**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 (~60 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 (\(\Phi \approx 0.5\)) 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.

\[
\begin{align*}
\text{Initiator} & \xrightarrow{\text{hv}} \text{species } X \\
X + \text{monomers} & \rightarrow \text{polymer} \\
X + \text{oligomers} & \rightarrow \text{cross-linked network}
\end{align*}
\]

**Radical photopolymerization**

a) Initiation

\[
\begin{align*}
\text{initiator} & \xrightarrow{\text{hv}} \text{X· + products} \\
\text{X·} + M & \rightarrow P_1·
\end{align*}
\]

b) Propagation

\[
P_1· + n M \rightarrow P_{n+1}·
\]

c) Termination

\[
P_n· + P_m· \quad \xrightarrow{\text{P - MH + vinyl - P}}
\]

\(M: \text{monomer}\)

**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.
Photochemistry of polymers

Examples of radical initiators for thermal- and photo-curing

a) Thermal decomposition

\[
\text{Fenton: } \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH}
\]

b) Redox reaction

\[
\text{Photoredox: } \text{Dye} + \text{HN} - \text{COOH} \quad \text{vis light} \quad \text{Dye}^{*} + \text{HN} - \text{COO}^- + \text{H}^+ \rightarrow \text{HN} - \cdot \text{CH}_2
\]

c) Photodissociation

\[
\text{Hydrogen abstraction: } \text{UV light} \quad \text{O} \quad \text{R} \cdot + \quad \text{OH} \quad \rightarrow \quad \text{R} \quad \text{H}
\]

Radical photopolymerization

Typical initiators of radical photopolymerization

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

\(^1\) Quantum yields in solution
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

\[
\text{initiator} \xrightarrow{\text{hv}} \text{products + X}^+ \text{ (Lewis acid)}
\]

b) Propagation

\[
\text{Initiation initiator} \xrightarrow{\text{hv}} \text{products + X}^+ \text{ (Lewis acid)}
\]

c) Termination

\[
\text{Termination} \xrightarrow{\text{hv}} \text{products + X}^+ \text{ (Lewis acid)}
\]
Examples of cationic photoinitiators

Diazonium salts

Advantage: colored, large extinction coefficient

Drawback: forms N₂ bubbles

\[
\text{Ph}^+ \text{N≡N}^- \xrightarrow{\text{vis light}} \text{Ph}^+ + N_2
\]

Iodonium salts

Drawback: low extinction coefficient

The reaction can however be photosensitized in the visible

\[
\text{Ph}^+ \text{I}^- \xrightarrow{\text{UV light}} \text{Ph}^+ + \text{I}^- \xrightarrow{\text{vis light}} \text{Ph}^+\text{IH}^- + \text{R}^- \xrightarrow{\text{hv}} \text{Ph}^+ + \text{R}^- + \text{H}^+
\]

Photochemistry of polymers

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.
Photochemistry of polymers

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.

![Chemical Reaction](image1)

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.

![Chemical Reaction](image2)

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.