

## 5. Photochemistry of polymers

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### 5.1 Photopolymerization and cross-linking

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#### Photopolymerization

The fundamental principle of photopolymerization is based on the photoinduced production of a reactive species, which then initiates thermal reactions of low-molecular weight products leading to polymer or network formation.

In general, such reactions are associated with low activation energies ( $\sim 60 \text{ kJ mol}^{-1}$  for radical chain polymerization). Therefore, these processes can also occur sufficiently fast at room temperature.

The photo-initiator present in the system creates the reactive species X in high yields ( $\Phi \simeq 0.5$ ) upon irradiation. The reactive species X can be a radical, or a cation (Brønsted or Lewis acid). Most commercially viable photopolymers are, however, formed via radical processes.



#### Radical photopolymerization

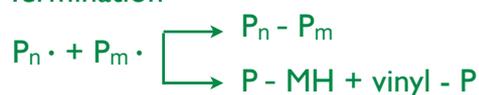
##### a) Initiation



##### b) Propagation



##### c) Termination

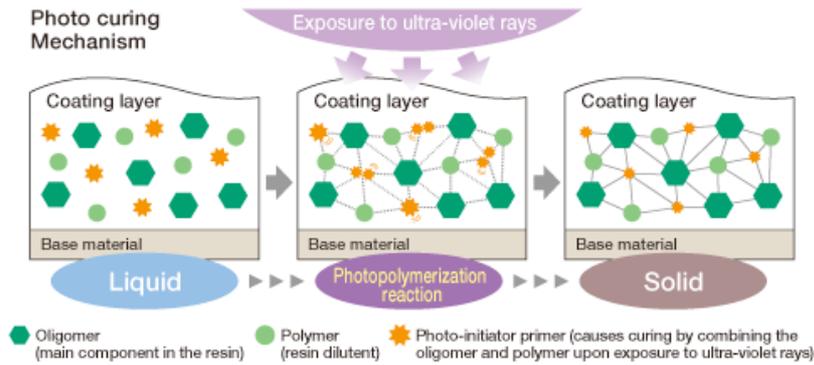


M : monomer

## Photopolymerization ("photocuring")

Depending on the concentration of the photoinitiators and their absorption coefficient, the photocuring depth varies from a few microns to at most 1-2 mm. This implies that the use of photopolymerization process is restricted in practice to thin coatings.

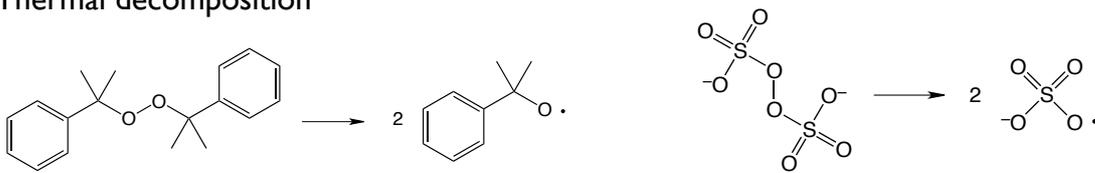
One of the prime application areas for UV curable coatings is clear films on substrates ranging from metals and wood to floors and paper. *Photocurable inks* and *photoresists* used in microlithography represent important technical applications of light-induced polymerization.



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## Examples of radical initiators for thermal- and photo-curing

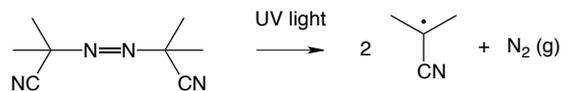
a) Thermal decomposition



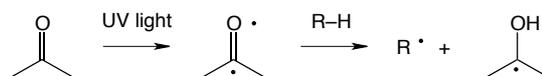
b) Redox reaction



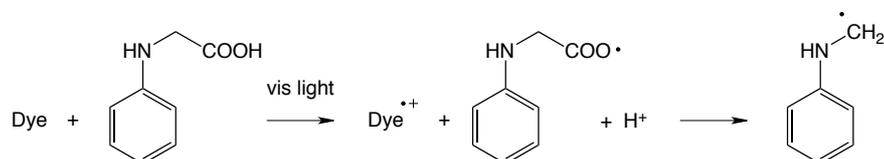
c) Photodissociation



Hydrogen abstraction



Photoredox



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## Radical photopolymerization

### Typical initiators of radical photopolymerization

Compounds	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}/\text{l mol}^{-1} \text{ cm}^{-1}$	$\Phi^1)$	Commercial products
Benzoin derivatives	320...350	150...300	0.5	Trigonal 14, Sensi B2
Benzil ketals; $\alpha, \alpha'$ -dialk-oxyacetophenones	320...350	150...300	0.5	DEAP, Irgacure 651
2-Hydroxyacetophenones	320...350	150...300	0.5	Darocure 1173, Irgacure 184
Aroylphosphine oxides	350...380	500...800	0.7	Paladal
Subst. benzophenones (+ amines)	320...370	100...200	0.2	Trigonal 14, Quantacure
Thioxanthenes (+ amines)	340...420	7,000	0.1	Lucirin 8513, Kaya-cure DETX
Dyes (+ amines)	450...800	10,000...50,000	0.1	Ro-Sensi, SATEA
$\alpha$ -Benzoyloxime esters	320...350	150...300	0.3	
Perhalogenides	350...360	20...80	0.4	Sandoray 1000
Aliph. azo compounds	330...360	10...20	0.5	
Peroxides	280...320	3...10	0.7	
Disulfides	350...420	10...30	0.7	
Quinones (+ amines)	340...460	900...2,000	0.2	

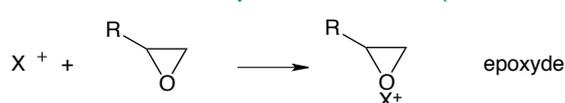
<sup>1)</sup> Quantum yields in solution

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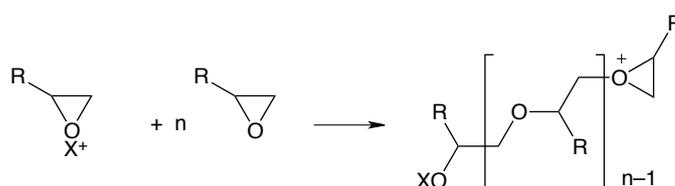
## Cationic photopolymerization

Radical polymerization is very sensitive to oxygen and, therefore, is hard to use for surface photocuring. Due to the same problem, anionic polymerization is practically useless. Cationic photocure systems are often deemed superior to free-radical photocuring processes since they are insensitive to oxygen inhibitors,

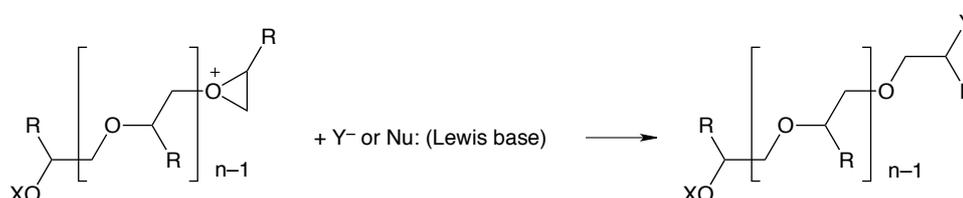
a) Initiation  $\text{initiator} \xrightarrow{h\nu} \text{products} + \text{X}^+ \text{ (Lewis acid)}$



b) Propagation



c) Termination



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## Cationic photopolymerization

### Typical initiators of cationic photopolymerization

Compounds	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max}^1)/\text{l mol}^{-1} \text{cm}^{-1}$	$\Phi^2)$
Aryldiazonium salts	270...600	10,000...30,000	0.02...0.5
Diaryliodonium salts	270...350	5...5,000	0.1...0.9
Triarylsulphonium salts	270...350	5...10,000	0.1...0.7
Tetraarylphosphonium salts	270...300	$\approx 3,000$	
Tetraarylammonium salts	270...300	$\approx 3,000$	0.1...0.5
Thiopyrylium salts	350...450	$\approx 20,000$	
Phenacylammonium salts	270...300	$\approx 9,000$	$\approx 1$
Dialkyl phenacylsulphonium salts	270...300	$\approx 9,000$	$\approx 1$
Sulfonic esters of hydroxyketones	320...350	20...1,000	
Perhalogenides	350...460	20...80	
Prototropic nitro compounds	320...360	600...10,000	
Metalocenes	360...500		0.2...0.6

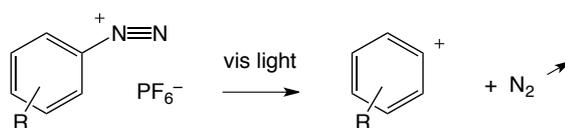
1) Maximum of long wavelength absorption

2) Quantum yield for formation of protonic acid in solution

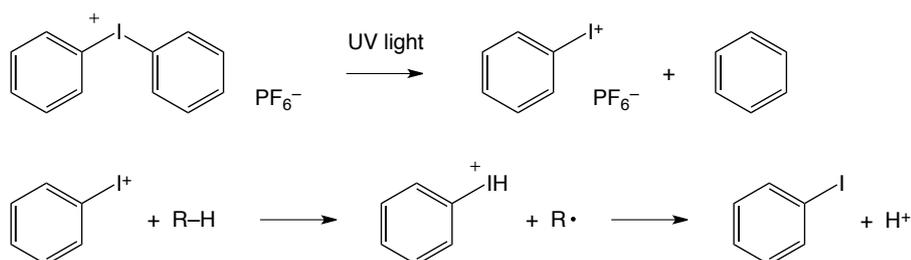
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### Examples of cationic photoinitiators

**Diazonium salts**      Advantage : colored, large extinction coefficient  
 Drawback : forms  $\text{N}_2$  bubbles

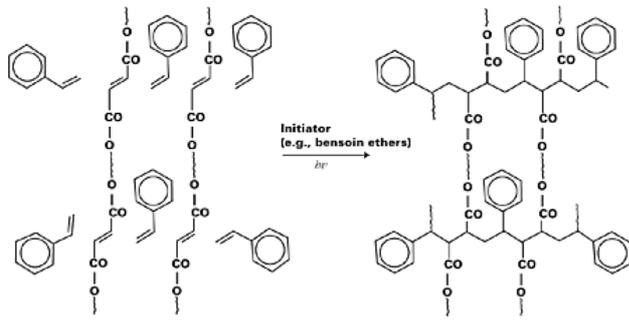


**Iodonium salts**      Drawback : low extinction coefficient  
 The reaction can however be photosensitized in the visible

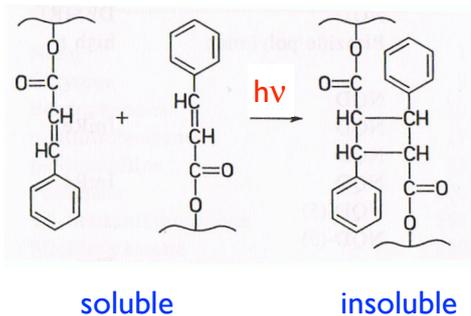


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## Photo-crosslinking of polymer chains



When polymer chains are linked together by cross-links, they lose some of their ability to move as individual polymer chains. Low cross-link densities transform gummy polymers into materials that have elastomeric properties and potentially high strengths. Very high cross-link densities can cause materials to become very rigid or glassy, such as phenol-formaldehyde materials.



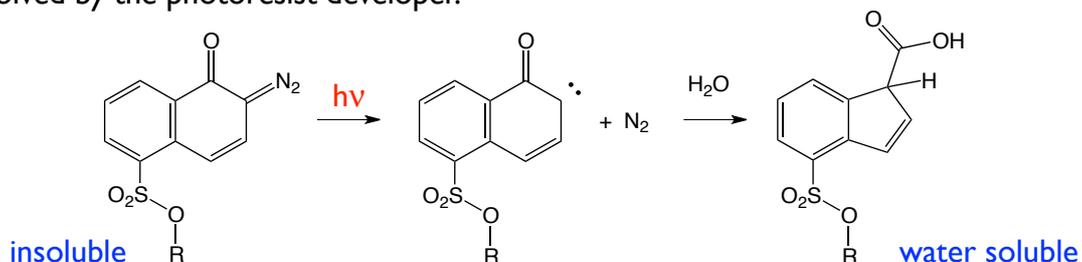
Poly(vinyl) cinnamates (lower figure) undergo photo-dimerization through photochemical [2+2] cycloaddition to form cyclobutanes. Photocrosslinking causes the material that is soluble in esters and chlorinated solvent to become insoluble.

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## Photoresists

A **photoresist** is a light-sensitive material used in several industrial processes, such as **photolithography**, to form a patterned coating on a surface upon irradiation through a mask. The polymeric material is used to "resist" a mechanical or a chemical attack of the coated substrate.

A negative resist, such as the poly(vinyl) cinnamate shown on previous slide, is a type of photoresist in which the portion of the photoresist that is exposed to light becomes insoluble to the photoresist developer. The unexposed portion of the photoresist is dissolved by the photoresist developer.



A positive resist is a type of photoresist in which the portion of the photoresist that is exposed to light becomes soluble to the photoresist developer (solvent). The portion of the photoresist that is unexposed remains insoluble to the photoresist developer.

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## Photolithography

**Photolithography** (or "optical lithography") is a process used in microfabrication to selectively remove parts of a thin film or the bulk of a substrate or to chemically treat it (doping). It uses light to transfer a geometric pattern from a photomask to a photoresist, or simply "resist," on the substrate. A series of chemical treatments then either engraves the exposure pattern into, or enables deposition of a new material in the desired pattern upon, the material underneath the photoresist. For example, in complex integrated circuits, a modern CMOS wafer will go through the photolithographic cycle up to 50 times.

