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DI TORINO

Roberta Bongiovanni

roberta.bongiovanni@polito.it

Department of Applied Science and Technology

Politecnico di Torino, Italy

Light and chemistry

SCIENCE

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CONTENTS

The Photochemistry of the Future: Professor Giacomo Ciamician 385

The First International Eugenics Congress: Professor Raymond Pearl 395

Industrial Education in the Philippines 396

Graduates from American Colleges and Universities 397

The Harpswell Laboratory 397

Scientific Notes and News 398

University and Educational News 400

Discussion and Correspondence:—
The Policy of the Geological Survey: Dr. Geo. Otis Smith. *School Grades—to What Type of Distribution shall they conform?* Dr. A. P. Weiss 401

Scientific Books:—
Colman on Nature's Harmonic Unity: Professor Arnold Emch. *Case's Revision of the Amphibia and Pisces of the Permian of North America:* Dr. Maurice G. Mehl. ... 407

Notes on Infectious Abortion in Cattle: Dr. Frank M. Surface 409

Special Articles:—
The Effects of Alkaloids on the Development of Fish (Fundulus) Embryos: Dr. J. F. McClendon. *On the Relationship between the Bilateral Asymmetry of the Unilocular Fruit and the Weight of the Seed which it produces:* Dr. J. Arthur Harris. *Heat Conductivity of Crystals:* Dr. R. W. Clark. *Some Curious Cases of Selective Reflection in Ultra-violet Light:* Gustave Michaud 412

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of Science, Garrison-on-Hudson, N. Y.

THE PHOTOCHEMISTRY OF THE FUTURE[1]

Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

G. Ciamician
Science 36 (926), 1912,. 385-394

1912

G. Ciamician (University of Bologna, Italy) conceptualized the development of a new chemistry based on light

Light and polymer chemistry

PHOTOPOLYMERISATION: *Polymerisation requiring a photon for the propagation step*

PHOTOINDUCED POLYMERISATION: *Polymerisation of a monomer by a free radical or ionic chain reaction initiated by photoexcitation*

PHOTOCURING*: Technical expression for the photoinduced hardening of a monomeric, oligomeric or polymeric substrate normally in the form of a film*

PHOTOGRAFTING*: Photoinduced reaction in which one or more species of block are connected to the main chain of a macromolecule as side-chains having constitutional or configurational features that differ from those in the main chain*

PHOTODEGRADATION*: Photochemical degradation of a macromolecule into lower molecular weight fragments, usually in an oxidation process*

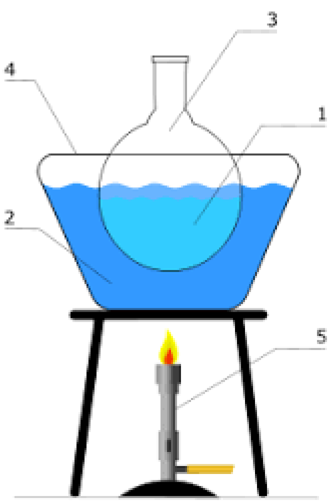
Photoprocesses have merged with new polymerization techniques (i.e. *controlled/living polymerization processes and supramolecular chemistry*)* resulting in the precise synthesis of complex architectures

J.V.Verhoeven *Glossary of terms used in photochemistry (IUPAC Recommendations 1996) Pure Appl. Chem. 68(12), 1996,* 2223-2286
K.Horie et al. Definitions of terms relating to reactions of polymers and to functional polymeric materials (IUPAC Recommendations 2003) Pure Appl. Chem., 76 (4), 2004, 889–906

Competiveness of photoprocesses/1

Comparison of energies available for activation

for a reactive systems at 25°C:



thermal bath:
1 unit of energy

1 mole of photons 350–450 nm:
100 unit of energy

SUSTAINABILITY

Competiveness of photoprocesses/2

- Photons are selectively taken by specific light harvesting molecules (chromophores) once the light is on, unlike thermal energy which is transferred throughout entire reaction mixtures.

- Production of light with great precision over the emission wavelength, without using expensive equipments

- Use of a large window of the electromagnetic spectrum

- Specific reaction paths can be activated "on demand"

→ precise and efficient transformations.

Overall pros of photoprocesses for polymers

- Room temperature operation
- Fast reactions (even few seconds of irradiation are enough)
- Spatially controlled reaction
- Temporal control of reaction: stop & go reaction (thermal processes due to heat and mass transfer reasons can not instantaneously switch ON/OFF)
- Extrinsic control of reaction rate (through change of Intensity/wavelength)
- Bulk process (with reduction of volatile emissions COV)
- Space saving (irradiation units are small)
- ….

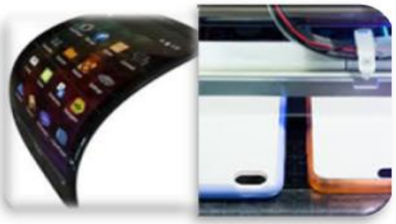
SUSTAINABILITY

Photopolymerisation potential /1

For the ability to react rapidly at r.t., photoinduced polymerization reactions are highly competitive and therefore ubiquitous


Photoresist for chip fabrication


Car finishing


Portable phone parts


Wood varnish


Card printing


Release coatings


Dental filling


Joining with adhesives


Contact lenses


Printing inks – Packaging

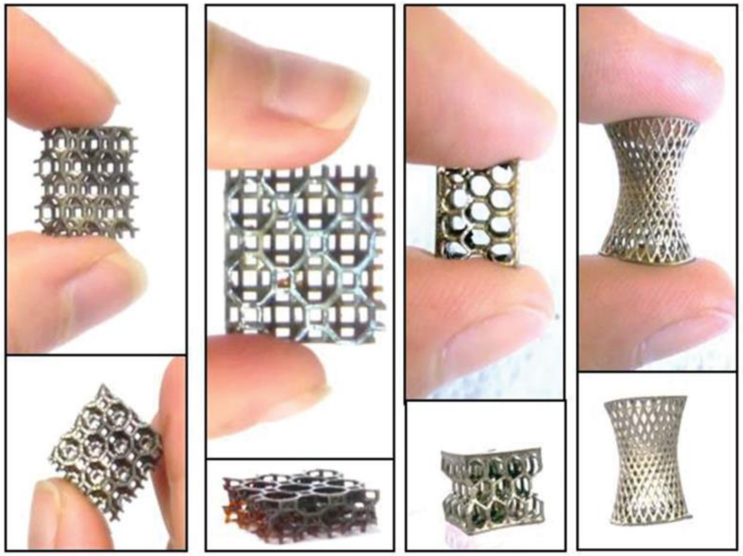

3D- printing


Nail lacquers

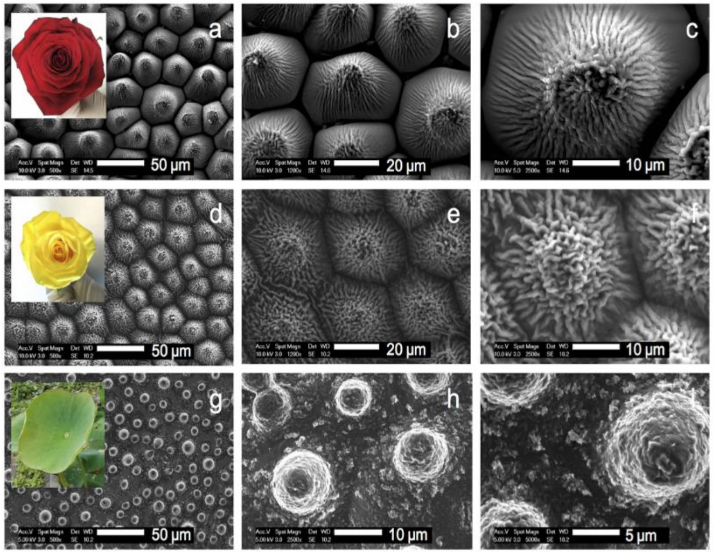
Photopolymerisation potential/2

For the intimate control in both time and space, photoreactions can be coupled with polymer processing techniques, e.g. patterning processes and 3D-printing

Some examples:

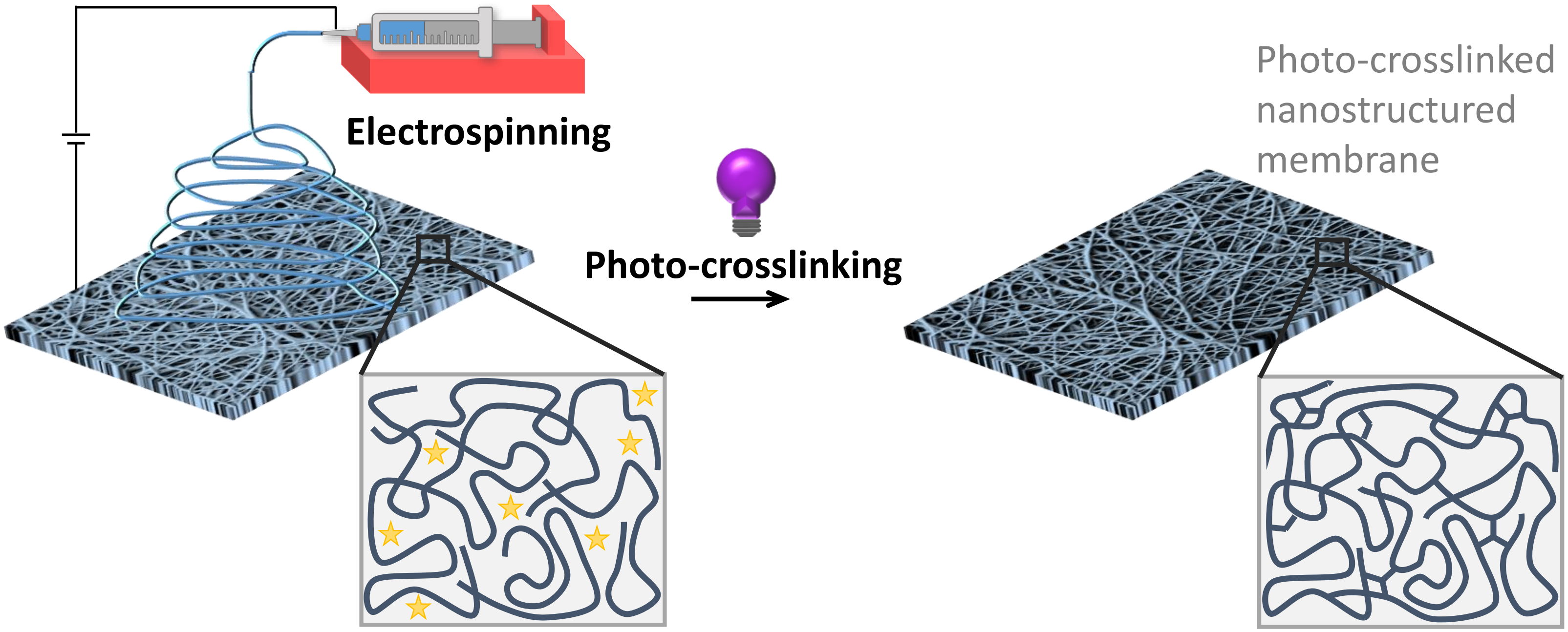


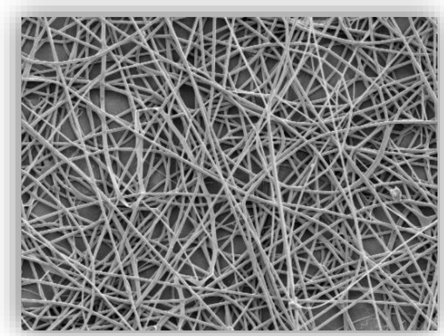
Fantino, E.; Chiappone, A.; Roppolo, I.; Manfredi, D.; Bongiovanni, R.; Pirri, C. F.; Calignano, F. Adv. Materials 2016, 28 (19), 3712–3717.



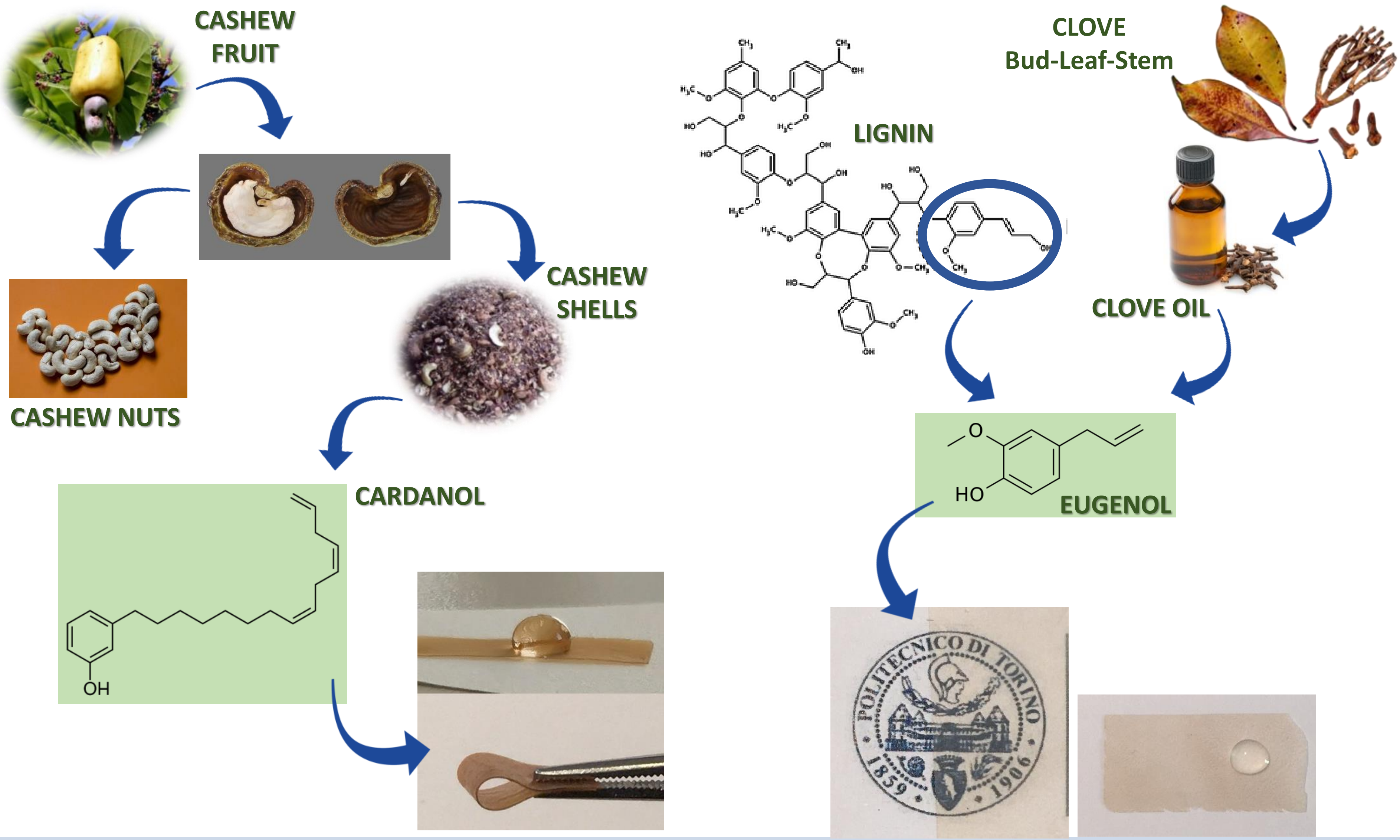
Wasser, L.; Dalle Vacche, S.; Karasu, F.; Müller, L.; Castellino, M.; Vitale, A.; Bongiovanni, R.; Leterrier, Y. Coatings 2018, 8 (12), 436

Photopolymerisation potential/3 polymer processings: electrospinning





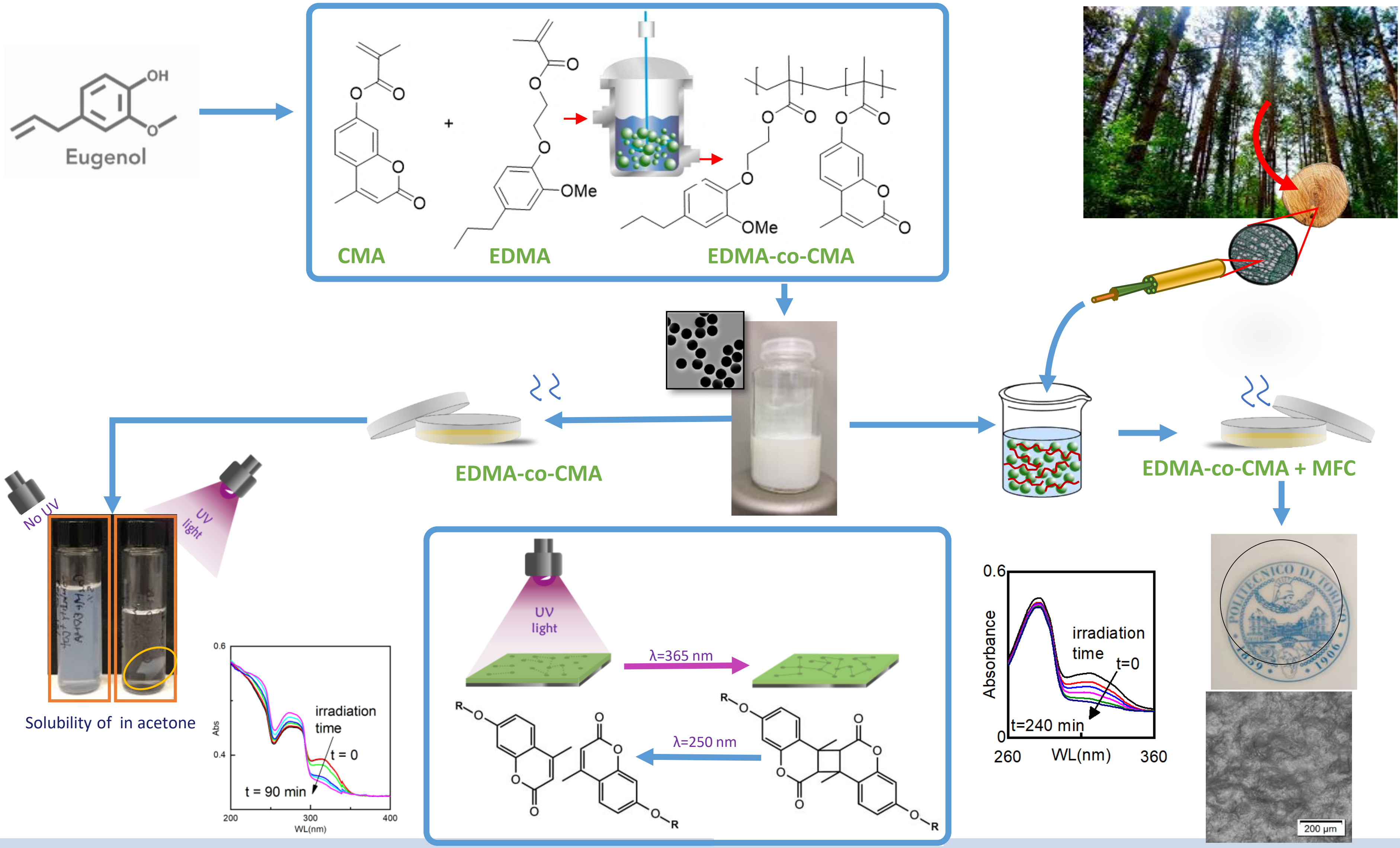
Our recent works on the use of biobased materials in photoinduced polymerisation



S. Dalle Vacche et al. *Molecules* **2019**, *24* (21), 3858; *J. Compos. Sci* **2021**, *5* (1), 11

S. Molina-Gutiérrez et al. *Molecules* **2020**, 25 (15), 3444

Our recent works on photoreversible curing (photoreversible networks



Grazie!
Thank you!
Merci!