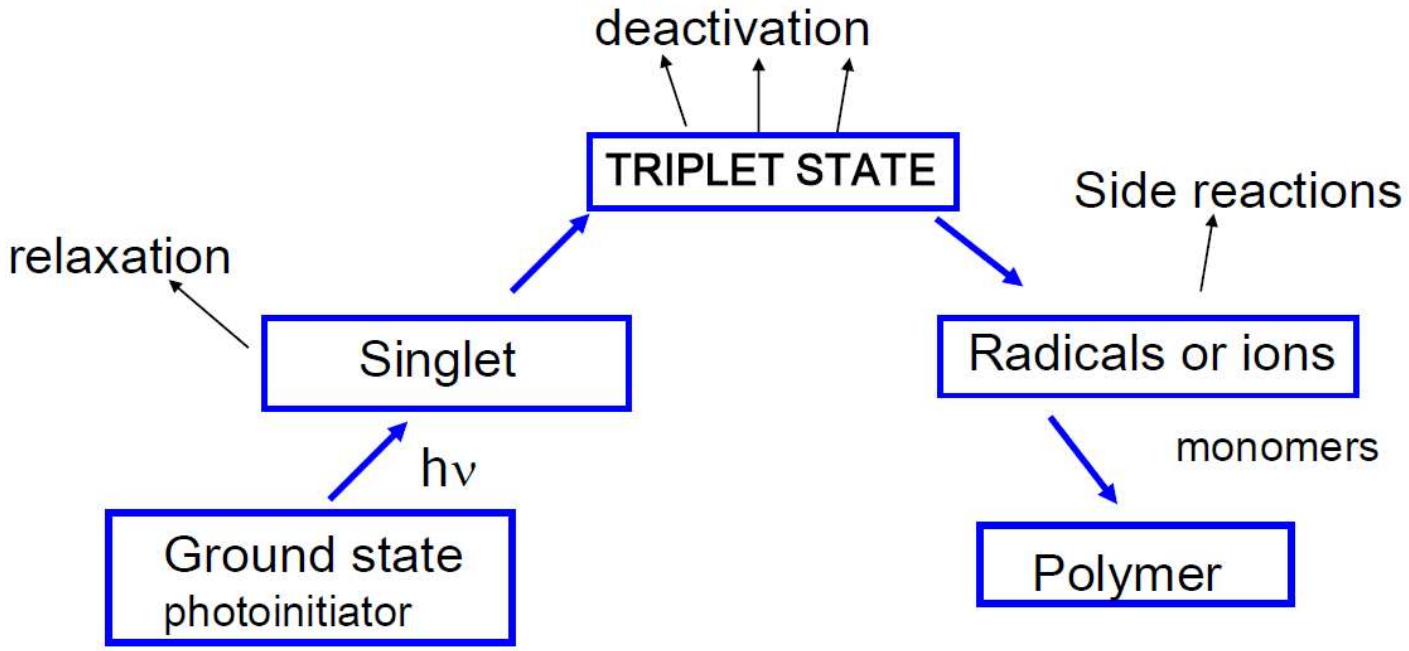


Photoinitiators have a key role in photopolymerisation. Important parameters are

- ε = extinction coefficient, Higher ε, less amount of photoinitiator = cost decrease, reduction of problems connected to thephotoinitiator
- Absorption window (especially for pigmented formulations check interference of pigments and colorants!)
- Photoinitiators synergism
- Volatility, extractability
- Photodegradation
- Oxygen quenching

Schematic diagram of the photoinitiation of a radical polymerisation

J.P.Fouassier in S.P. Pappas (Ed.), Radiation Curing, Science and Technology, Plenum Press, New York, 1992, Chapter 2, fig.2.16



Blue arrows: pathways which efficiently initiate the polymerisation

The triplet excited state may be deactivated through several processes:

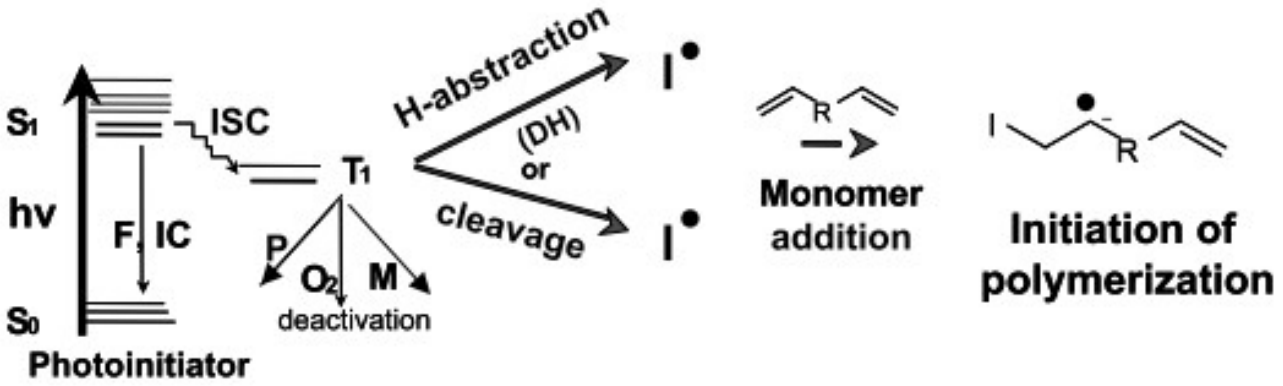
- Quenching by oxygen;

- Chemical formation of products;

- Reaction with other molecules;

- Quenching by the monomers through a process which does not undergo any chain initiation;

Initiation

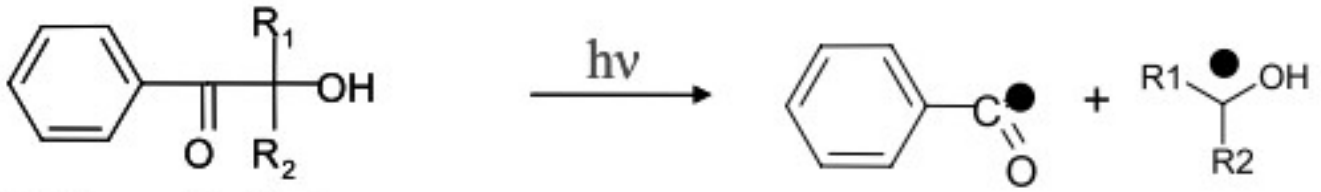


F = fluorenscense
IC = internal conversion
P = phosphorescense
O_2 = oxygen quenching
M = monomer quenching
ISC = intersystem crossing

$$\Phi_{ini} = \Phi_{ISC} * \Phi_{cleavage} * \Phi_{monomer\ addition}$$

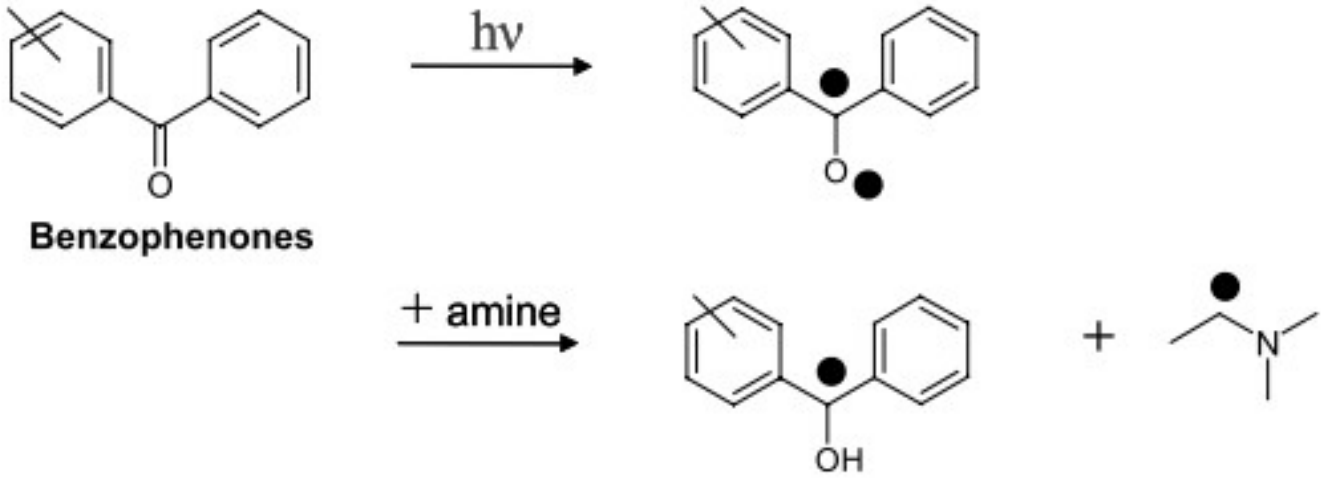
Quantum Yield of initiation

α - cleavage type photoinitiators (type I)



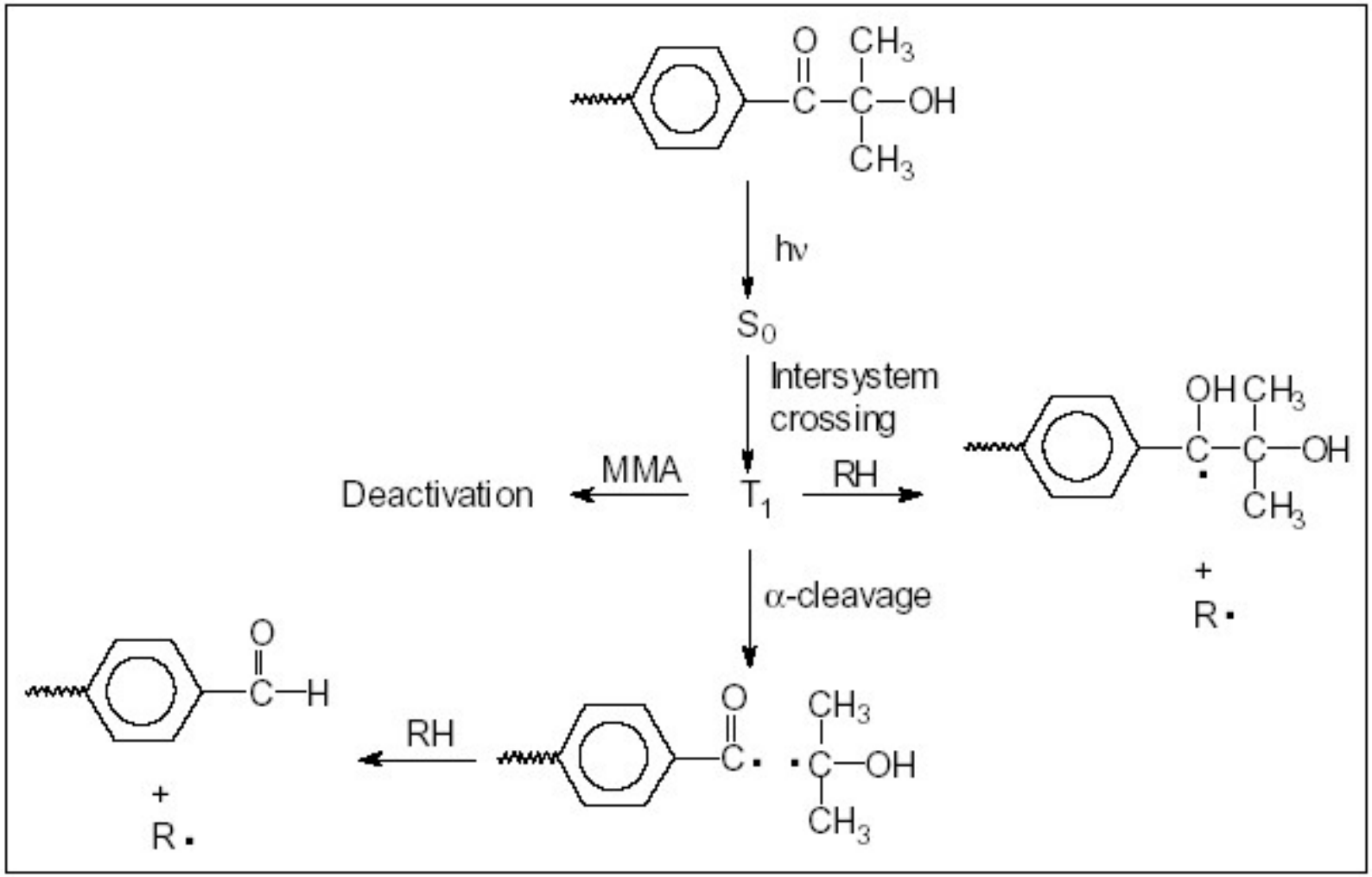
Hydroxy alkyl ketones

H-abstraction type photoinitiators (type II)

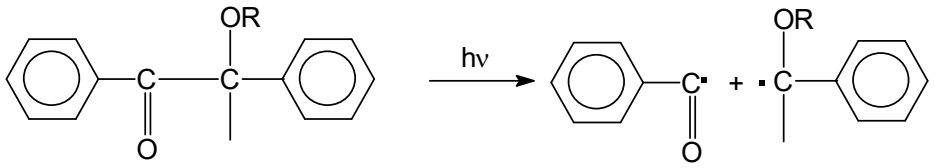


Benzophenones

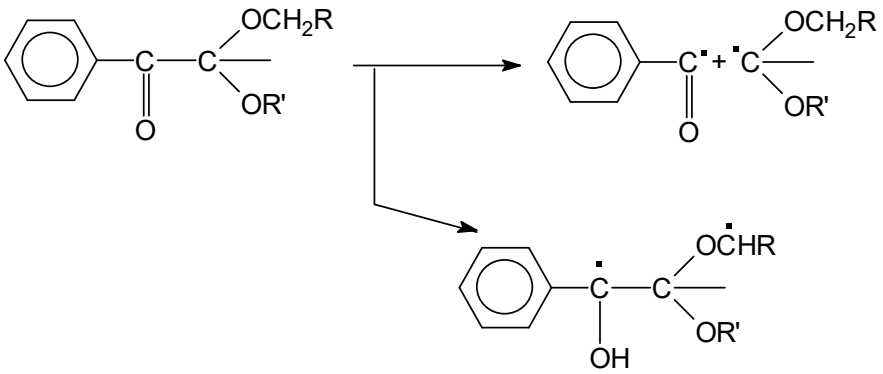
NORRISH TYPE I PHOTOINITIATOR



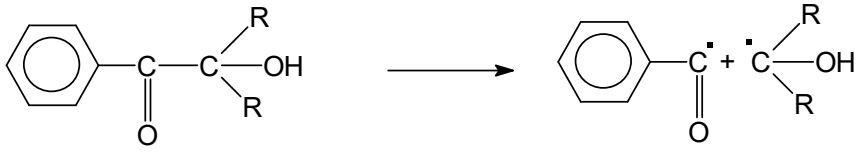
Benzilketals



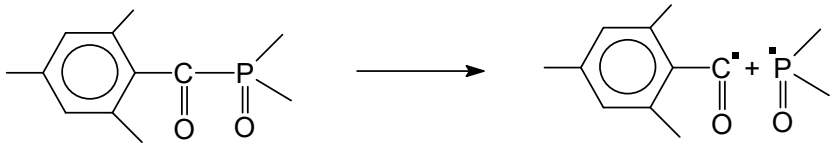
Dialkoxyacetophenones



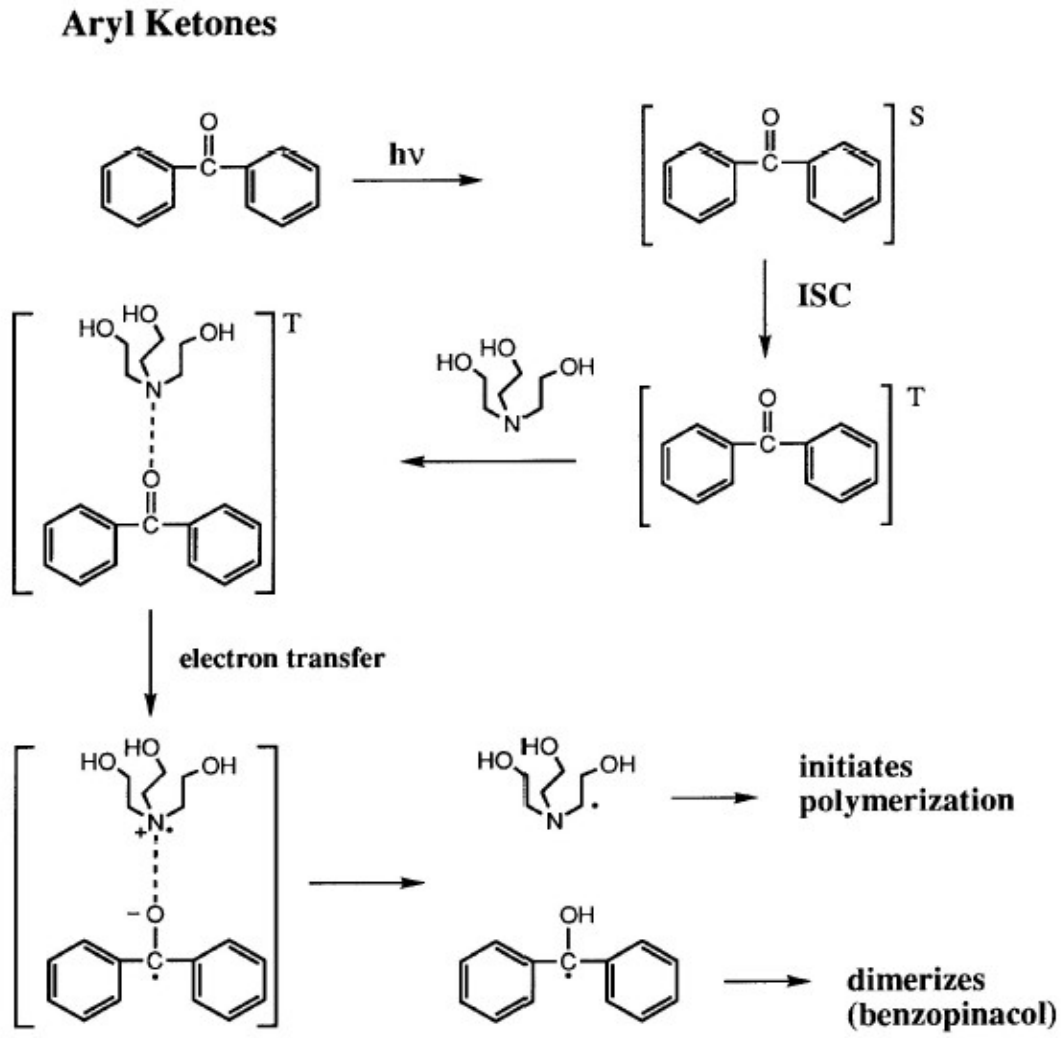
Hydroxyalkylphenyl ketones



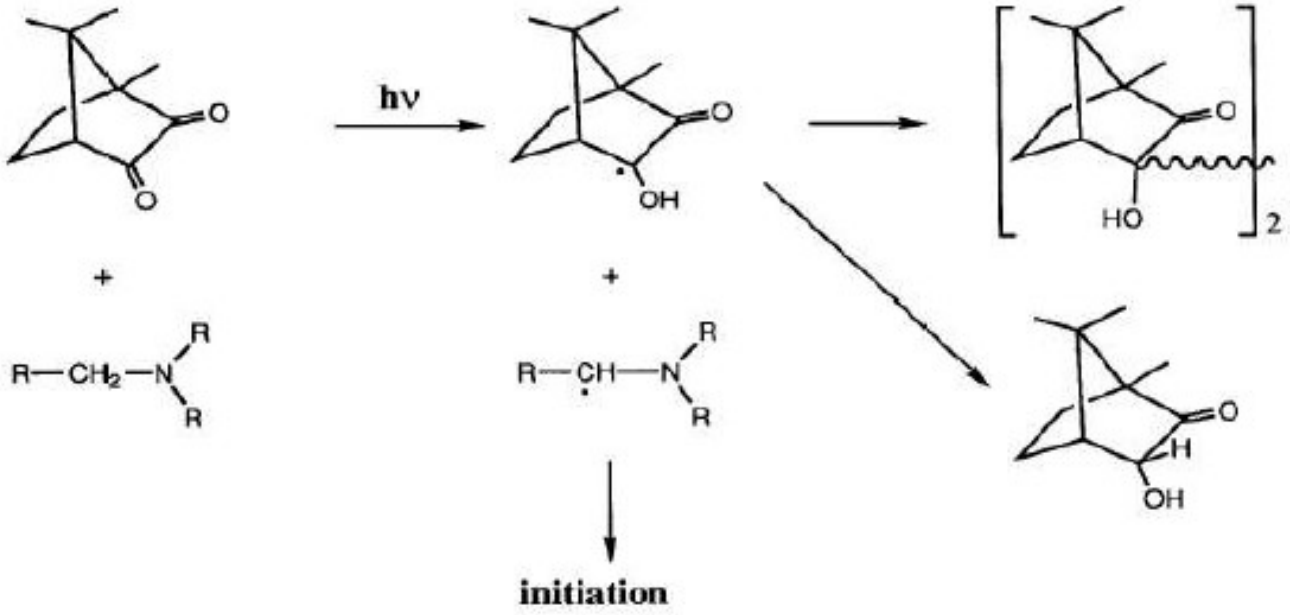
Benzoyol phosphine oxides



NORRISH TYPE II PHOTOINITIATOR

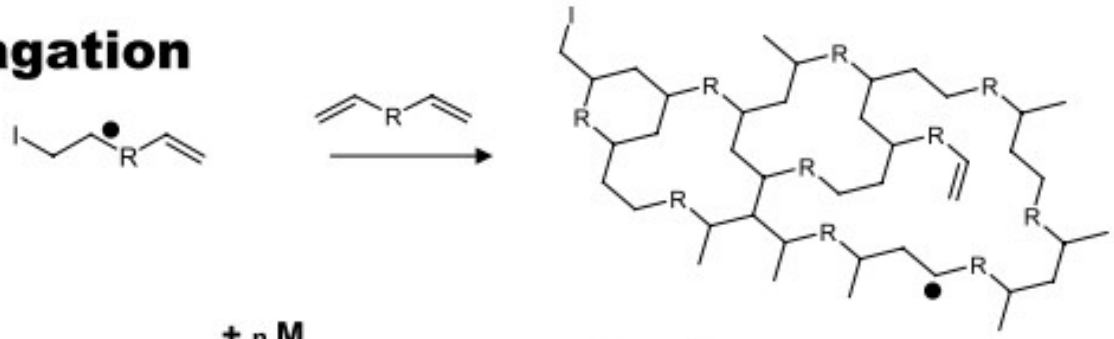


Camphor Quinone - Amine Systems



visible light initiators
(400-500 nm)
dental applications

Propagation



$$I\text{-}M^{\bullet} \xrightarrow{+\ n\ M} I\text{-}M_n^{\bullet}$$

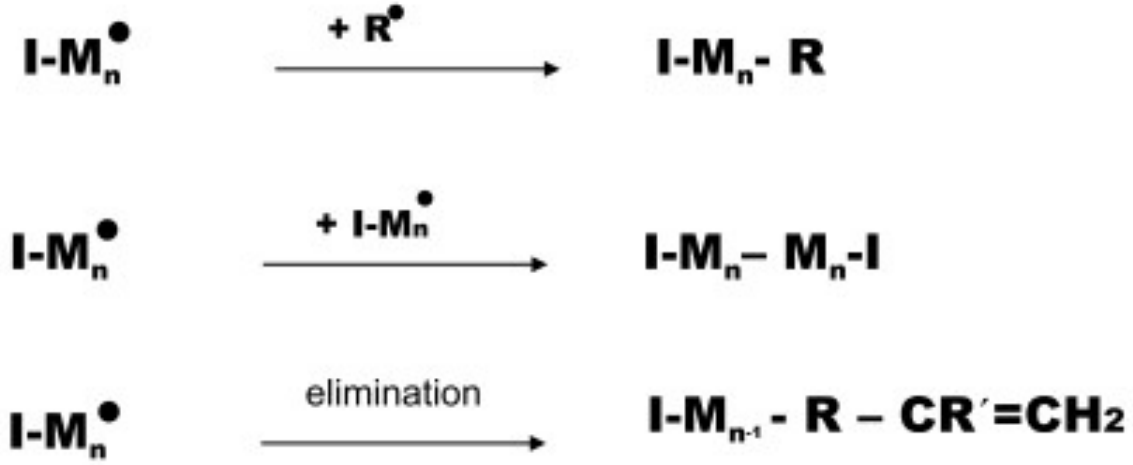
.. and Transfer

$$I\text{-}M_n^{\bullet} \xrightarrow{+\ R\text{-}H} I\text{-}M_n\text{-}H + R^{\bullet}$$

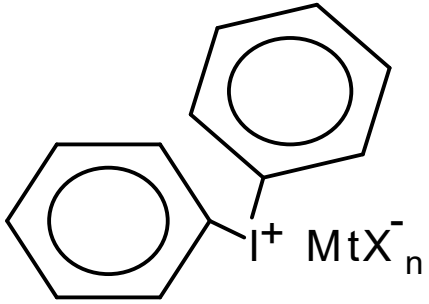
$$I\text{-}M_n^{\bullet} \xrightarrow{+\ O_2} I\text{-}M_n\text{-}OO^{\bullet} \xrightarrow{+\ R\text{-}H} I\text{-}M_n\text{-}OOH + R^{\bullet}$$

$$R^{\bullet} \xrightarrow{+\ n\ M} R\text{-}M_n^{\bullet}$$

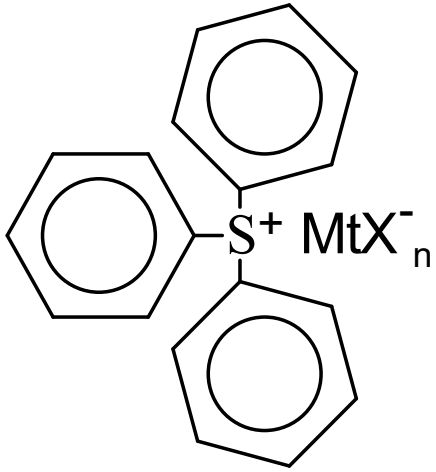
Termination



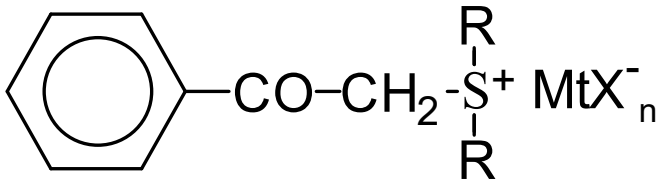
CATIONIC PHOTOINITIATORS



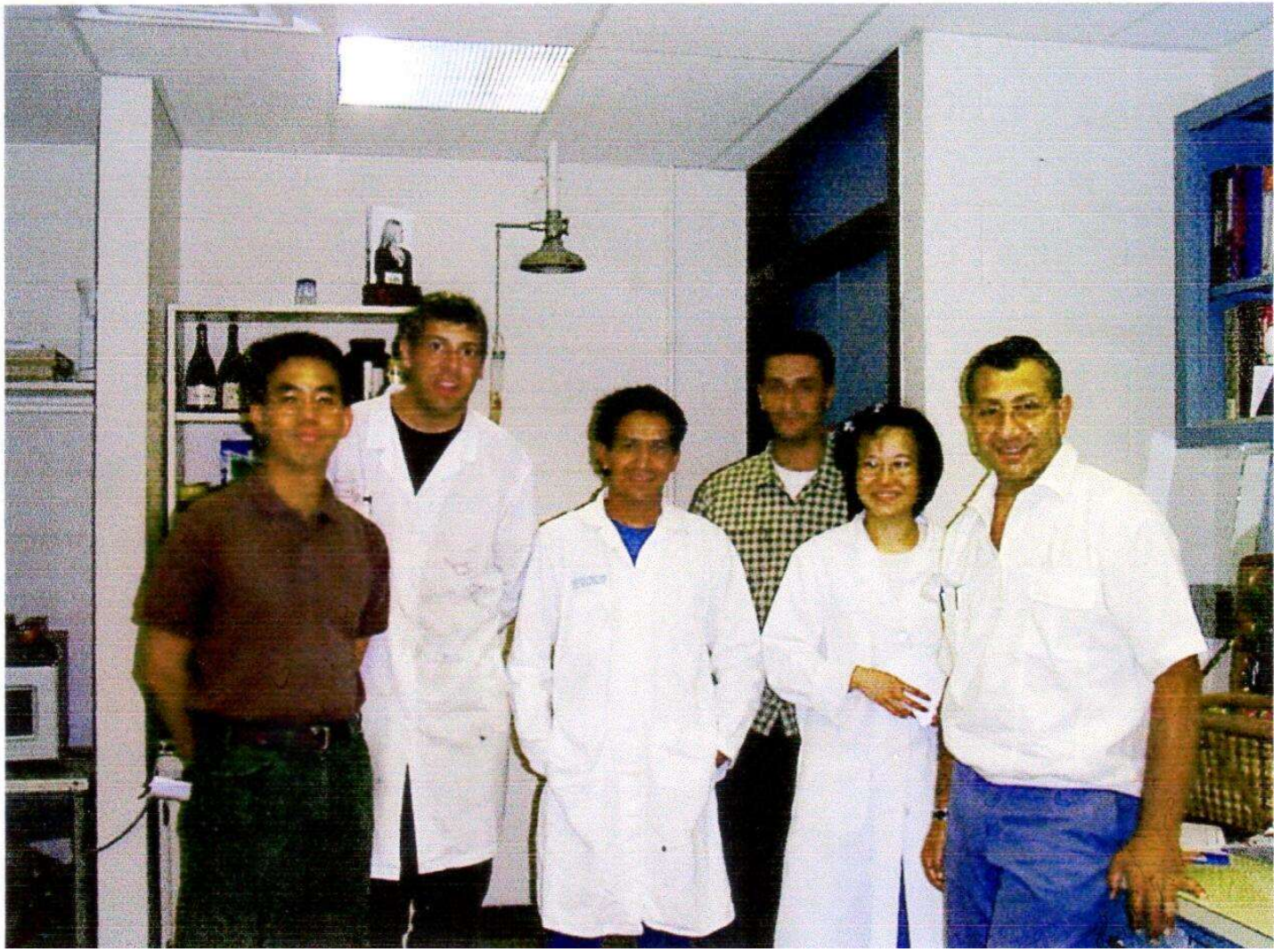
Diaryliodonium salt



Triarylsulfonium salt



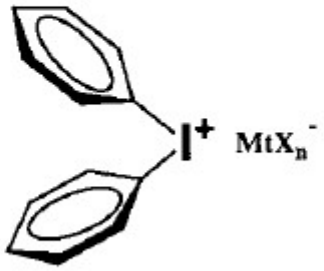
Phenacylsulfonium salt



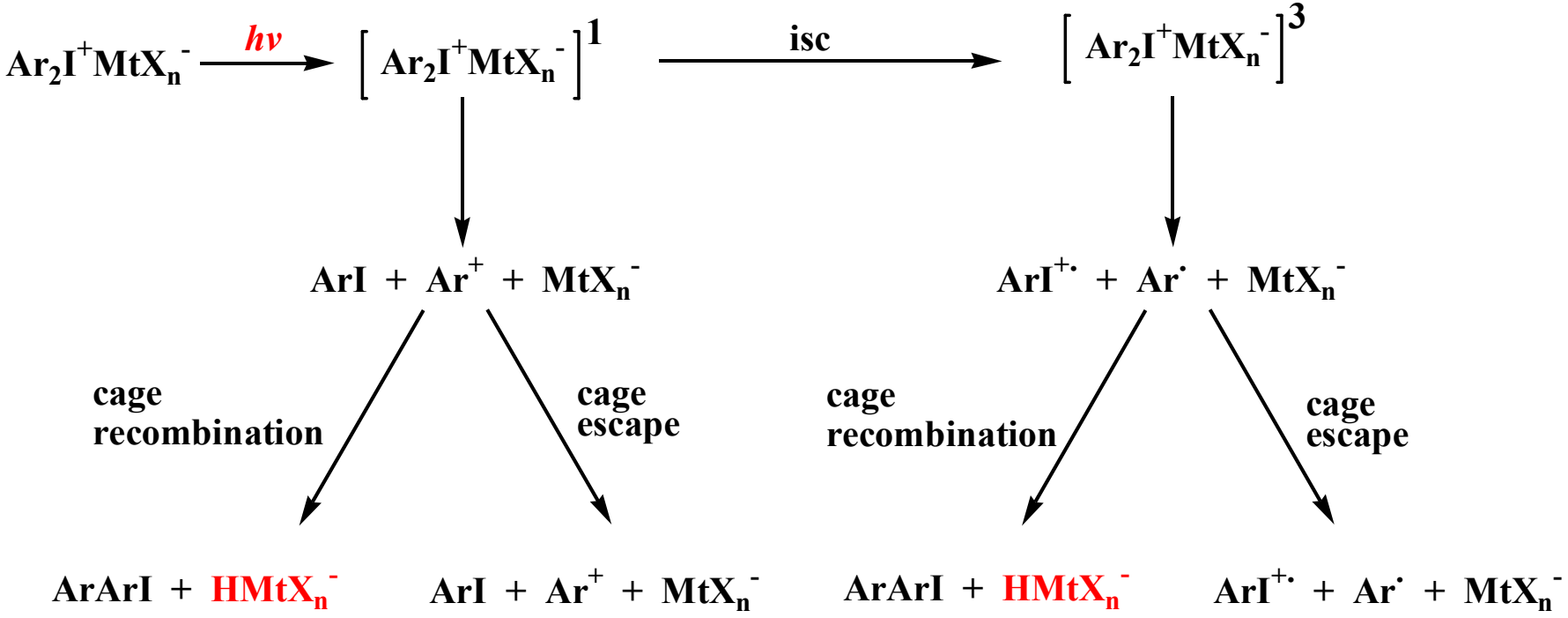

24/06/2009

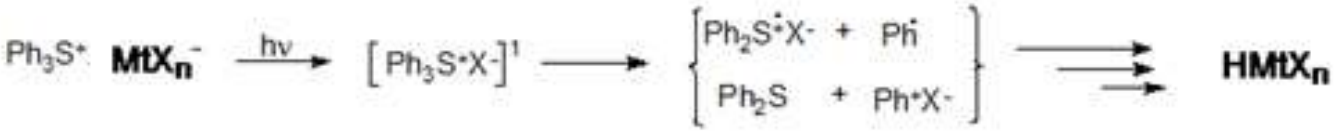
ANATOMY OF AN ONIUM SALT

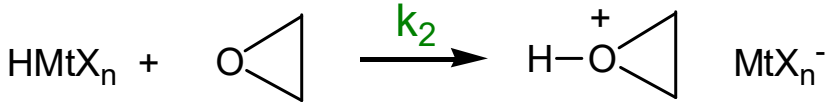
PHOTOINITIATOR



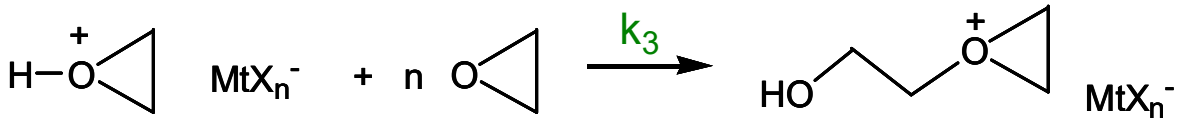
CATION	ANION
DETERMINES PHOTOCHEMISTRY	DETERMINES POLYMER CHEMISTRY
λ_{max}	acid strength
molar absorption coefficient	nucleophilicity (ion pairing)
quantum yield	anion stability
photosensitization	initiation efficiency
thermal stability	propagation rate constants


Ar2I+MtXn- hv [Ar2I+MtXn-]1 isc [Ar2I+MtXn-]3
ArI + Ar+ + MtXn-
ArI+· + Ar· + MtXn-
cage recombination
cage escape
cage recombination
cage escape
ArArI + HMtXn-
ArI + Ar+ + MtXn-
ArArI + HMtXn-
ArI+· + Ar· + MtXn-

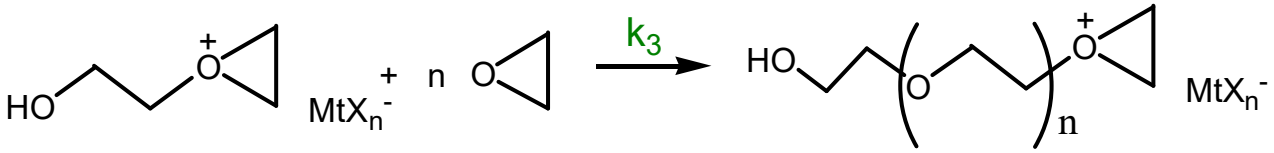




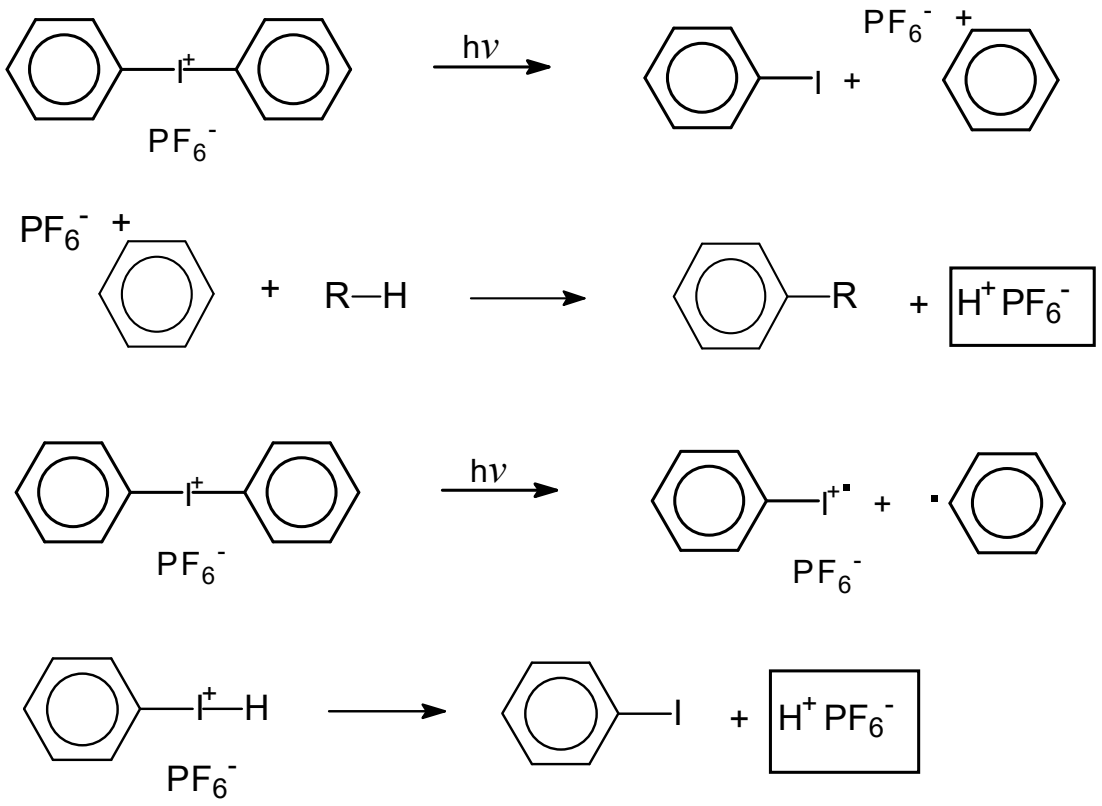
2º Oxiranium Ion



3º Oxiranium Ion



Direct Initiation

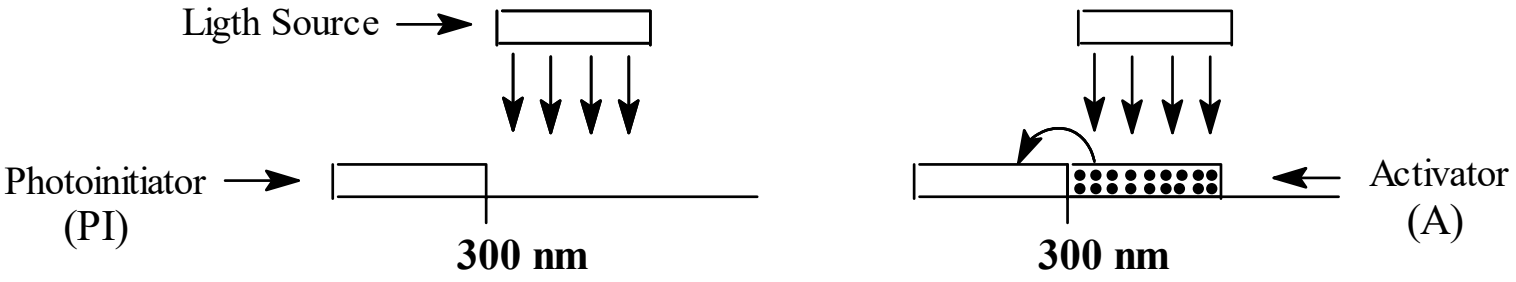


λ = 260-330 nm

Onium salts may be viewed as photoacid generators capable of producing acids of whatever strength desired depending on the starting anion. The anion employed are capable of generating 'superacids' with Hammet acidities (H_0 values) ranging from –15 to –30. The larger the negatively charged anion, the more loosely it is bound and the more active the propagating cation species is in the polymerization.

The order of reactivity is: SbF_6^- > AsF_6^- > PF_6^- > BF_4^-

Indirect Initiation



Activator

A) Free Radical Photoinitiator

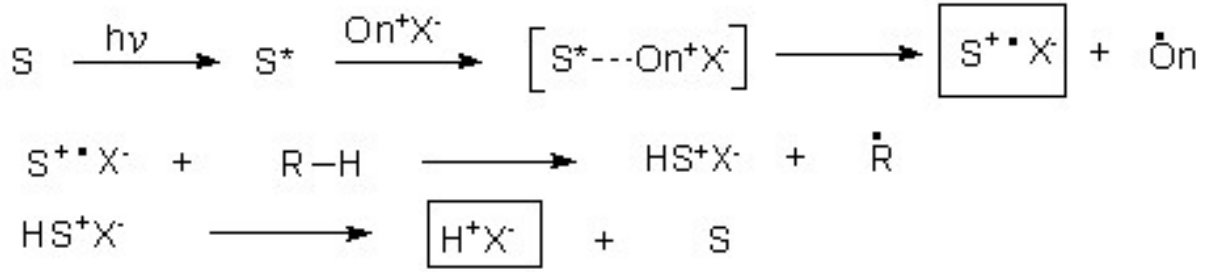
B) Photosensitizer

A) Radical Oxidation

$$\Delta G = F\,[E^{ox}_{1/2}(R^{\cdot}) - E^{red}_{1/2}(On^{+})]$$

λ = 330-650 nm
limited to electron donating radicals

B) Sensitization via Exciplexes



S=Anthracene, Perylene, Phenothiazine

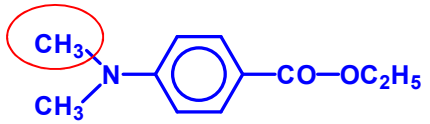
λ > 350 nm

$$CC \xrightarrow{h\upsilon} [CC]^1 \xrightarrow{ISC} [CC]^3$$

$$\mathbf{E} = \mathbf{h}\nu = \mathbf{h} \cdot \left(\frac{\mathbf{c}}{\lambda}\right) = 6.62 \cdot 10^{-34} \cdot \left(\frac{3 \cdot 10^{8}}{500 \cdot 10^{-9}}\right) = 3.97 \cdot 10^{-19}\,\mathbf{J}$$

$$[CC]^3 + M^{-}H \longrightarrow M^{\bullet}$$

$$M^{\bullet} + Ar_2I^{+}MtX^{-} \longrightarrow M^{+}MtX^{-} + Ar_2I^{\bullet}$$



$$\left(\begin{array}{l} Ar_2I^{\bullet} \longrightarrow Ar^{\bullet} + ArI \\ M-H + Ar^{\bullet} \longrightarrow M^{\bullet} + Ar-H \end{array} \right)$$

$$M^{+} + M \longrightarrow \text{Polimero}$$

The **efficiency of the photoinitiator** can be divided:

Quantum yields of initiation **(ϕi)** = number of starting polymer chains per photons absorbed

Quantum yields of polymerization **(ϕm)** = number of monomer units polymerized per photon absorbed

In absence of chain transfer reaction

$$\phi m = \phi i \times DP$$

In the photoinduced polymerization reaction the rate of polymerization is given by the following equation

$$R_p = K_p[M]\left(\frac{\Phi I_a}{K_t}\right)^{1/2}$$

Where Ia is the light intensity and Φ is the quantum initiation yield previously described.

The light intensity Ia can be obtained by Lambert-Beer law in the form:

$$I'_a = I_0 - I_0 e^{-\alpha[A]D}$$

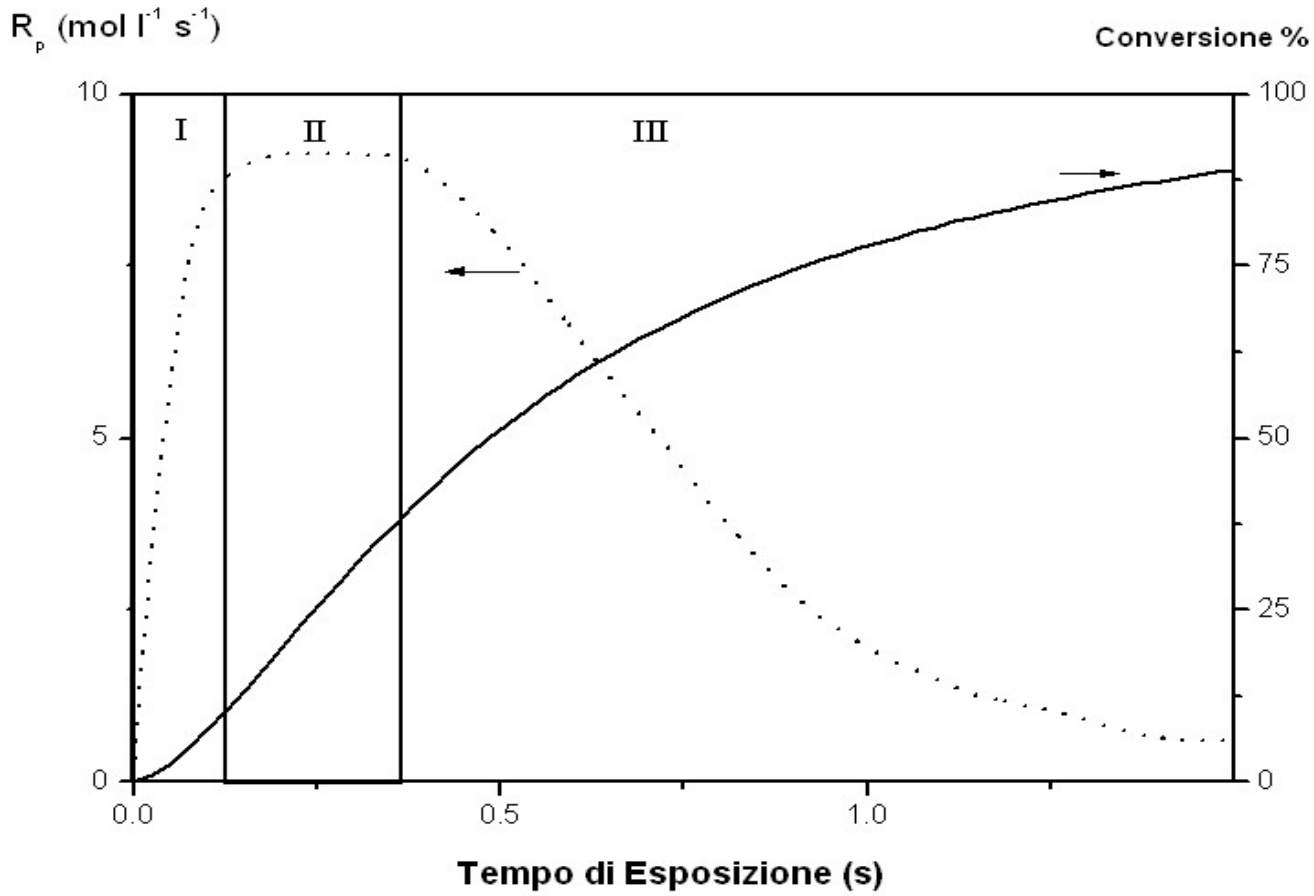
Where Io is the incident light intensity in the external part of the reactive system, and Ia' is the absorbed light intensity at the distance D (cm) inside of the reative system. Ia, and Rp, change by varying the thickness D in the reactive system. The change of Ia as a function of D can be calculated with the differential equation

$$I_a = \frac{dI'_a}{dD} = \alpha[A] I_0 10^3 e^{-\alpha[A]D}$$

The term 10^3 is a conversion factor which make it possible to change Ia from $molcm^{-3}s^{-1}$ to $molL^{-1}s^{-1}$

Rp becomes the local polymerization kinetics, the polymerization kinetic at a given distance D from the surface of the reactive system. From a practical point of view, it is possible to observe an attenuation of light intensity by increasing the thickness of the system. As a consequence the dependence of the kinetic of polymerization as a function of monomer concentration, photoinitiator concentration and light intenisty becomes more complex.

$$R_p = K_p[\mathrm{M}]\left(\frac{\phi\alpha[\mathrm{A}]I_0 10^3 e^{-\alpha[\mathrm{A}]\mathrm{D}}}{K_t}\right)^{1/2}$$



From the slope of the kinetic curves as a function of irradiation time it is possible to calculate the polymerization rate (Rp) at any istant during the irradiation.

The rate and degree of polymerization are functions of 4 parameters:

- Monomer concentration
- Optical density of the solution
- Incident light intensity
- Quantum yield of initiation

Quantum yield of initiation is a function of several parameters:

- Quantum yield of intersystem crossing
- Rate constant of different processes
- Light intensity
- Concentration of initiator

Three types of factors govern the rate and degree of polymerization:

- The experimental conditions (light sources, light intensity, monomer and initiator concentration….)
- The nature of the monomer
- The nature of the photoinitiator

DEPTH OF CURE

In contrast to electron beam curing that develops uniformly throughout the irradiated coating, photoinitiated curing follows a surface to depth gradient because of the limited penetration of light in those systems. In a clear formulation, UV radiation is absorbed mainly by the photoinitiator, so that the cure depth is directly controlled by the PI and its concentration.

For each specific application, the best compromise must be found between cure speed and cure depth.

Recently, photocuring has found applications in the production of thick polymers and composites. To effectively cure a thick section, not only the initiator system must be carefully selected to ensure that light can effectively penetrate the sample, but also the wavelength is very important.

Ideally, the initiation wavelength should be selected so that The initiator is the only absorbing species (the monomer or such should be non absorbing).

By selecting an initiation wavelength that the monomer does not absorb, we can significantly increase the maximum photoinitiation rate and increase the rate of spatial propagation of the polymerization front.

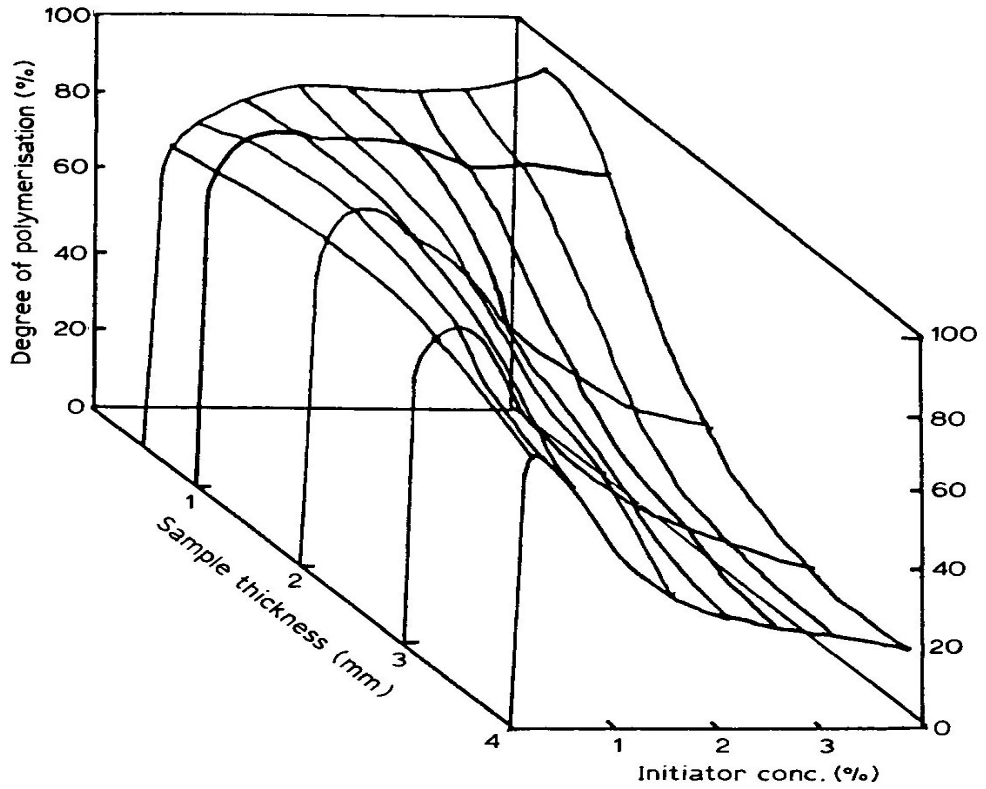
It is advantageous to use photobleaching initiators in which light absorption by the initiator products is lower than that by the original photoinitiator molecule, thereby allowing more light to pass through the system.

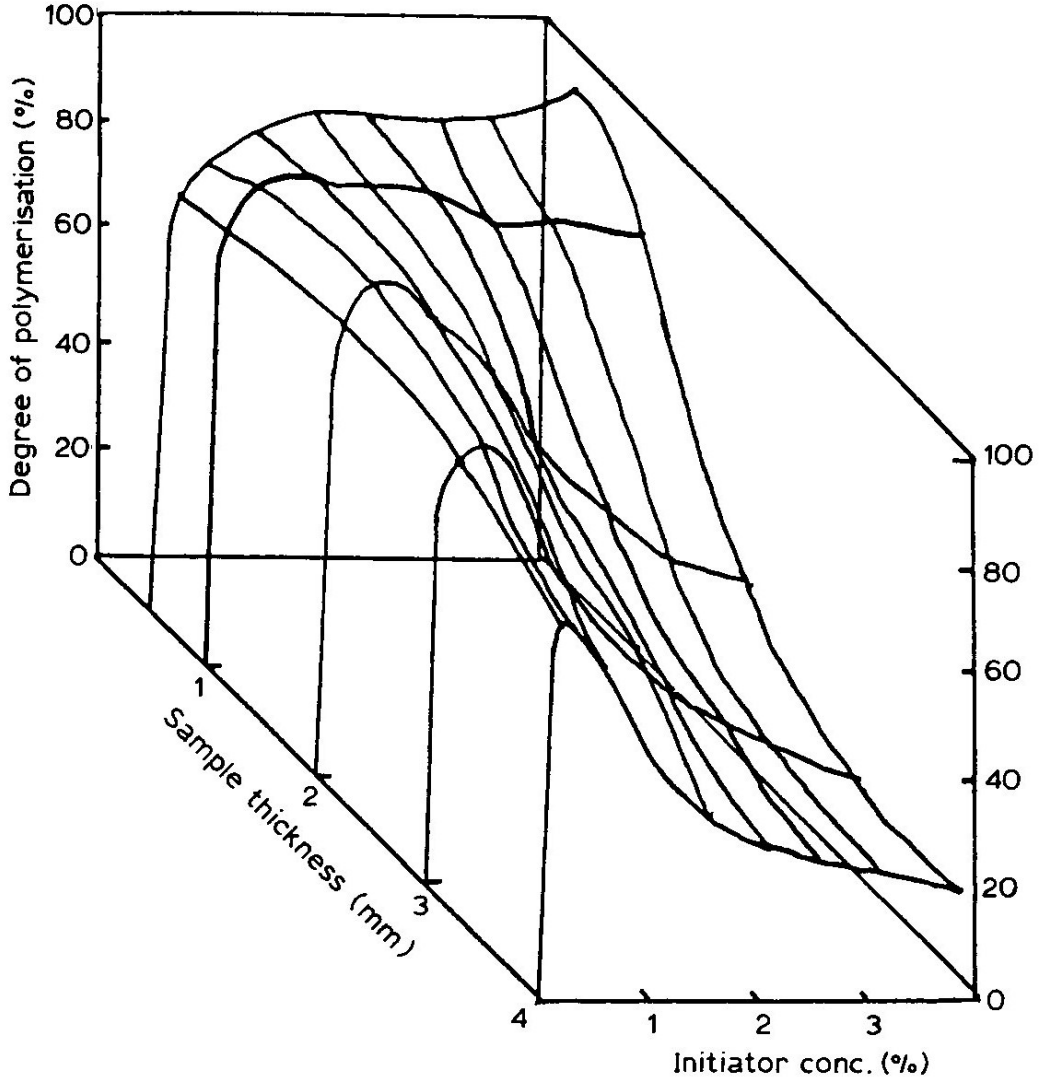
Simulation results have confirmed that, at any given time, the initiation **rate profile resembles a wave front**, and the breadth of this front is determined by factors such as:

- Initial initiator concentration;
- Molar absorptivity;

The simulation results suggest that there is an **optimum initiator concentration** for the efficient photopolymerization of thick samples.

As the initiator concentration is increased, the initiation rate at the of the wave front is increased, although the rate of propagation of the front through the sample is decreased;




Degree of polymerisation (%)
100
80
60
40
20
0
Sample thickness (mm)
1
2
3
4
Initiator conc. (%)
1
2
3
100
80
60
40
20
0

A lower initiator concentration and/or extinction coefficient photoinitiator than for the photocuring of thin films is needed.

- A low molar absorptivity allows more efficient penetration of light into the samples; however, a higher molar absorptivity leads to higher rates of photon absorption and higher rates of bleaching;

- As the initiator molar absoprtivity increases, the maximum initiation rate increases, the breadth of the propagating front decreases, and the rate of spatial propagation through the sample decreases;

PIGMENTED COATINGS

The curing of pigmented coatings is difficult due to the high light absorption by the pigment, which is detrimental to the own absorption of light by the photoinitiator.

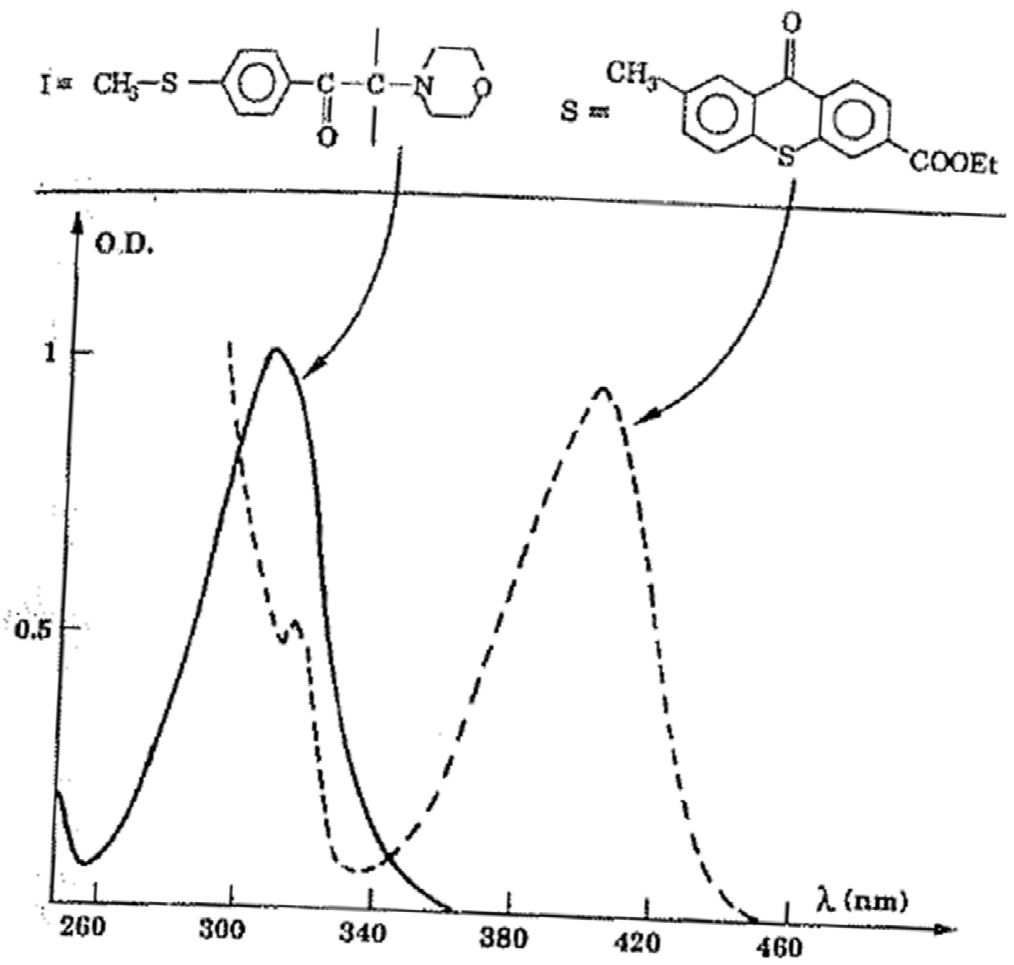
It can be solved:

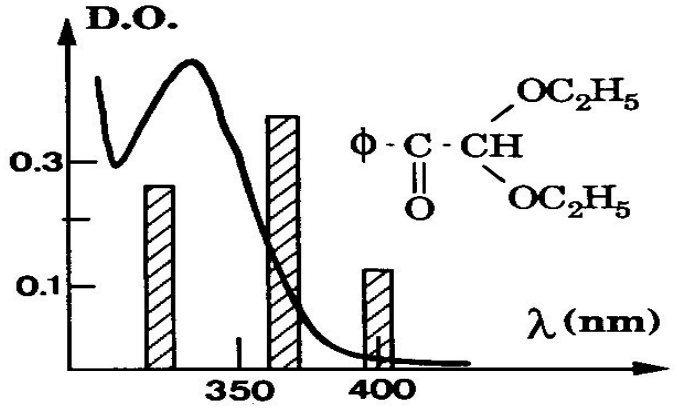
1. **By designing red-shift absorbing molecule acting as photoinitiator**
2. **By using a photosensitizer able to absorb at long wavelength and to transfer its excitation to a photoinitiator**
3. **Choosing a suitable spectral “window”**

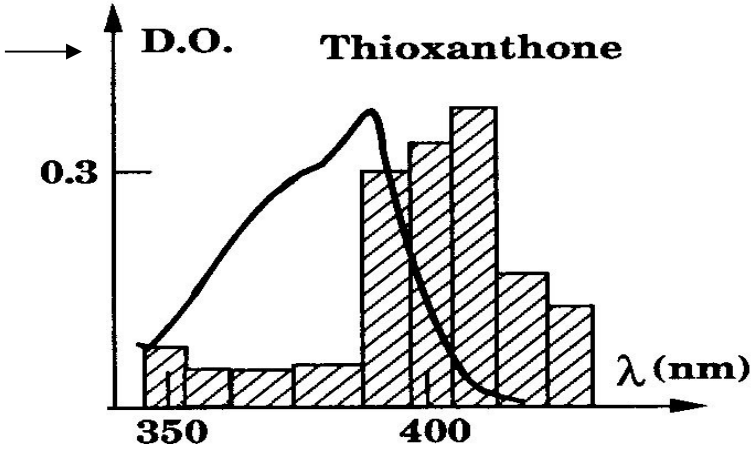
The efficiency of longer wavelegth photoiniatitor is due to a large light absorption in the near–UV range where the mercury lamp has its strongest emission, and where the pigment becomes more transparent.

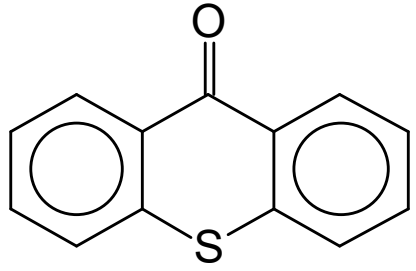
In addition, these photoiniatitors undergo a photo-bleaching process, thus allowing UV radiation to penetrate progressively deeper into the sample.

In fact, if the PI photoproducts absorb at shorter wavelength (photo-bleaching effect) than the photoinitiator; therefore UV radiation can progressively penetrate deeper into the coating rendering the process more uniform.


I =
CH3–S
C
C
N
O
O
S =
CH3
O
S
COOEt
O.D.
1
0.5
λ (nm)
260
300
340
380
420
460

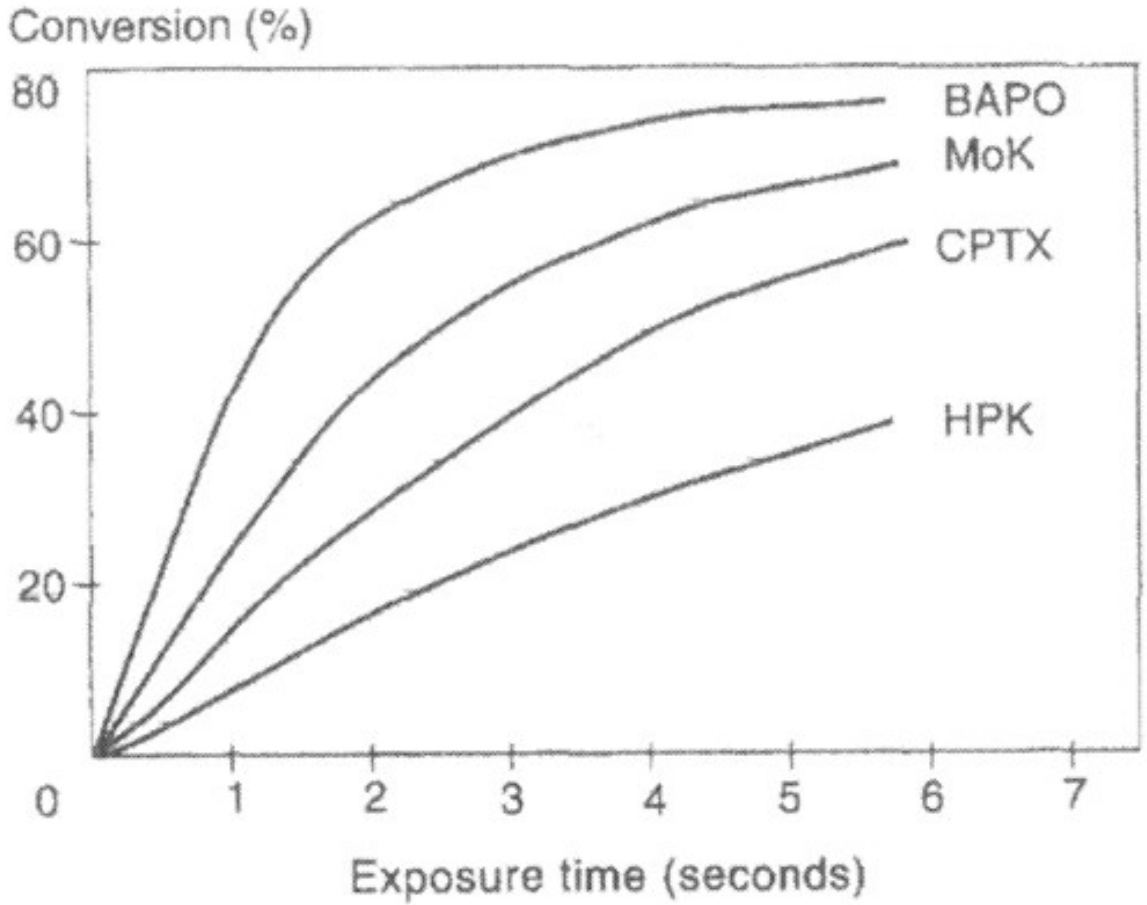




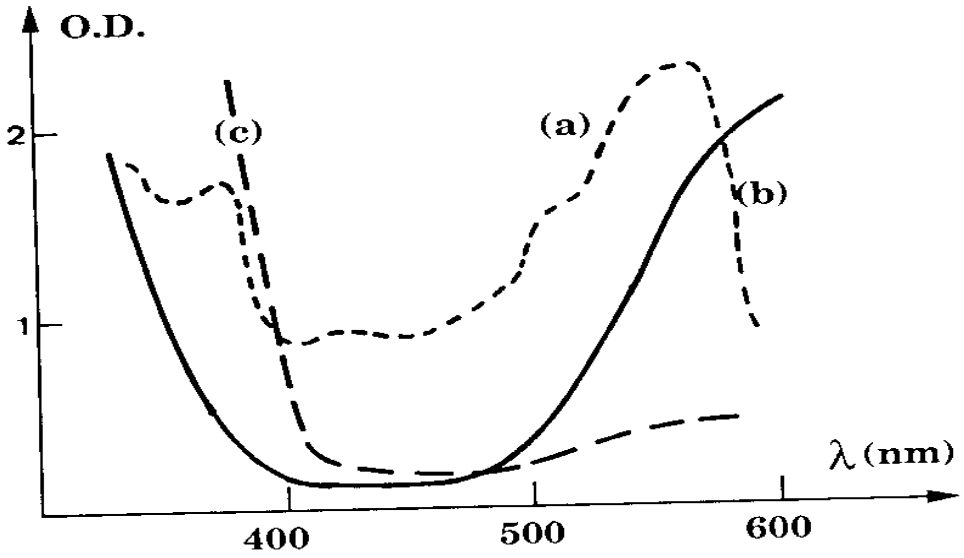


Photosensitizer (T1) + Photoinitiator (S0) ⟶

Photosensitizer (S0) + Photoinitiator (T1)



Influence of the photoinitiator (2%) on the photoinitiated polymerisation of a white polyester-acrylate lacquer. Hydroxyalkylphenone (HPK), chloropropoxythioxanthone (CPTX), morpholino ketone (MoK), bisacylphosphine oxide (BAPO).



Paint absorption spectra: (a) red, (b) blue and (c) white.

In the presence of a pigment a spectral window has to be found and the most suitable photoinitiator must be used, as well as the irradiation sources with the best adapted emission spectra