Science and Technology of UV-Induced Polymerization

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MSE-703, Doctoral Program in Materials Science and Engineering
February 2-4, 2022, Room DIA004, EPFL
https://epfl.zoom.us/j/65934361301

COURSE PROGRAM

https://epfl.zoom.us/j/65934361301

Wednesday Feb 2

14h15-15h00 Introduction to radiation processing (MS, YL)
15h15-16h00 Fundamentals (MS)
16h15-17h00 Components of photocurable formulations: photoinitiators, monomers, additives (MS)

Thursday Feb 3

zoom only

9h15-12h00 Analytical methods: state of the art and new developments (SDV)
14h15-16h00 Laboratory demonstration of UV methods and processes (YL)

Friday Feb 4

9h15-10h30 Advances in UV-induced polymerization research 1 (SDV) zoom only
10h45-12h00 Advances in UV-induced polymerization research 2 (MS)
14h15-15h00 Structure-property relations in UV curable polymers (YL)
15h15-16h00 Application to surfaces, nanostructures and devices (YL)
16h15-17h00 UV inks and coatings (EN)

EXAM!

The course provides 1 ECTS, based on a written report (maximum 10 pages) on a topic relevant to UV polymers. The report should synthesize three technical papers A, B and C from open scientific literature and develop a short case study (for example using equation from paper A and data from paper B to model results from paper C, or designing a process method (formulation, UV intensity, time) using inputs from the 3 papers).

The following topics are proposed. Other topics are welcome.

Free-radical vs cationic UV systems: mechanisms, drawbacks and benefits
Humidity effect on cationic UV curing
Oxygen effects on free-radical cure
Analytical methods: state of the art, limitations and future developments
Analysis and modeling of process induced stresses in UV coatings
Hybrid UV-cured organic-inorganic coatings
UV-curable nanocomposites: formulations and applications
Process equipment for micro/nano structuring using UV polymers
Comparison of thermal NIL (nano imprinting lithography) and UV NIL
UV-curing applications in automotive industry
Process technologies for UV inks

Deadlines:

- selection of project (1 student / topic): Feb 3, 2022
- report (pdf) by email to yves.leterrier@epfl.ch: Feb 28, 2022

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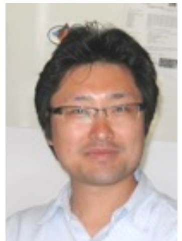
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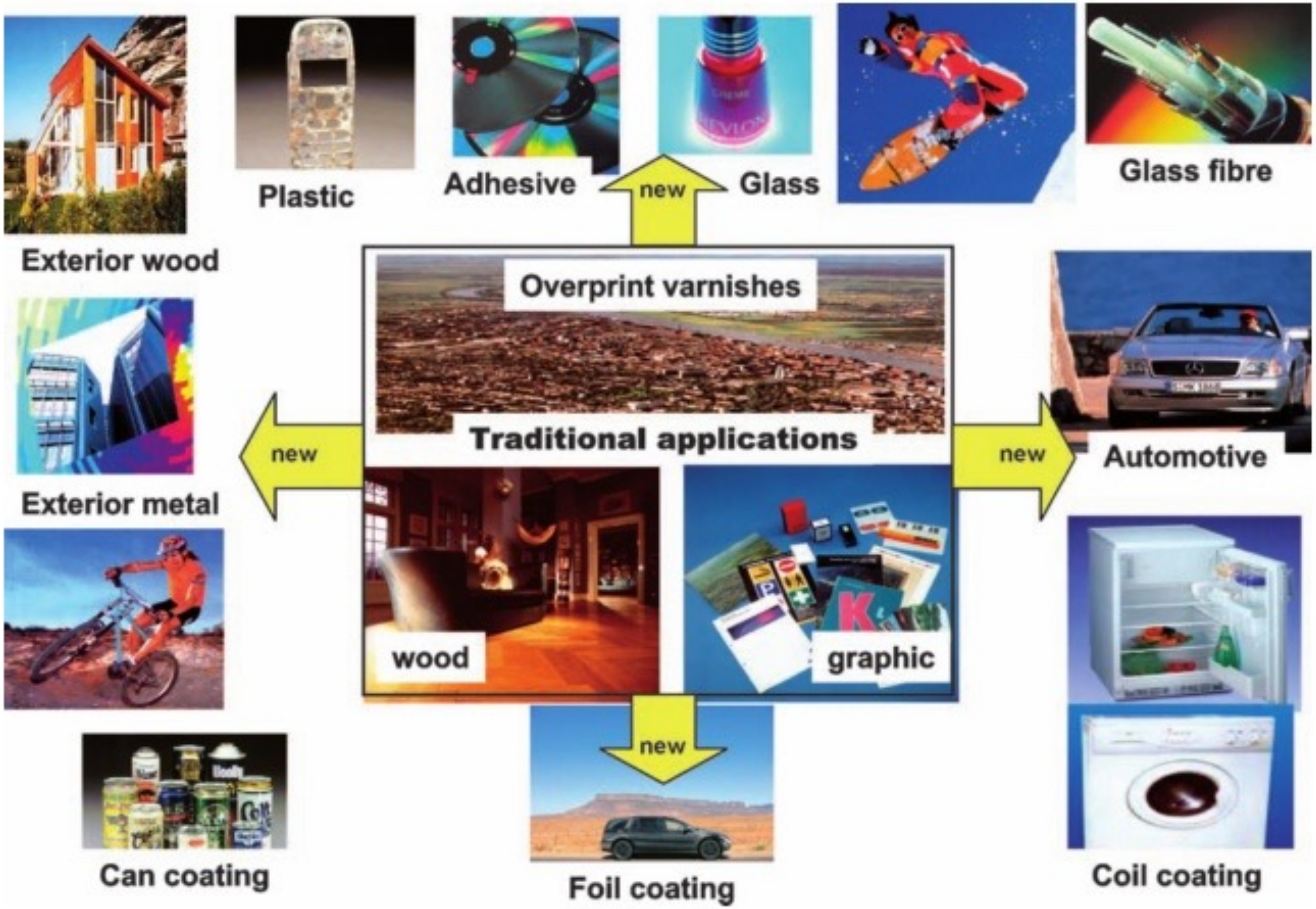
THE PHOTOPOLYMERIZATION PROCESS IS A RAPID TRANSFORMATION OF A LIQUID MONOMER INTO A SOLID POLYMER INDUCED BY LIGHT.

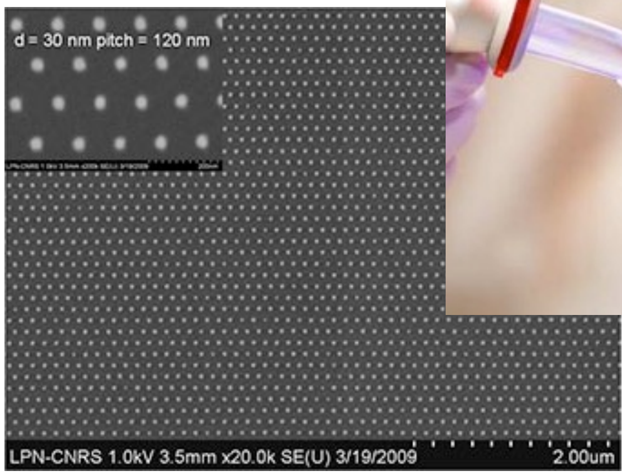
WHEN MULTIFUNCTIONAL MONOMERS ARE USED AS STARTING MATERIALS A POLYMER NETWORK IS FORMED.

WHY PHOTOPOLYMERIZATION



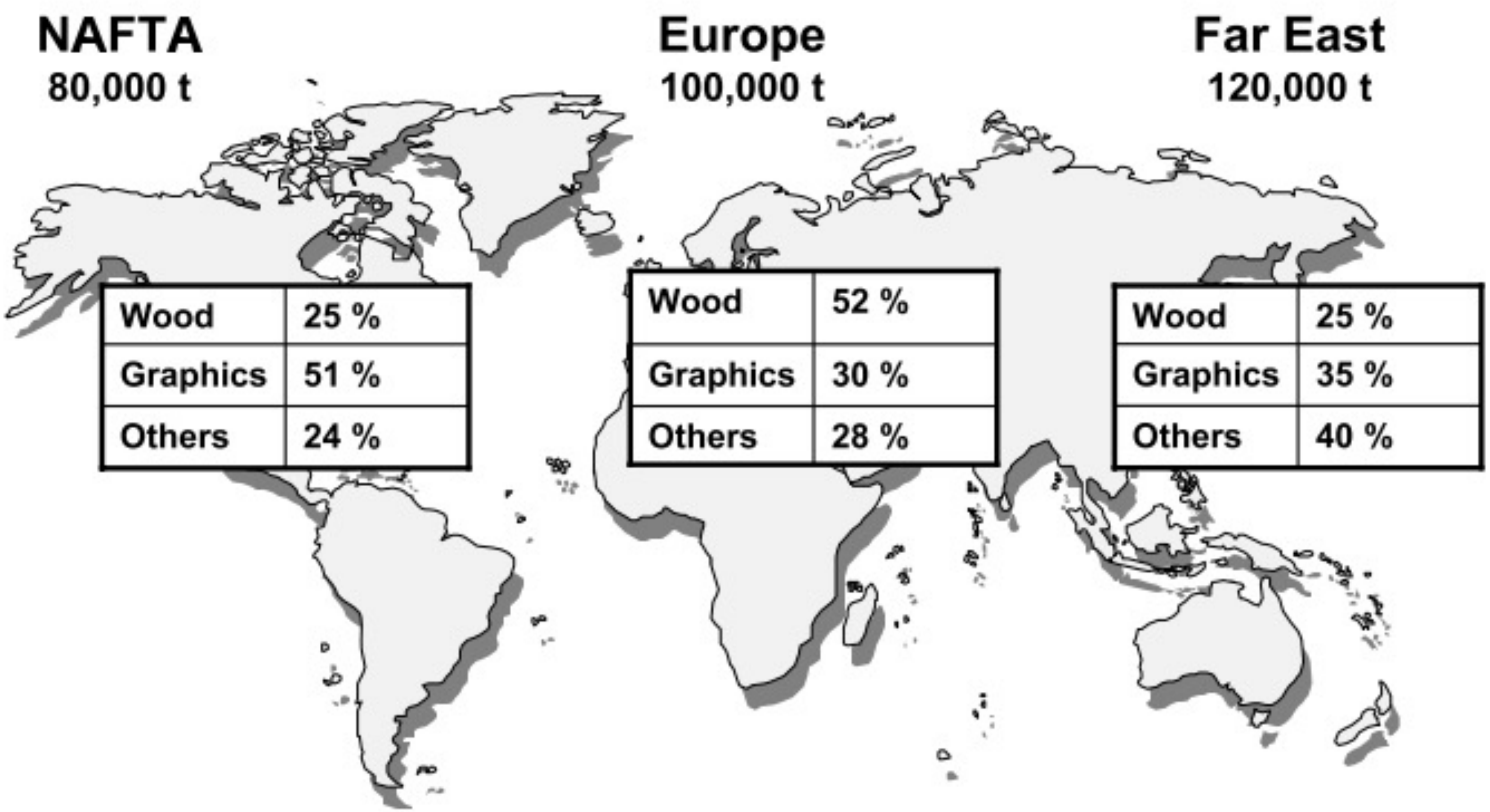
UV coatings – from traditional to new applications.

WHY PHOTOPOLYMERIZATION



MARKET OF INDUSTRIAL COATINGS

Market of industrial coatings in Europe and share of UV acrylates.



MARKET OF INDUSTRIAL COATINGS

https://www.psmarketresearch.com/market-analysis/uv-curable-resins-market

FIELDS OF APPLICATIONS

Decorative coatings: Book covers, posters, vinyl flooring, etc.

Protective coatings: for plastic lenses, corrosion protection, etc.

Printing industry: Printing plates and ink manufacture

Optics: Optical fiber and coatings, protective coatings for compact discs

Electronics: Organic polymer conductive materials, etch resists, insulation layers for printed circuits

Adhesives: Primers for metal and glass coatings, adhesive layers for laminated safety glass

Miscellaneous: Dental filling compounds sealing compounds, traffic markings, etc.

PHOTOPOLYMERIZATION: ADVANTAGES

Economical advantages

- Energy saving (commonly rapid cure at room temperature)
- High production speed, spatial and time control (on/off)
- Small space requirements
- Immediate post cure processing possible

Ecological advantages

- In general solvent free formulations (VOC reduction)
- Possibility of easy recycling (waste reduction)
- Energy saving

Performance advantages

- Low substrate heating
- High product durability
- Application versatility
- High scratch resistance and chemical resistance
- Exceptional abrasion, stain and solvent resistance
- Superior toughness

PHOTOPOLYMERIZATION: DISADVANTAGES

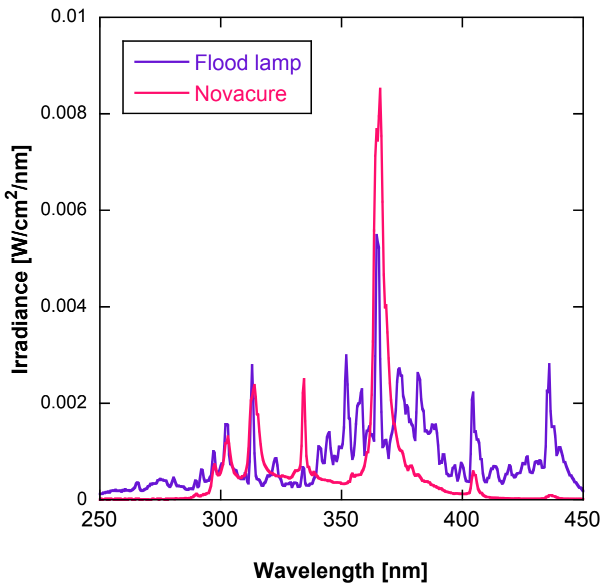
Drawbacks

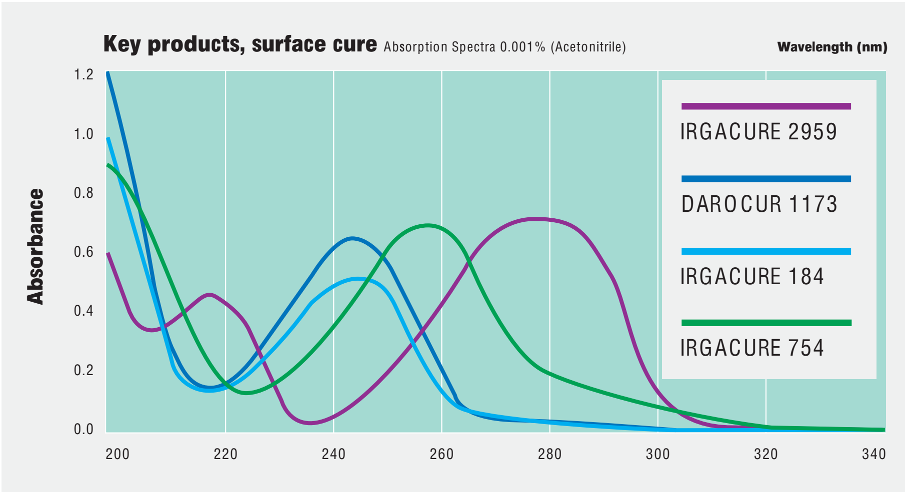
- Material costs are higher than, e.g., alkyds, polyesters or epoxies
- 3D curing equipment development is in its infancy
- UV curing in the presence of UV stabilizers decelerated
- Oxygen inhibition at the surface (in many radical curing systems)
- Sensitivity to moisture (cationic curing system)
- Difficult through-cure of pigmented coatings (at thicknesses $>5\ \mu m$)
- For bio-applications: energy of light, possible heat of reaction, formation of radicals, toxicity of photoinitiators…

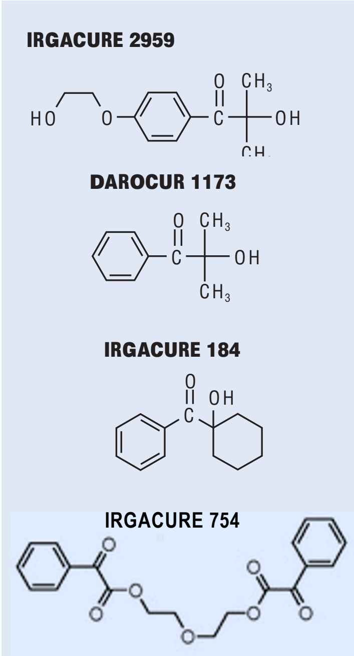
WHAT AND HOW PHOTOPOLYMERIZATION

In photopolymerizable formulations only the first reaction step, which is the production of an initiating species, is a photochemical reaction. The polymerization itself is exclusively a thermal chain reaction. This chain process amplifies the first photochemical event by a factor of several hundreds and explains in part why photopolymerization is very efficient and therefore an industrially acceptable process.

UV-radiation <–> photoinitiator







LIGHT

Photochemistry is concerned with all aspects of light absorption by matter, which results either in a chemical change of the original molecule or a recovery of this molecule without any modification.

WHAT IS LIGHT?

characterized by:

Frequency ν

speed c

wavelength λ

Light obeys the relationship

$$\nu = c / \lambda$$

LIGHT is that which is perceived by the human eyes, but it can be more amply defined to as optical radiations with a wave-like and corpuscular character characterized by its frequency (ν), its wavelength (λ) and transport an energy (E)

$$\mathbf{E = hc/\lambda = h\nu}$$

they fall into several classes:

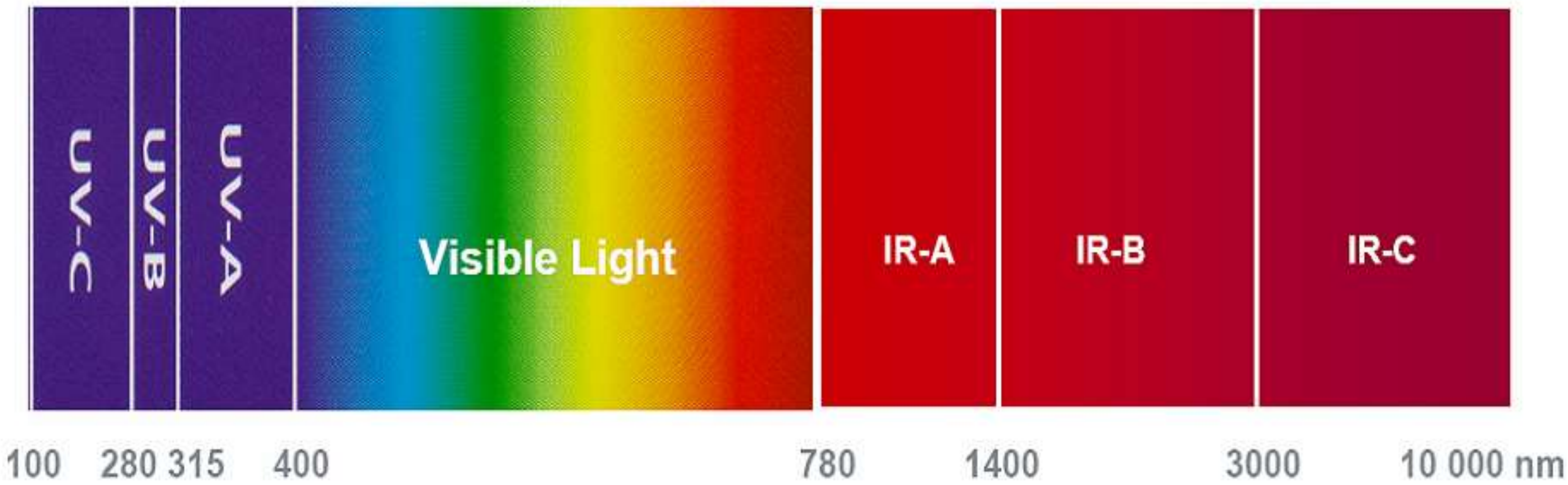
UV 200-400 nm

VIS 400-700 nm

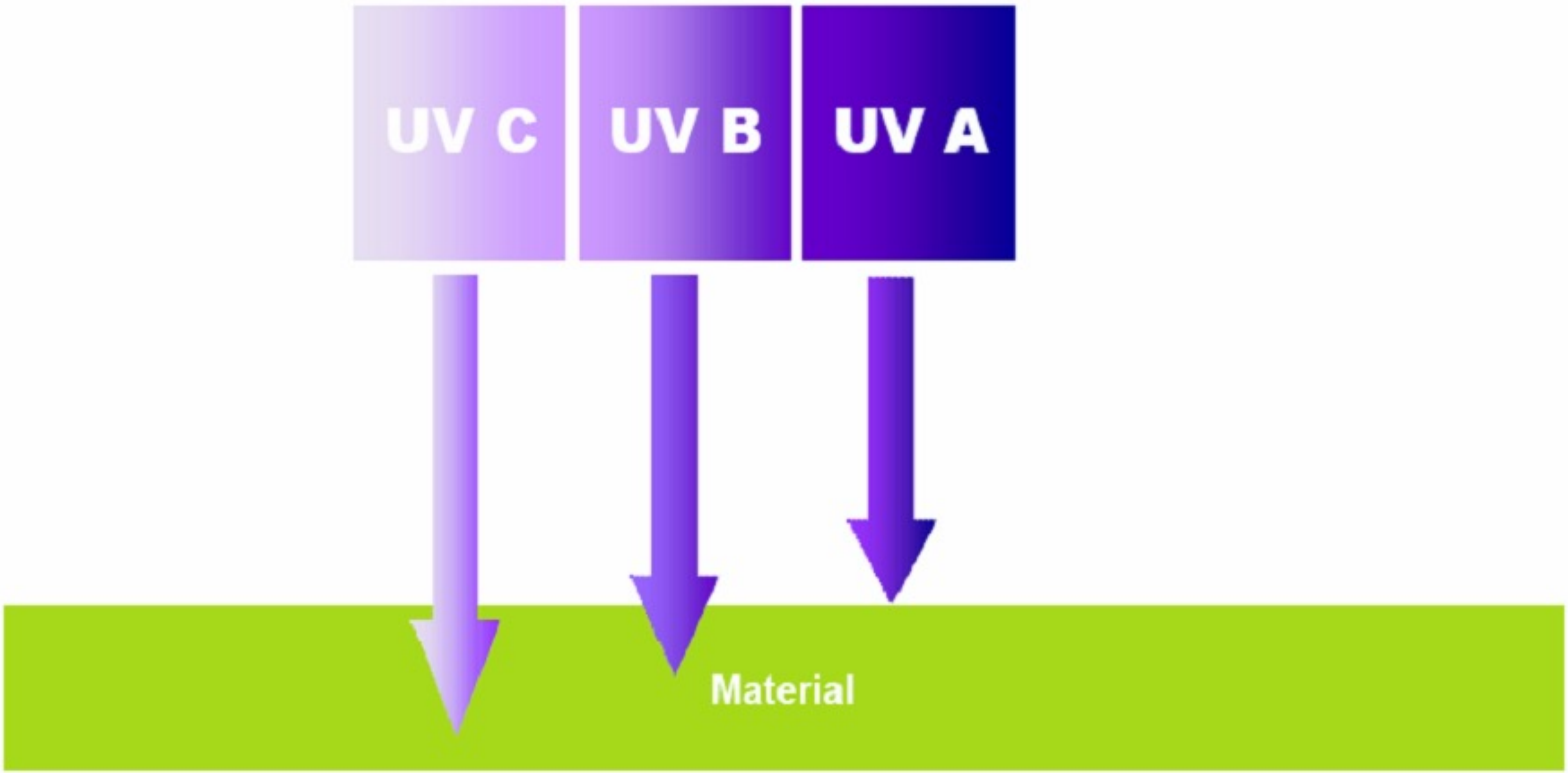
IR 700-1000 nm

THE ELECTROMAGNETIC SPECTRUM

$$E = hc/\lambda = h\nu$$



Penetration of the Material by UV Radiation



A molecule can absorbs a quantum of radiation and thus becomes energetically excited.

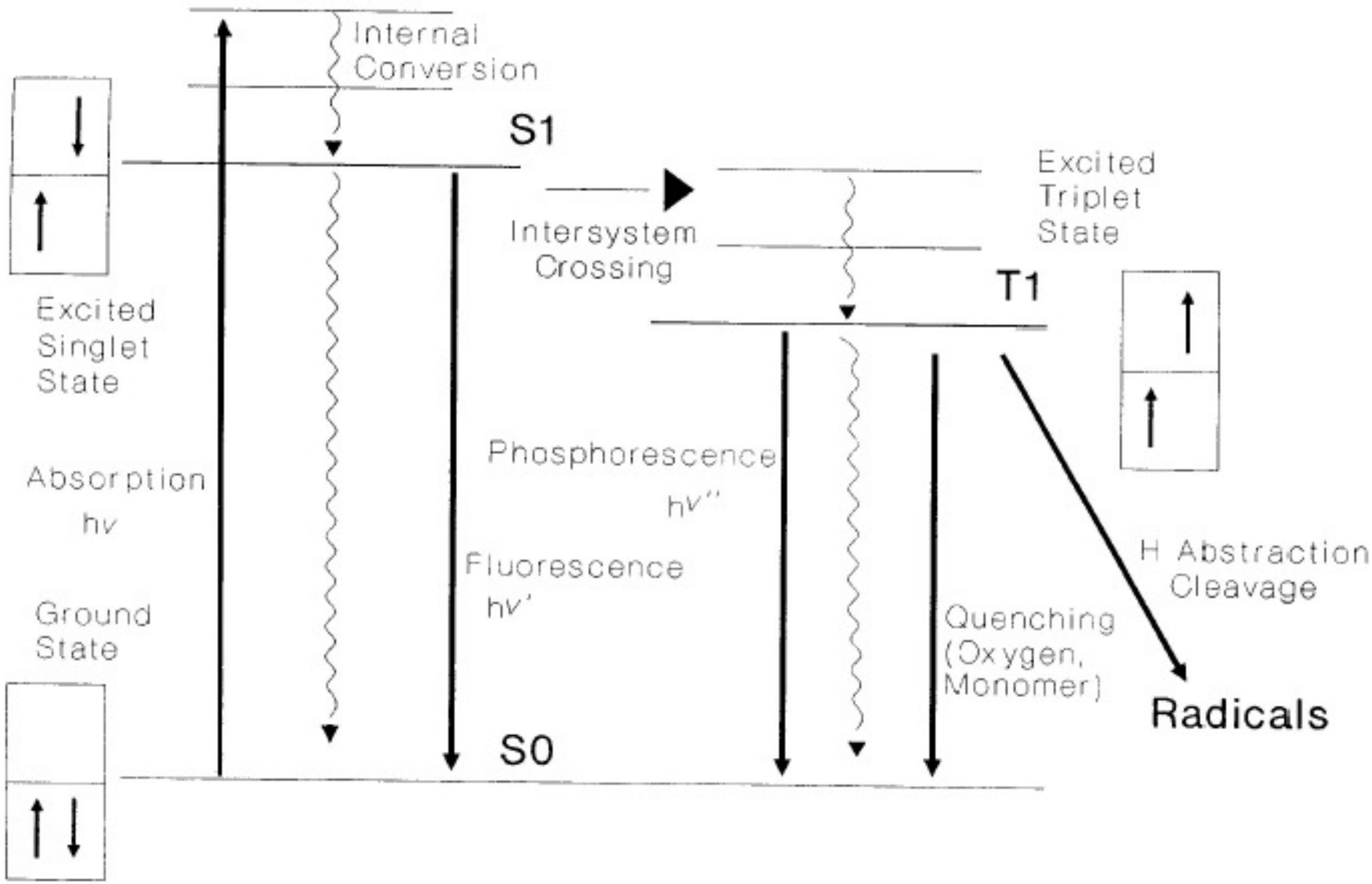
The energy of the photon absorbed should correspond to the exact difference in energy between the initial state E^0 (ground state) and the final state E^1 (excited state).

$$E^1 - E^0 = h\,\nu$$

Because of Pauli's principle, the spins of two electrons in the same orbital must be paired: as a result, there is not net spin and such a configuration corresponds to a singlet ground-state (**S_0**).

If one electron moves up to an unoccupied orbital, a singlet excited state **S_1** is formed, from which a triplet excited state **T_1** can be generated (the two electrons now possess parallel spins).

PERRIN-JABLONSKI'S DIAGRAM



BASIC STEPS IN PHOTOPOLYMERIZATION

1. **Absorption of light**
2. **Bond cleavage (generation of reactive species)**
3. **Addition of reactive species to monomers (initiation)**
4. **Chain growth (propagation)**
5. **Termination**

FORMULATION

A photopolymerizable formulation contains 4 types of compounds:

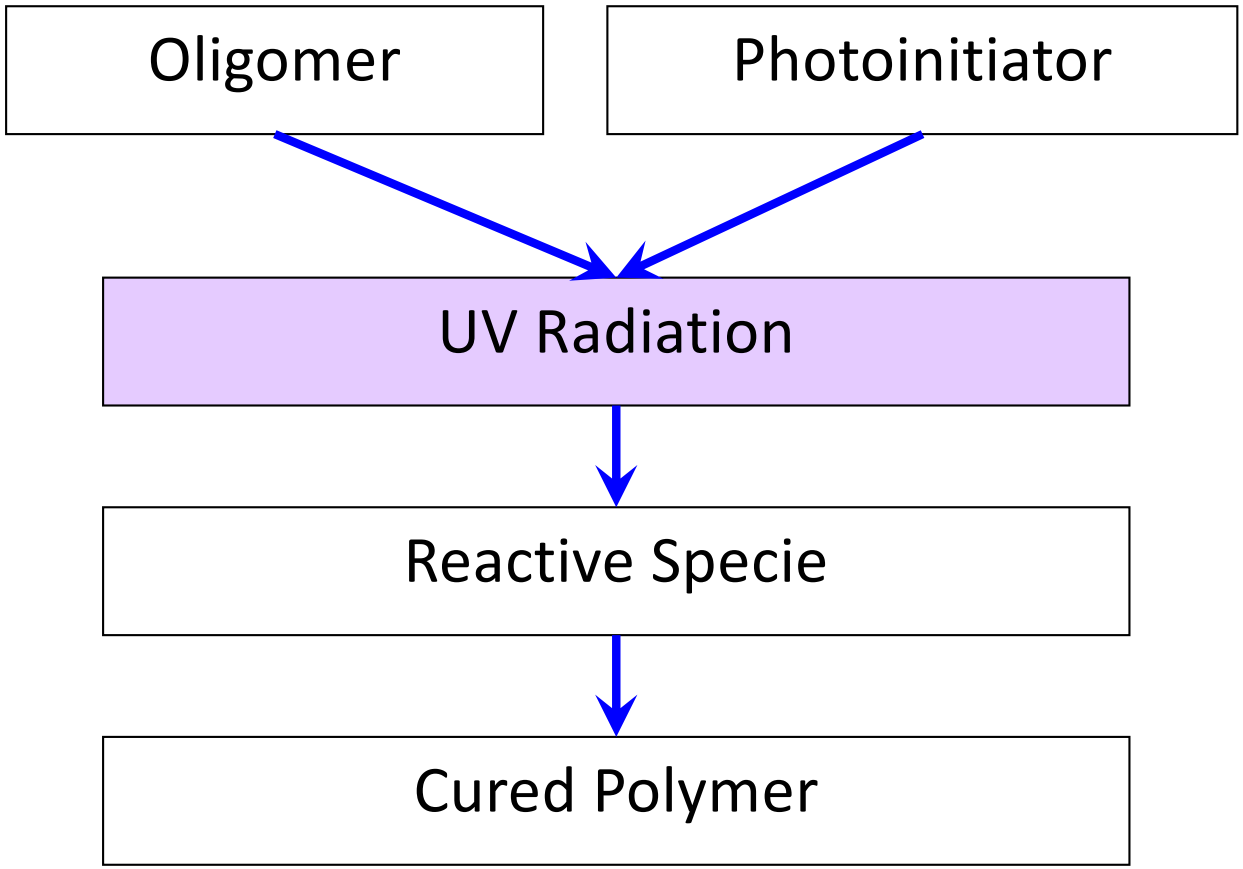
1. **A Photoinitiator**: in addition, there are often several photoinitiators and photosensitizers, giving a symergistic effect.
2. **A reactive diluent**: whose role is to adjust the viscosity and it also participate to the polymerization reaction.
3. **An oligomer**: this is generaly a multifunctional monomer which gives a crosslinking polymerization. The backbone of the oligomers has a chemical structure which can be varied and confers to the polymers its properties.: hardness, abrasion resistance, solvent resistance, elasticity, adhesion, permeability, etc…
4. **Additives**: the role of additives is to provide special properties: fillers, pigments, stabilizers, wetting agents, ati-foam, etc…

FORMULATION

General composition and function of an UV lacquer

Component	Share (%)	Function
Oligomeric resin	25–90	Film formation Basic properties
Reactive diluents	15–60	Viscosity adjustment X-link density
Photoinitiator	1–8	Initiation
Additives	1–50	Surfactants, pigments, fillers, stabilizers, etc.

WHAT AND HOW PHOTOPOLYMERIZATION



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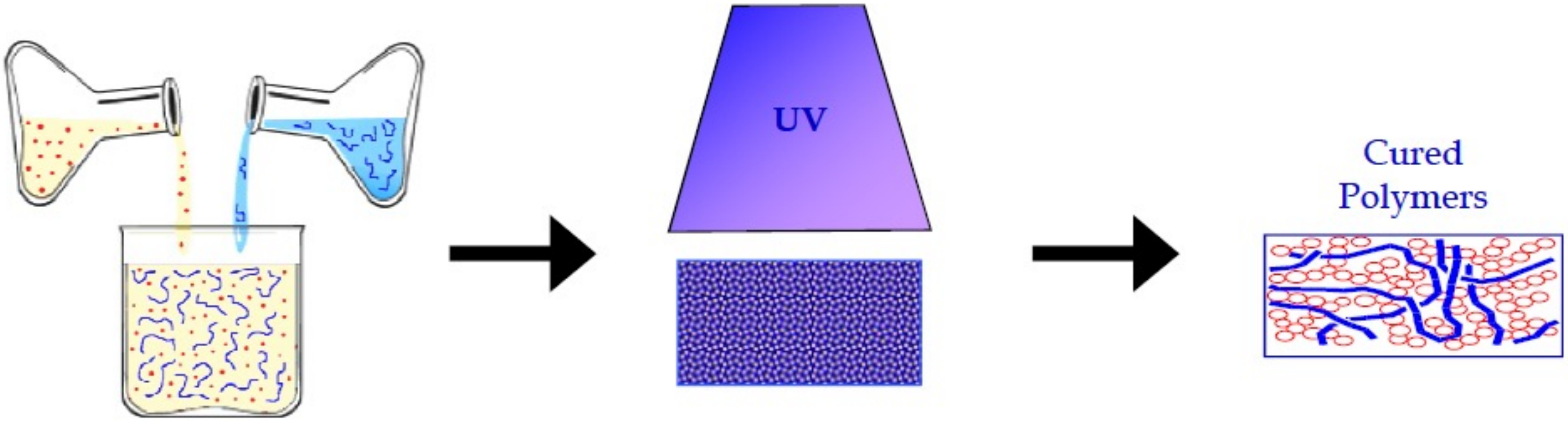
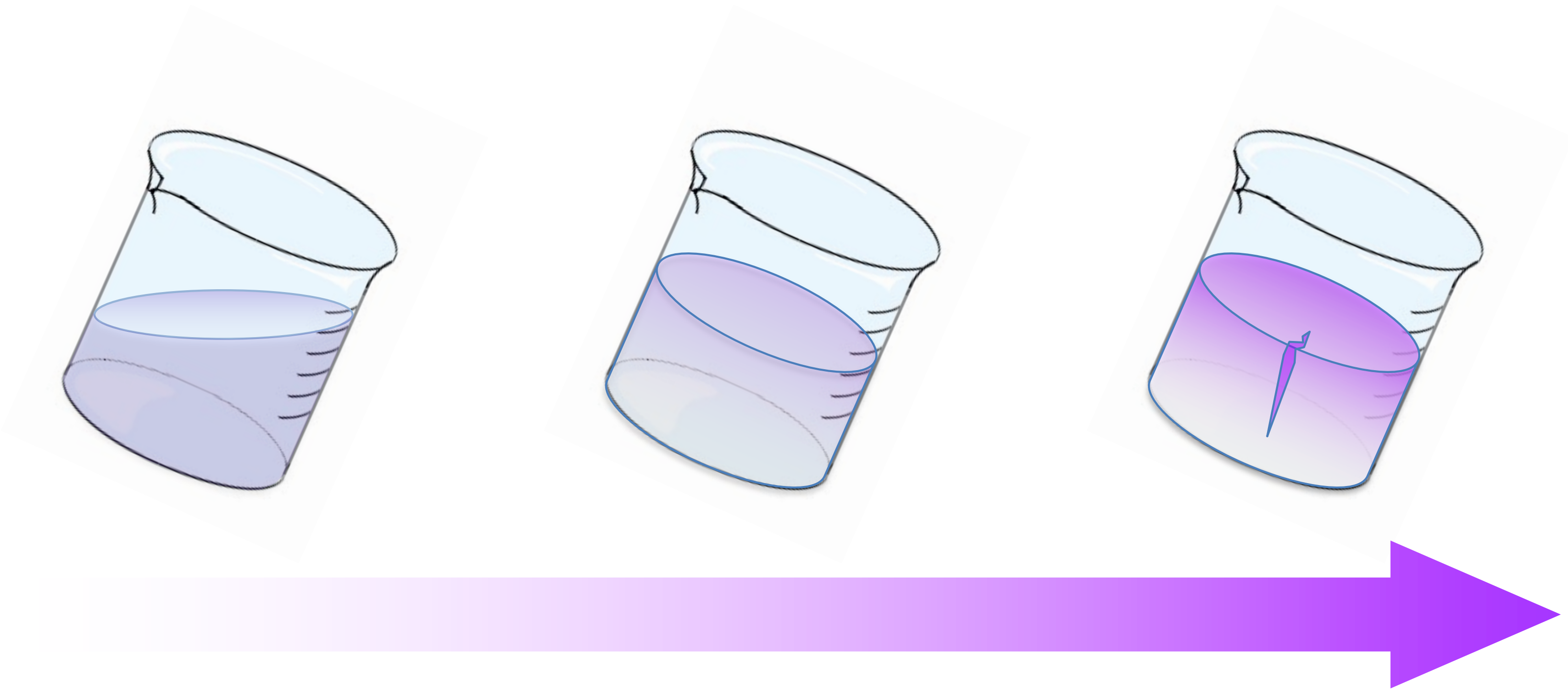


WHAT AND HOW PHOTOPOLYMERIZATION



WHAT YOU WILL LEARN

- What are the main classes of photopolymer systems
- What are the main factors, which control the photopolymerization process
- How to select the right formulation for a given application
- What are the standard methods to characterize the process-structure-property relations, and what new methods are developed
- What new materials and new applications are being developed

WHAT YOU WILL READ

BOOKS

- “Photopolymerization of surface coatings“ C.G. Roffey, Wiley, New York, 1982.
- “Radiation Curing Science and Technology”, S.P. Pappas Ed., Plenum Press, New York, 1992.
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REVIEW ARTICLES

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- C. Decker, “Photoinitiated Crosslinking Polymerization” Progress in Polymer Science, Vol. 21, 593, 1996.
- Y. Yagci, S. Jockusch, N. J. Turro, “Photoinitiated Polymerization: Advances, Challenges, and Opportunities”, Macromolecules, 43, 6245-6260, 2010.
- M. Sangermano, R. Bongiovanni, G. Malucelli, A. Priola “New developments in cationic photopolymerization: process and properties” in “Horizons in Polymer Research”, R.K. Bregg Ed., Nova Science Publisher Inc., New York, 61-82, 2006.
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