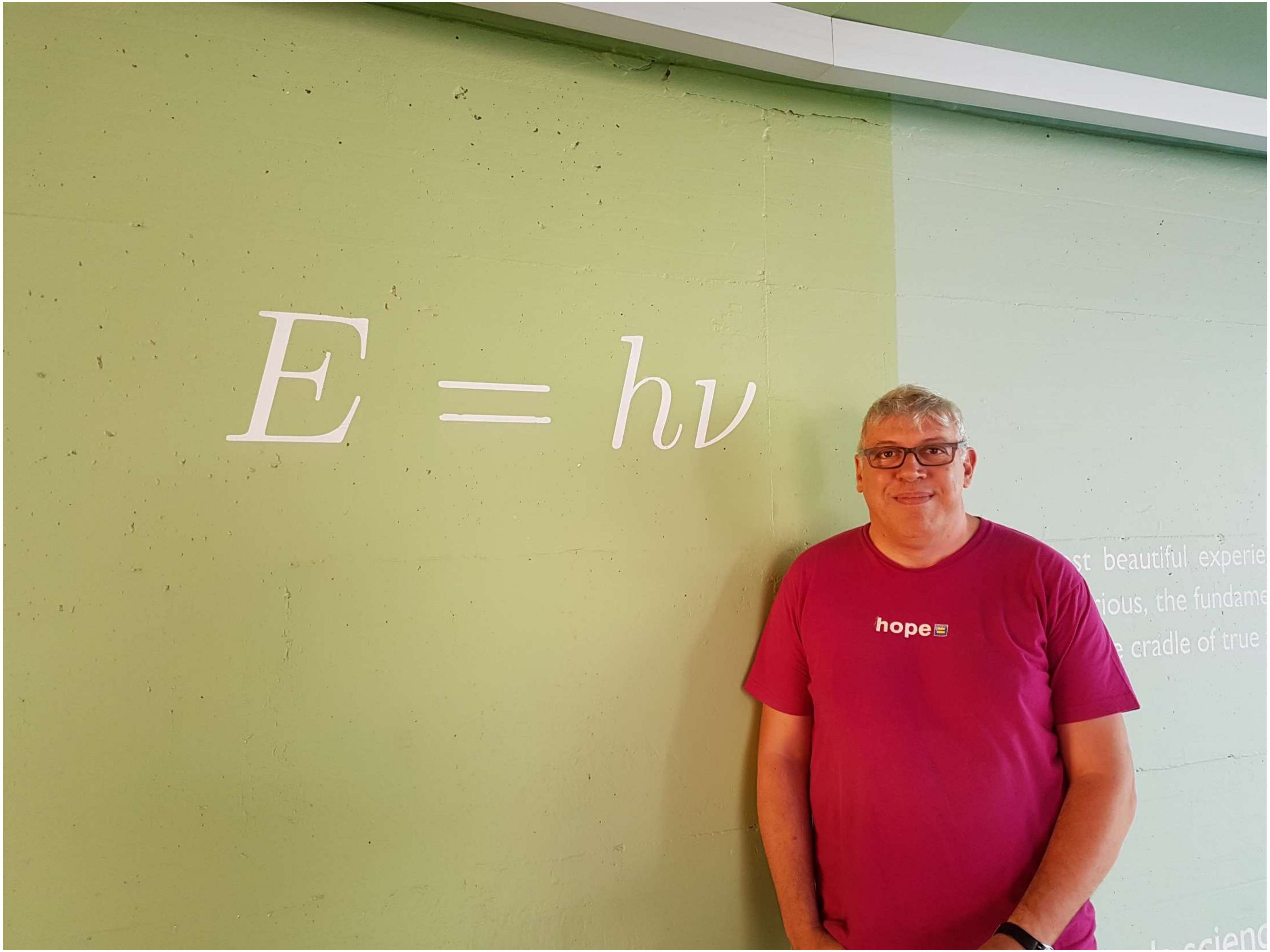
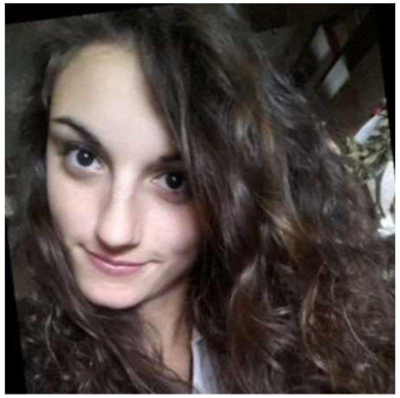

$E = h\nu$
hope
beautiful
cradle of true

POLITECNICO DI TORINO

Polymer Research Group

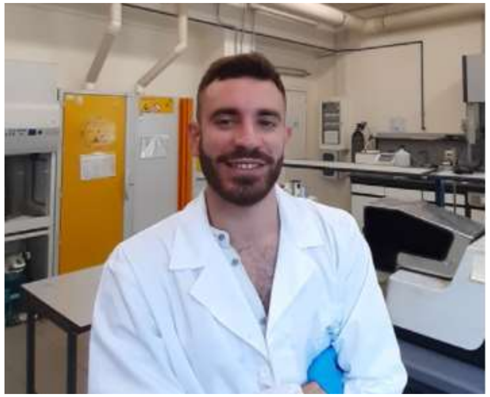
Marco Sangermano

PhD students



Camilla Noè

Andrea Cosola

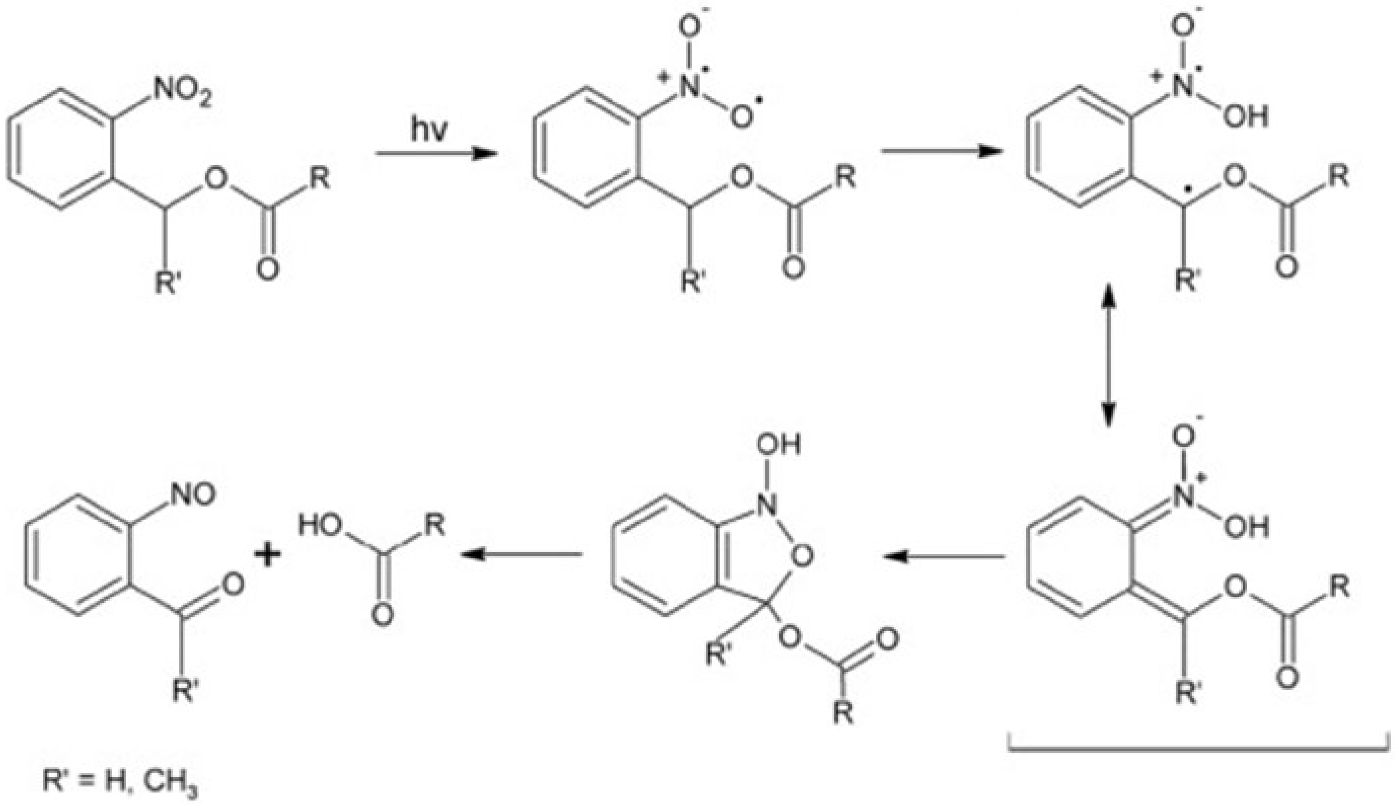


Michael Zanon

Lorenzo Pezzana

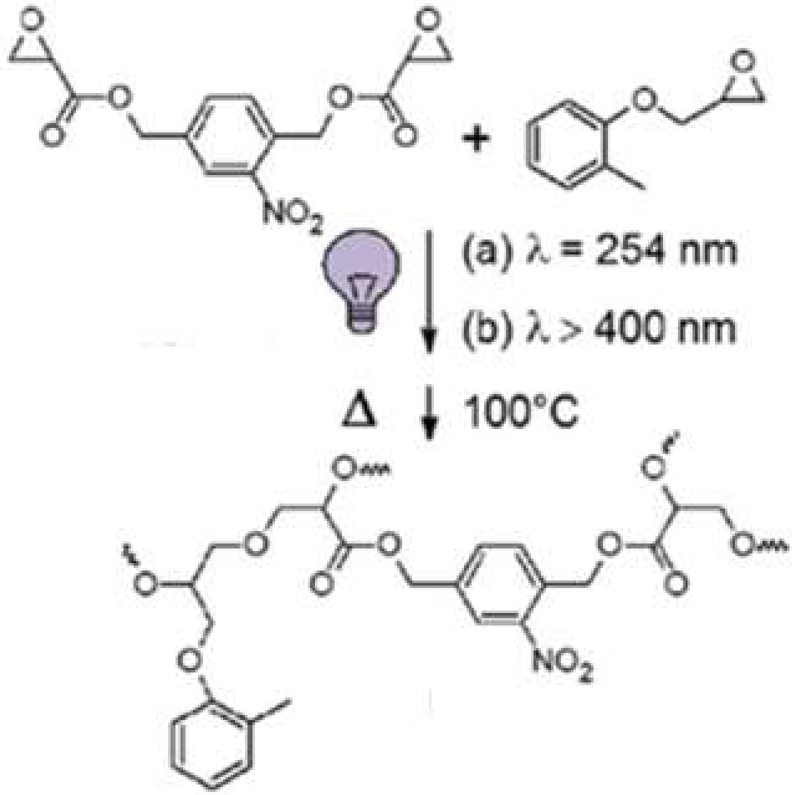
Photopatterning

Photodecrosslinking

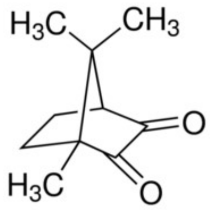


S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

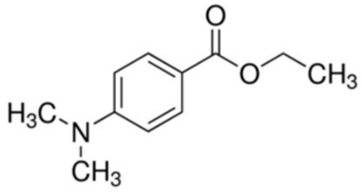
Epoxy-NBE



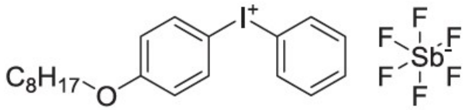
Visible light (>400 nm)



Camphorquinone

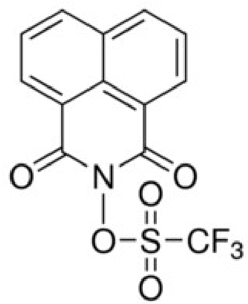


Ethyl 4-(dimethylamino)benzoate



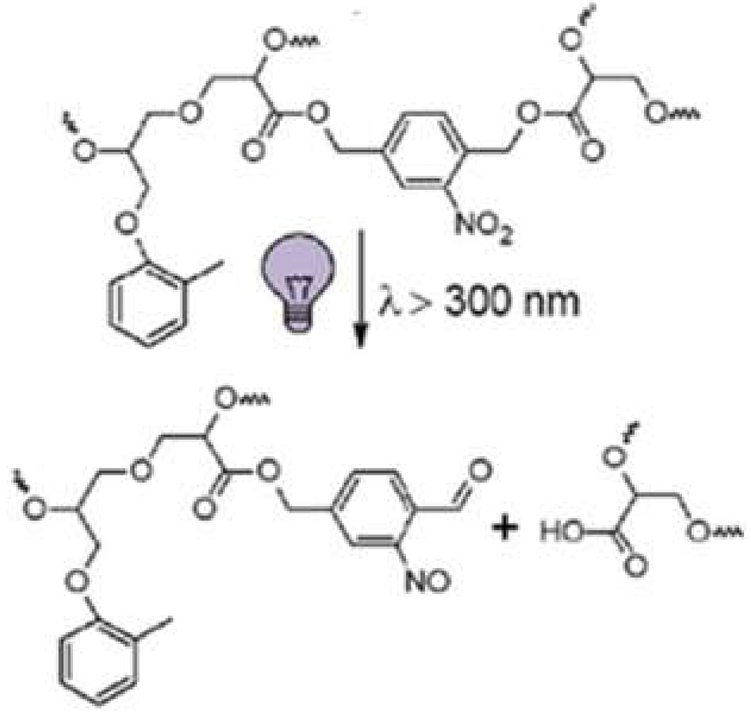
Iodonium Salt Photoinitiator

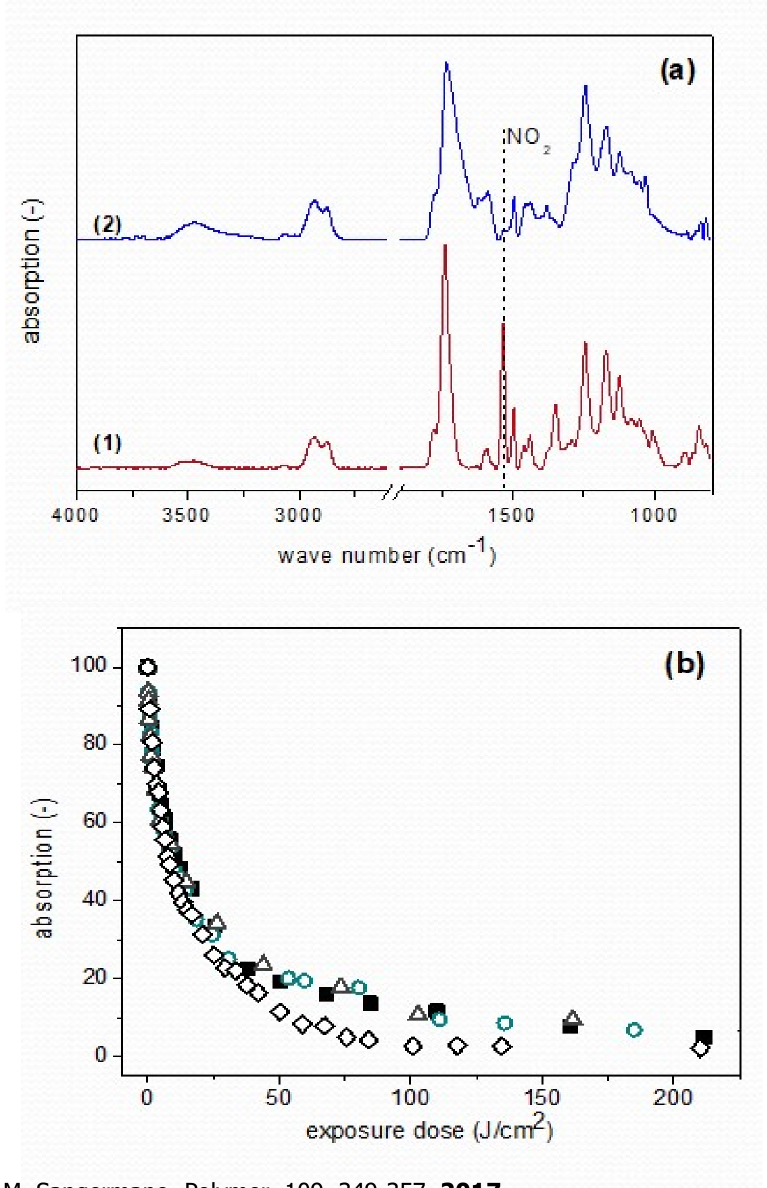
Deep UV (254 nm)



N-Hydroxynaphthalimide triflate

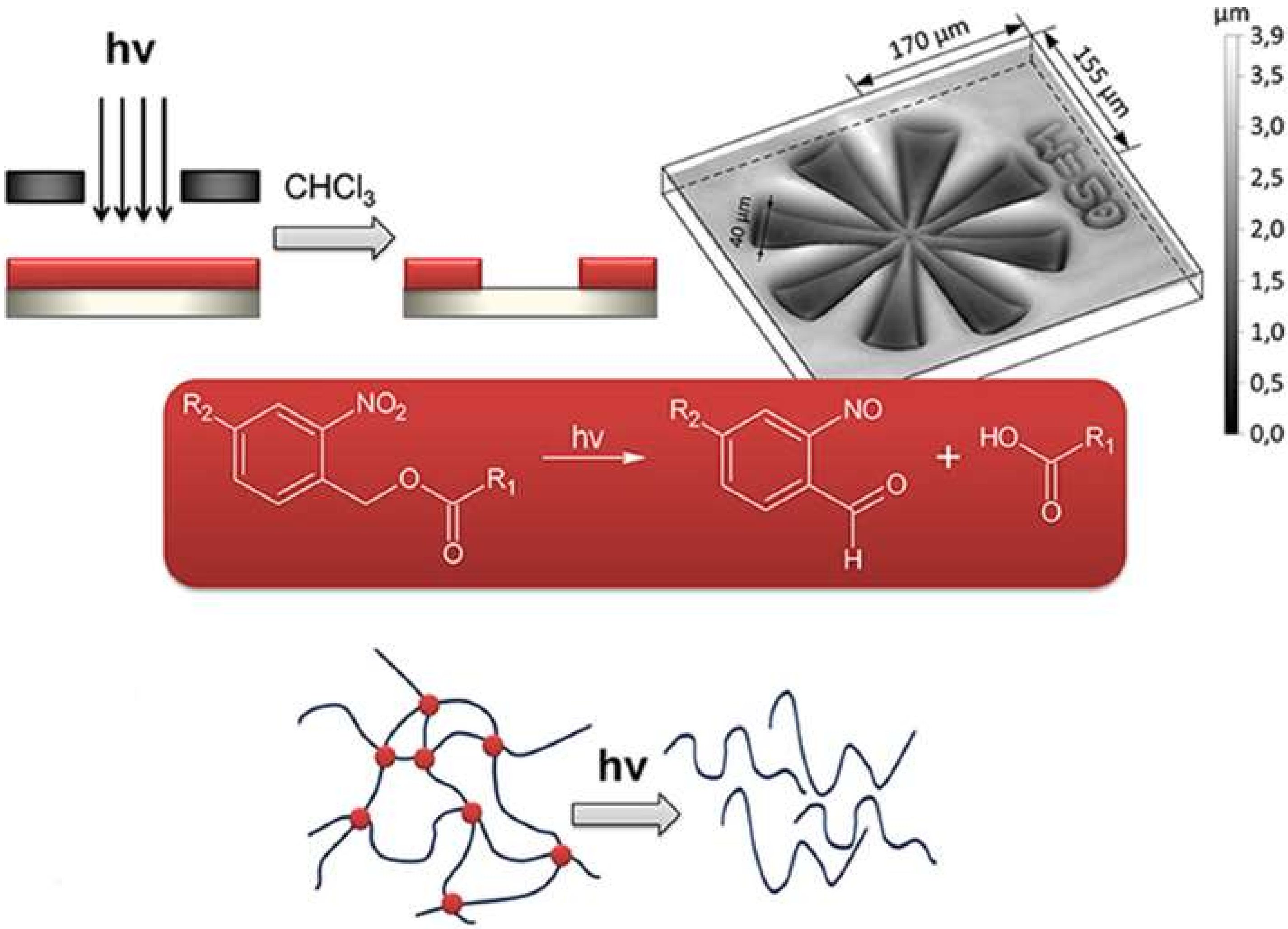
Photoclevage





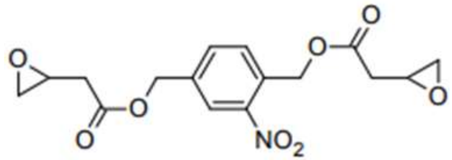
S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

Photoclevage

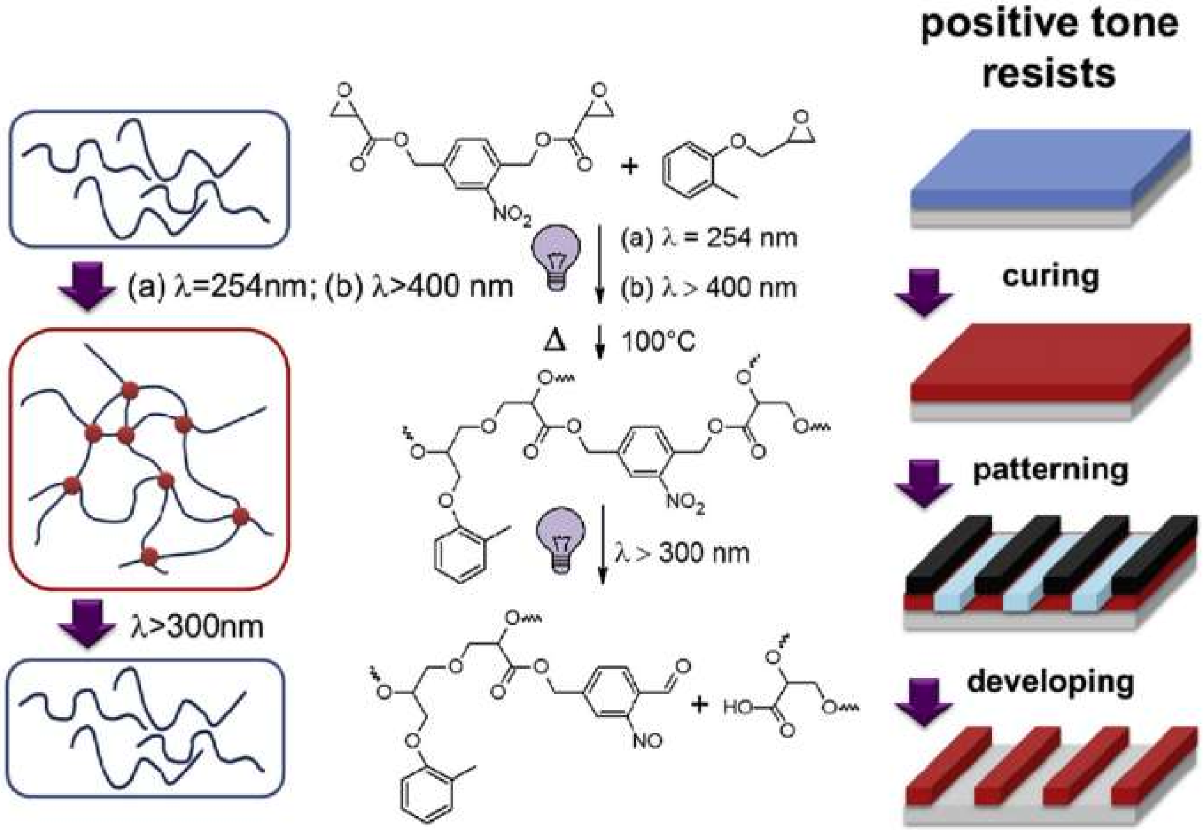


S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

Epoxy-NBE



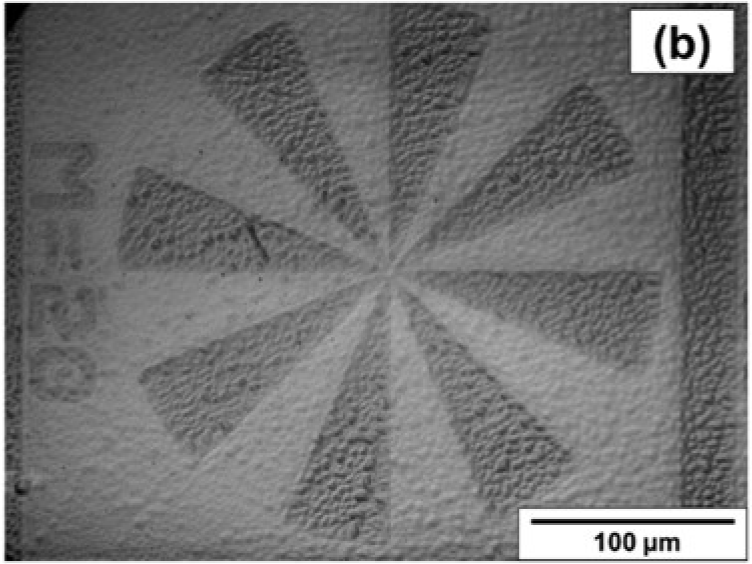
epoxy-**NBE**

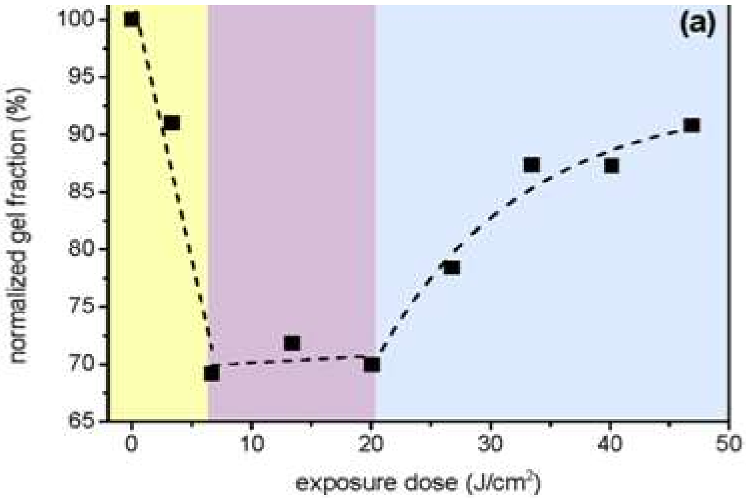


S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

Photoclevage

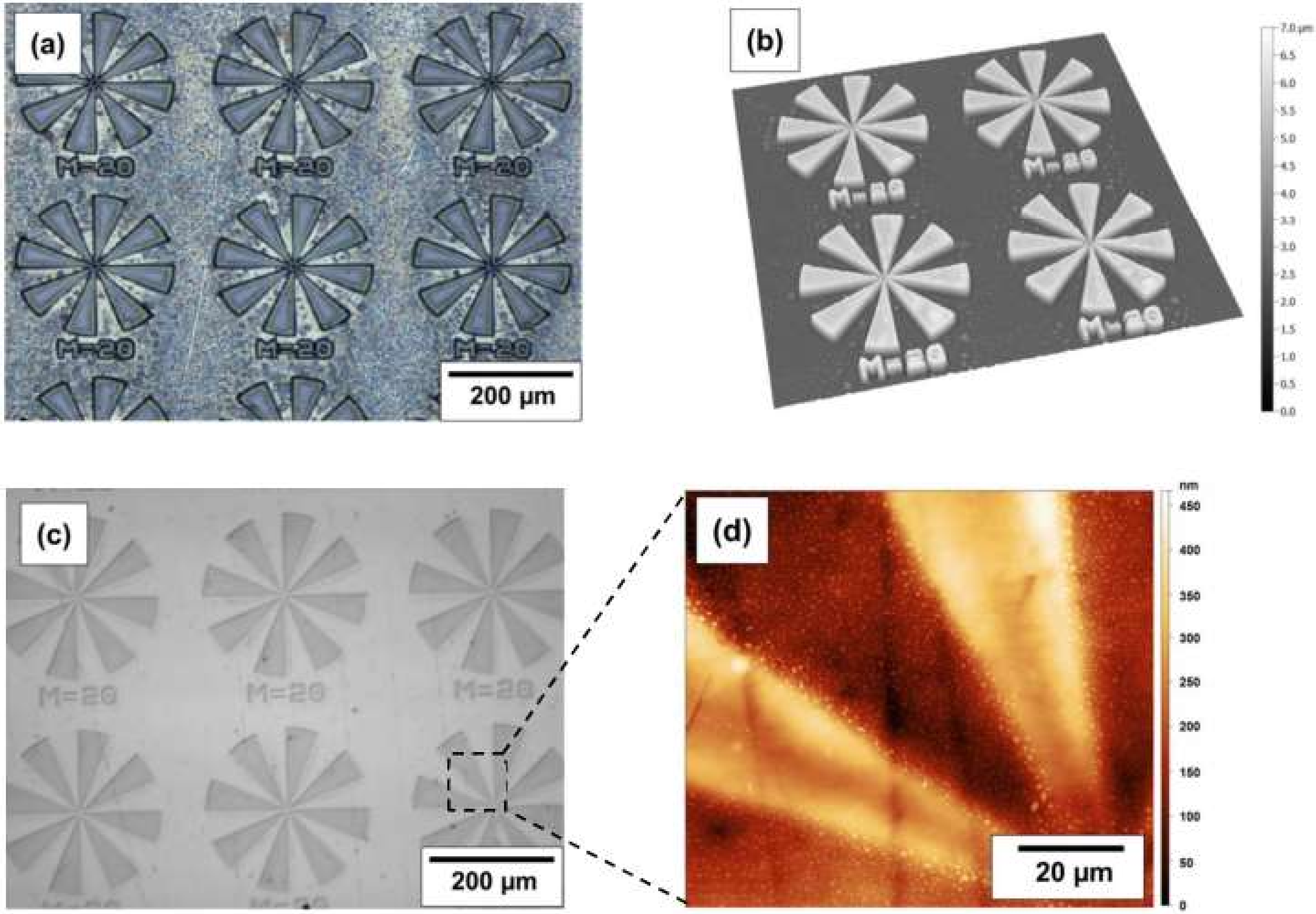
- Crosslinking points
- Film thickness (efficient decrosslinking in the firsts µm)
- Exposure dose





S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

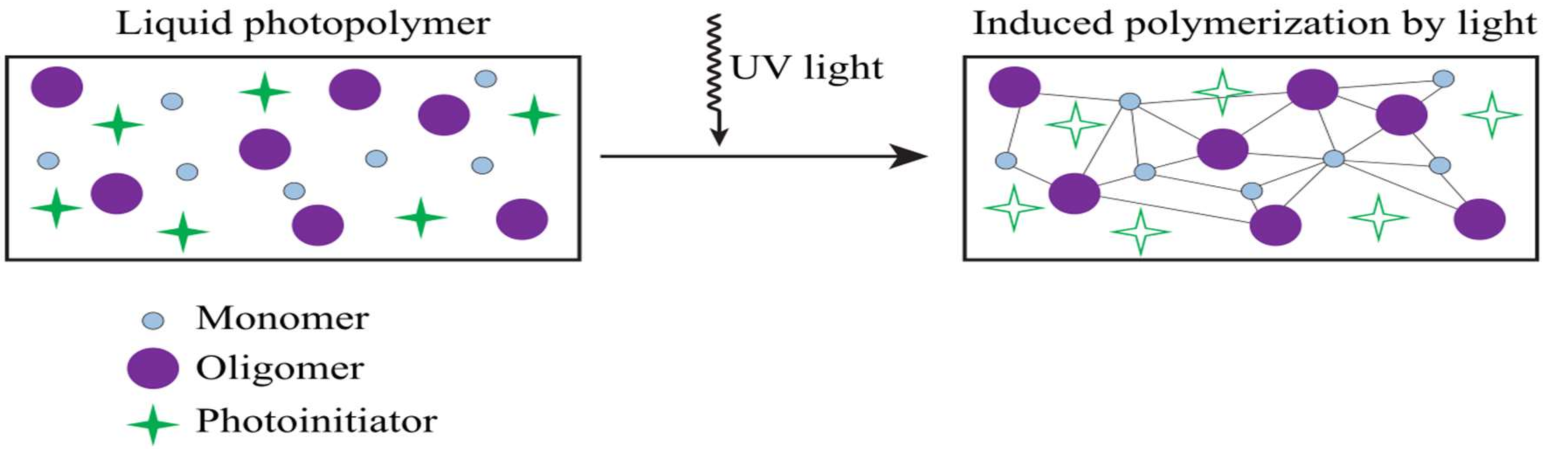
Selective Patterns



S. Radl, I. Roppolo, K. Pölzl, M. Ast, J. Spreitz, T. Griesser, W. Kern, M. Sangermano, Polymer, 109, 349-357**, 2017**

Frontal Polymerization

Photopolymerization



Advantages:

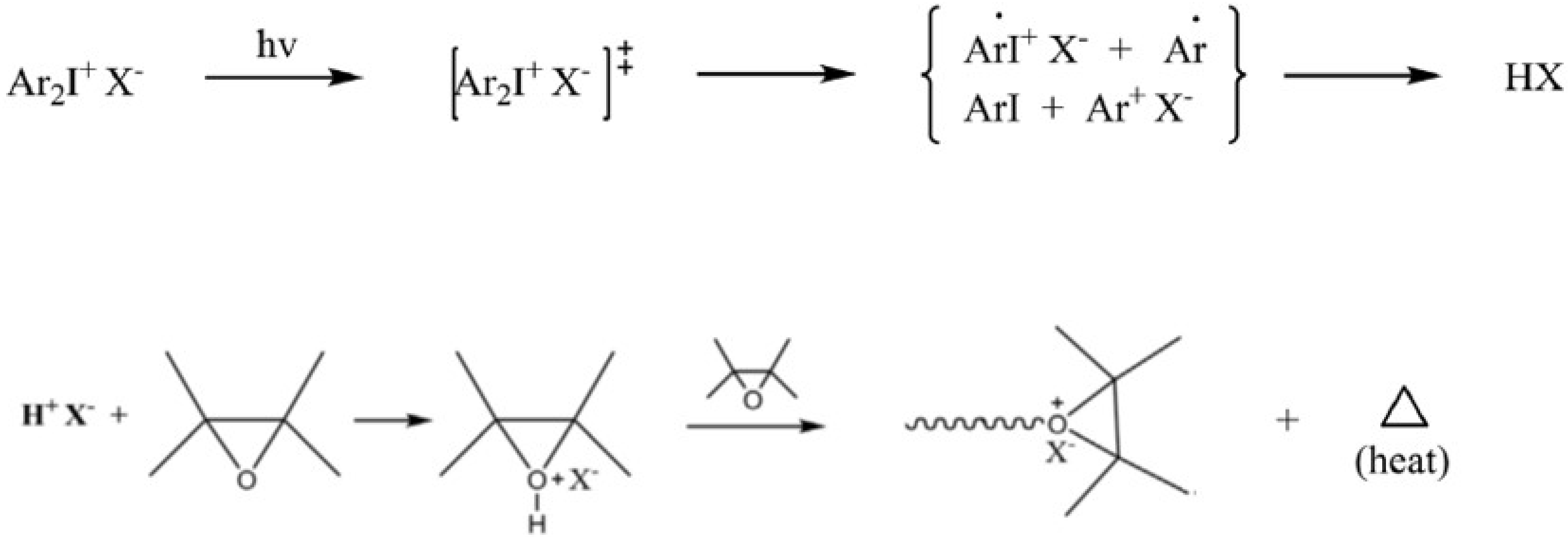
-High cure rate
-Process at room temperature
-Environmental friendly technique

Disadvantages:

-Limited curable thickness
-Difficult cure in the presence of fillers

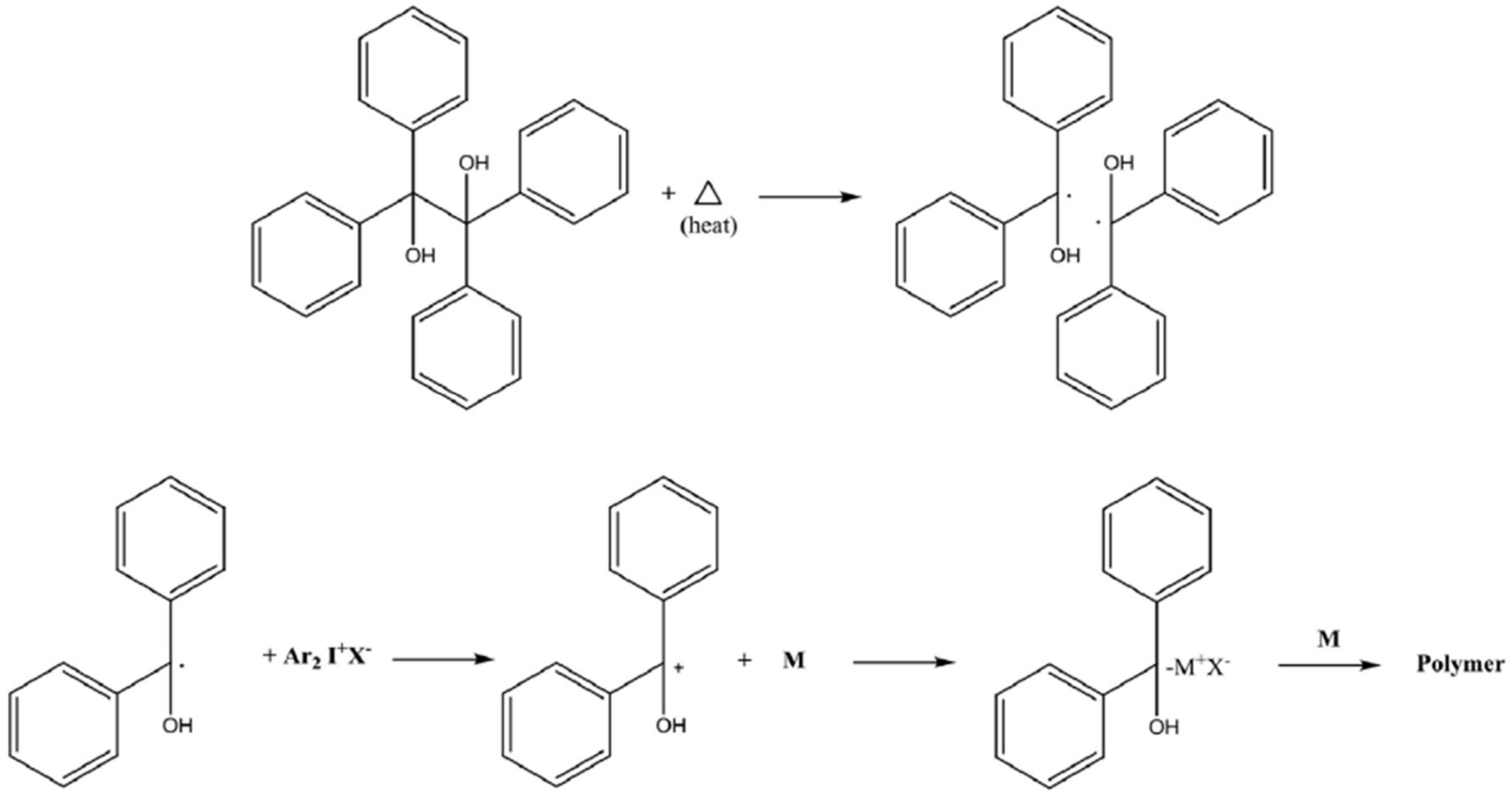
"Radiation Curing in Polymer Science and technology", Vol. I-IV, J.P. Fouassier, J.F. Rabek ed., Elsevier London, **1993**.

Radical Induced Cationic Frontal Polymerization



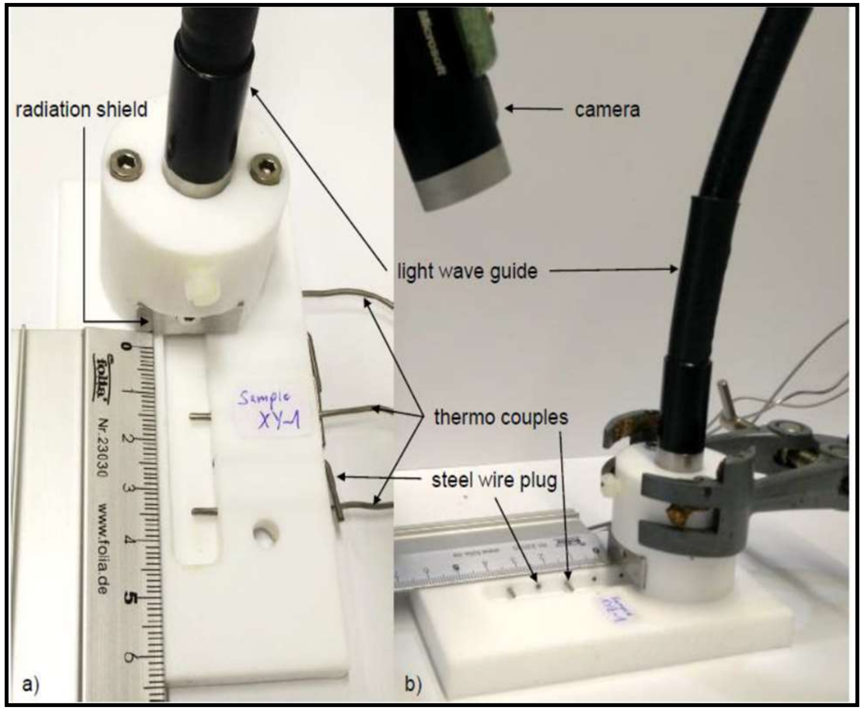
N. Klikovits, R. Liska, A. D’Anna, M. Sangermano, Macromolecular Chemistry and Physics, 218, 1700313-1700317, **2017**

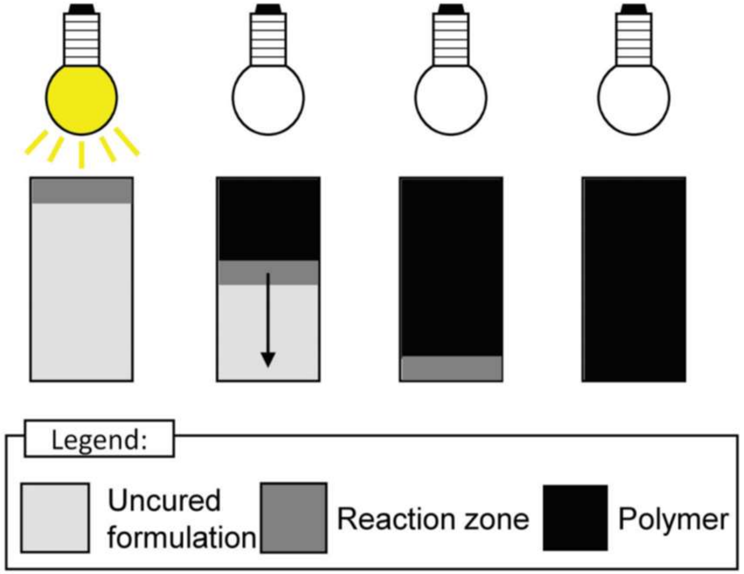
Radical Induced Cationic Frontal Polymerization

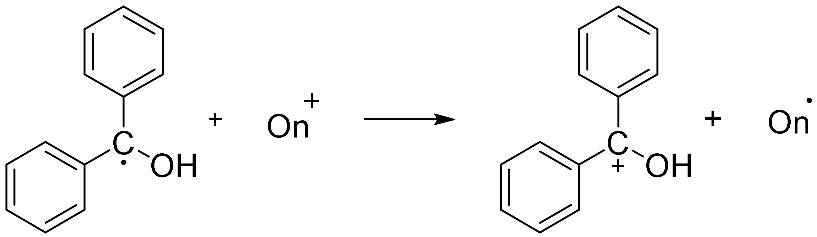


N. Klikovits, R. Liska, A. D’Anna, M. Sangermano, Macromolecular Chemistry and Physics, 218, 1700313-1700317, **2017**

Frontal Polymerization

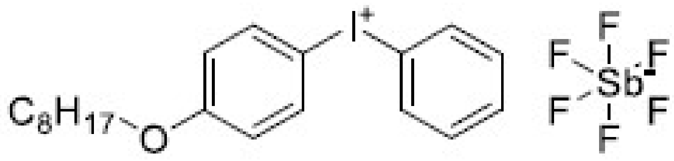






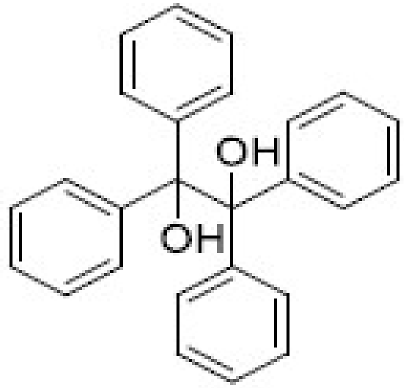
N. Klikovits, R. Liska, A. D'Anna, M. Sangermano, Macromolecular Chemistry and Physics, 218, 1700313-1700317, **2017**

Materials



IOC-8 SbF_6

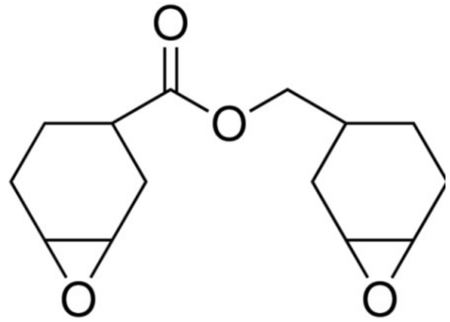
p(octyloxyphenyl)phenyliodonium hexafluoroantimonate



TPED

1,1,2,2-Tetraphenyl-1,2-ethandiol

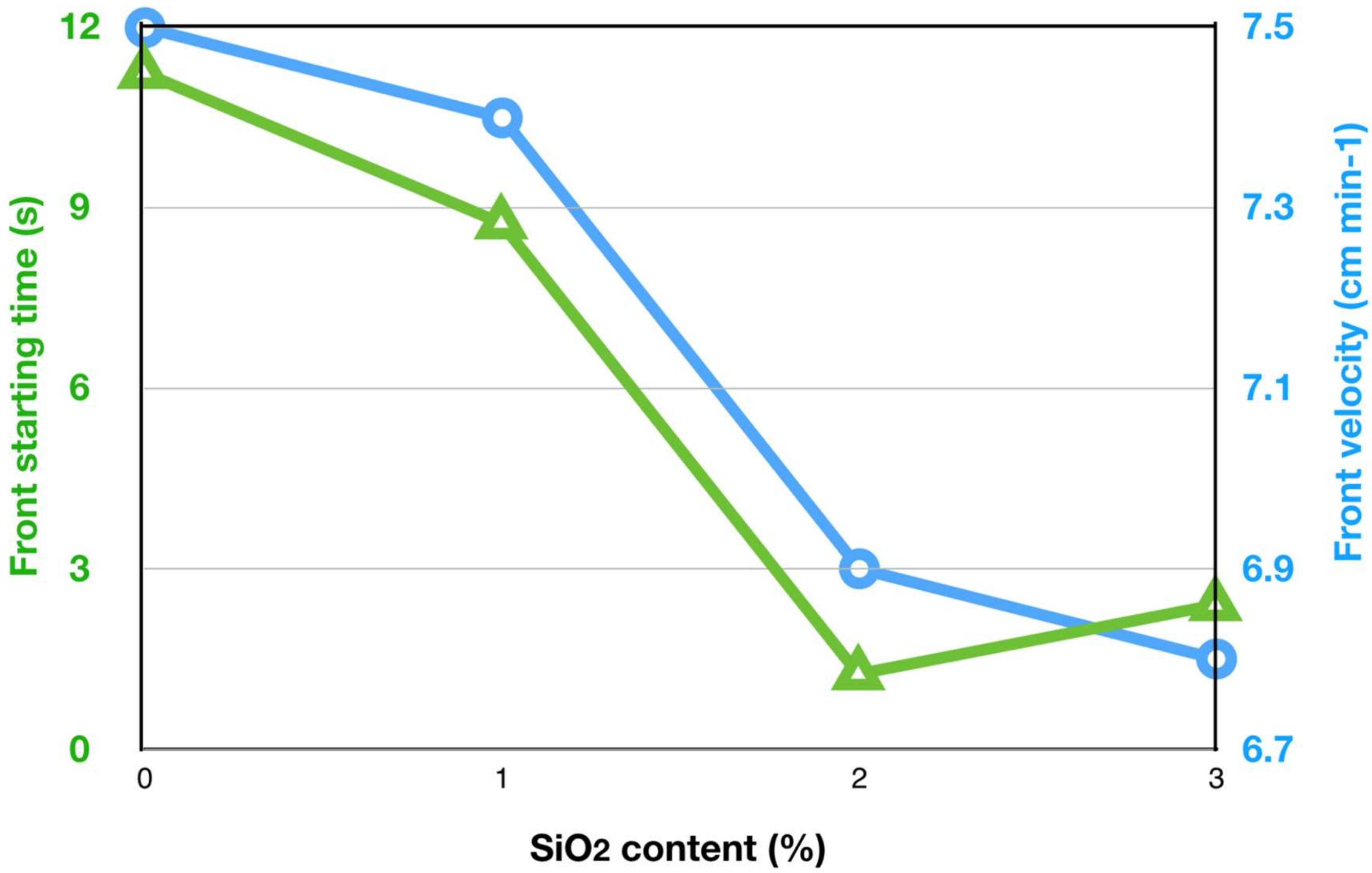
SiO2 or glass fibres



Epoxy Resin

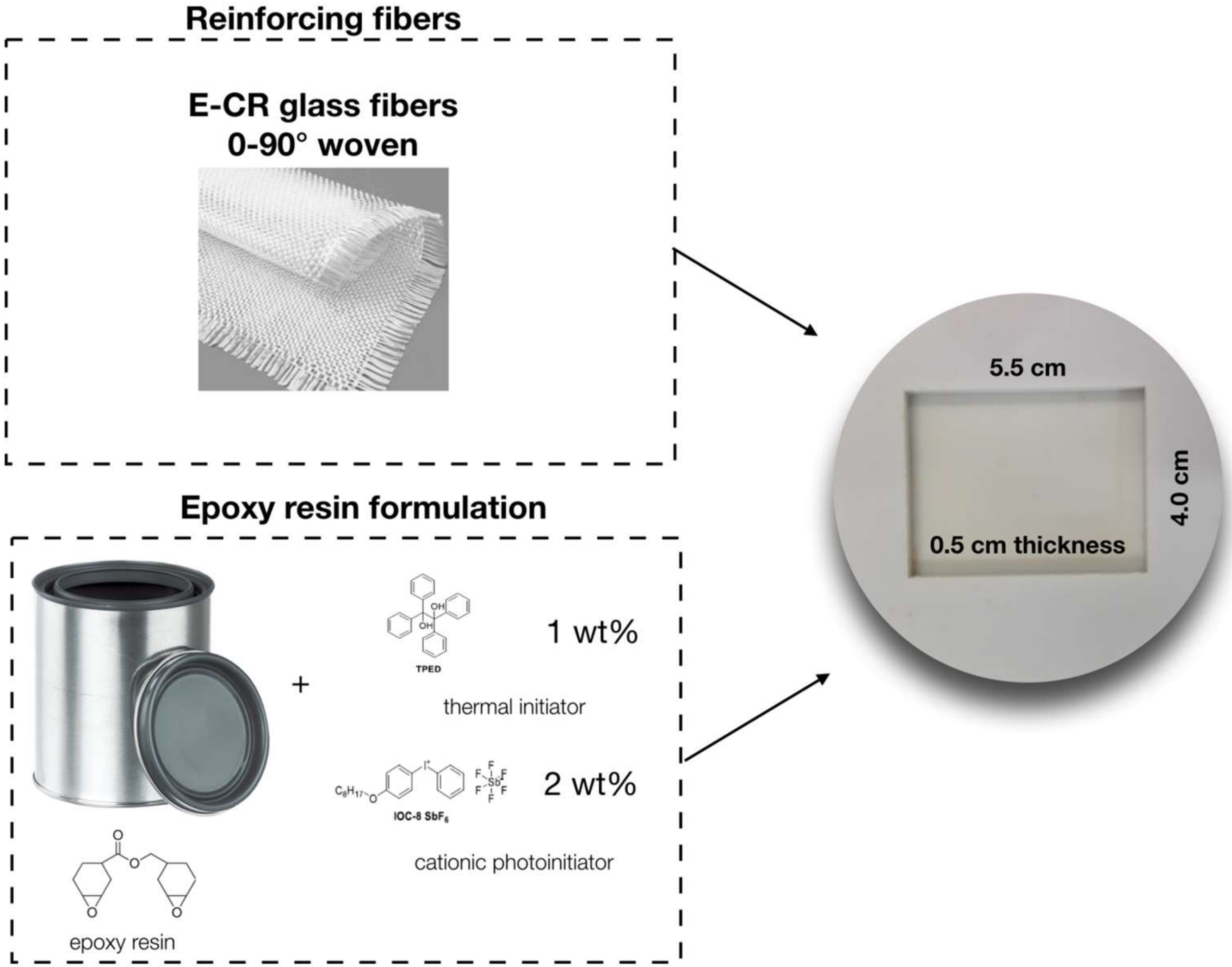
N. Klikovits, R. Liska, A. D'Anna, M. Sangermano, Macromolecular Chemistry and Physics, 218, 1700313-1700317, **2017**

Frontal Polymerization



N. Klikovits, R. Liska, A. D’Anna, M. Sangermano, Macromolecular Chemistry and Physics, 218, 1700313-1700317, **2017**

Epoxy Composites

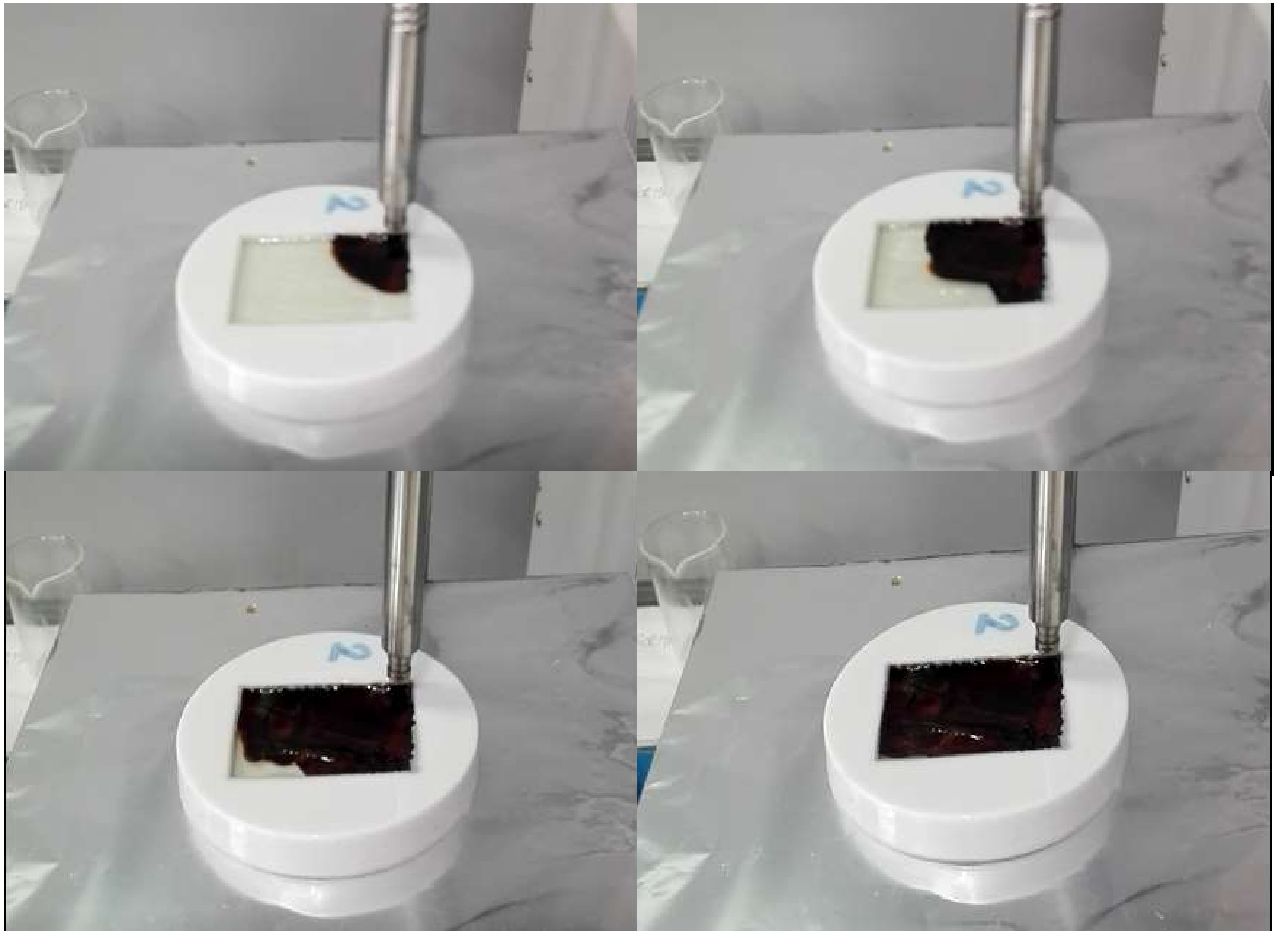


Frontal Polymerization

M. Sangermano, A. D'Anna, C. Marro, N. Klikovits, R. Liska, Composites part B: Engineer, 143, 168-171, **2018**

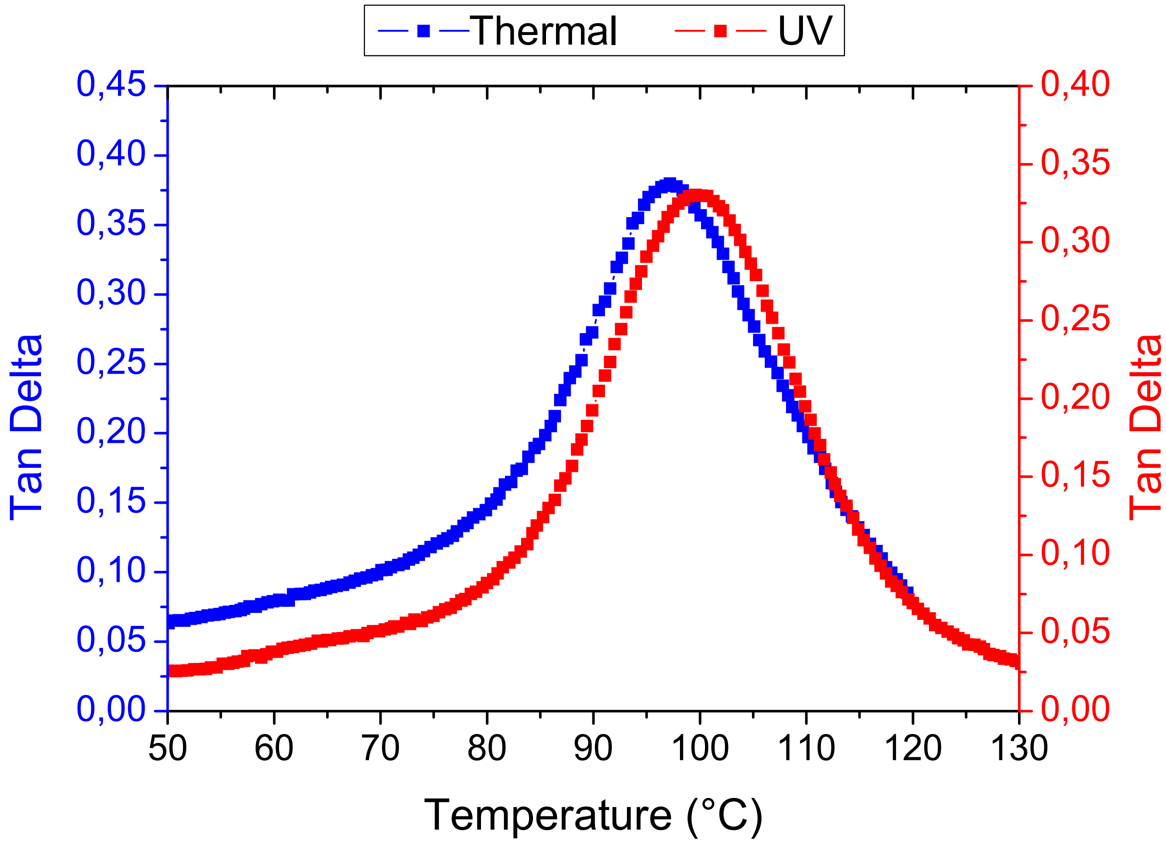
POLITECNICO DI TORINO

Frontal Polymerization



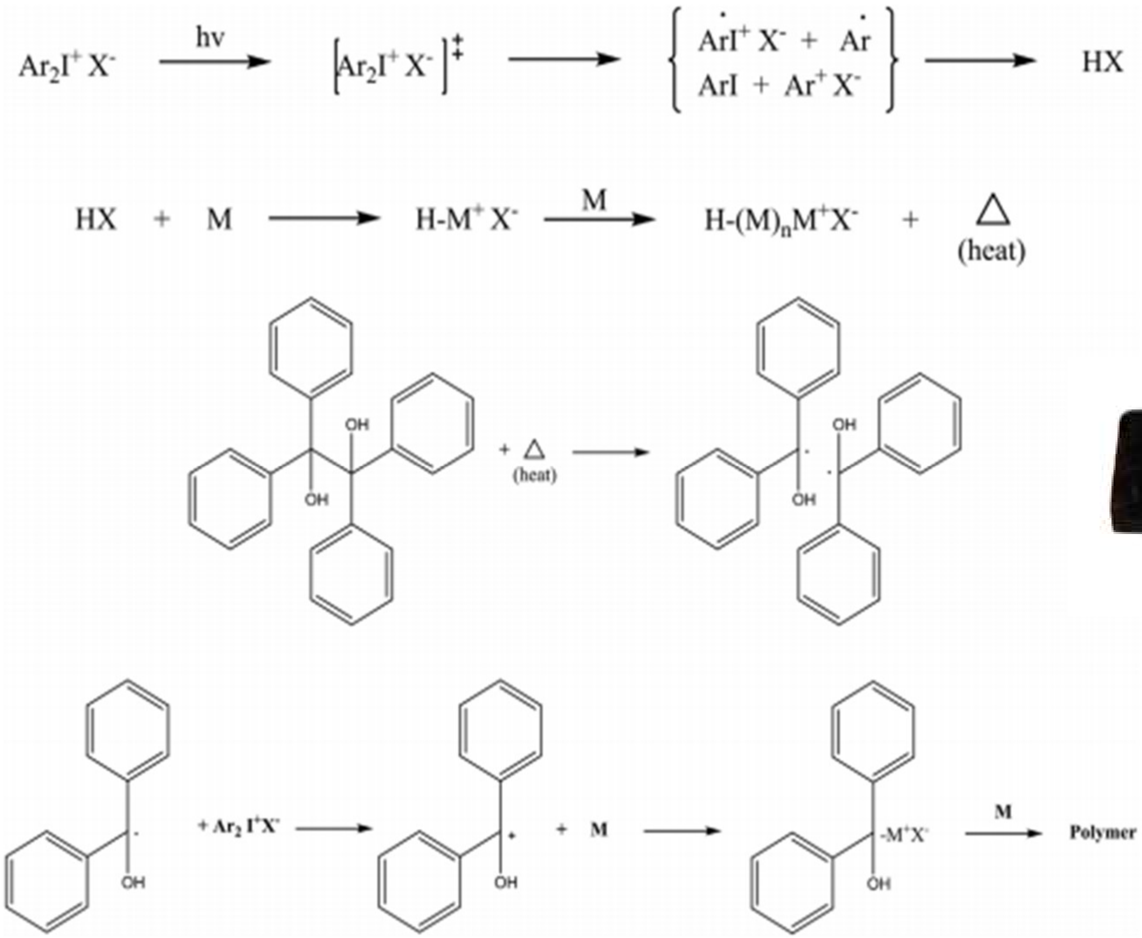
From the video the **front starting time was calculated to be 10 seconds**. This is why the mould was irradiated for 10 seconds with light. From the same video we could evaluate a **front velocity of about 5 cm/min,** so the entire sample contained in the mould was completely crosslinked in less than a minute.

Properties of Composite



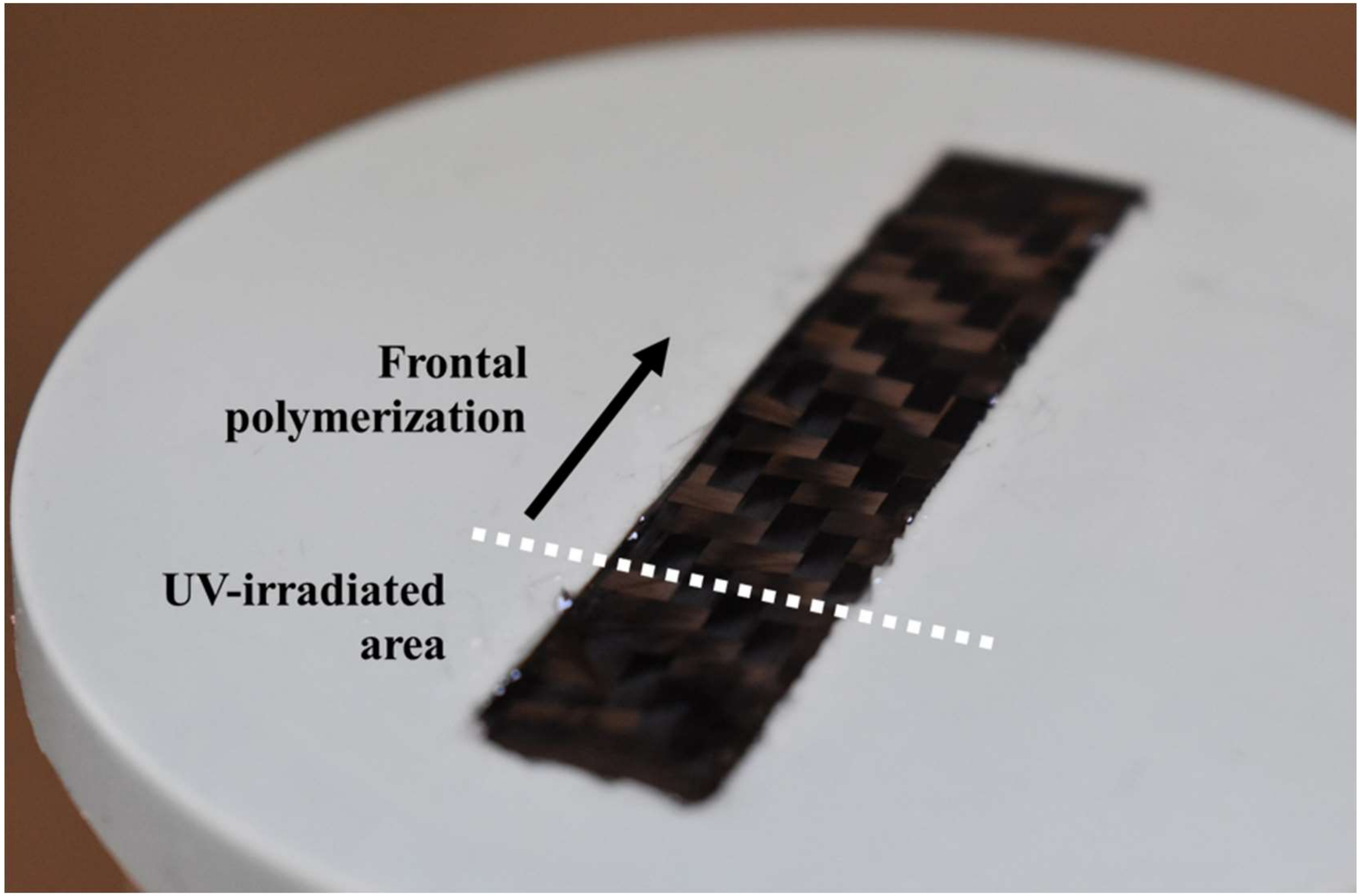
Sample	Tg (°C)[1]	Tensile Strength (MPa)[2]	Tensile Modulus E (GPa)[3]
UV-Cured	105	367±14	23.5±1.3
Thermally Cured	95	345±23	21.8±2.8

Frontal carbon composites



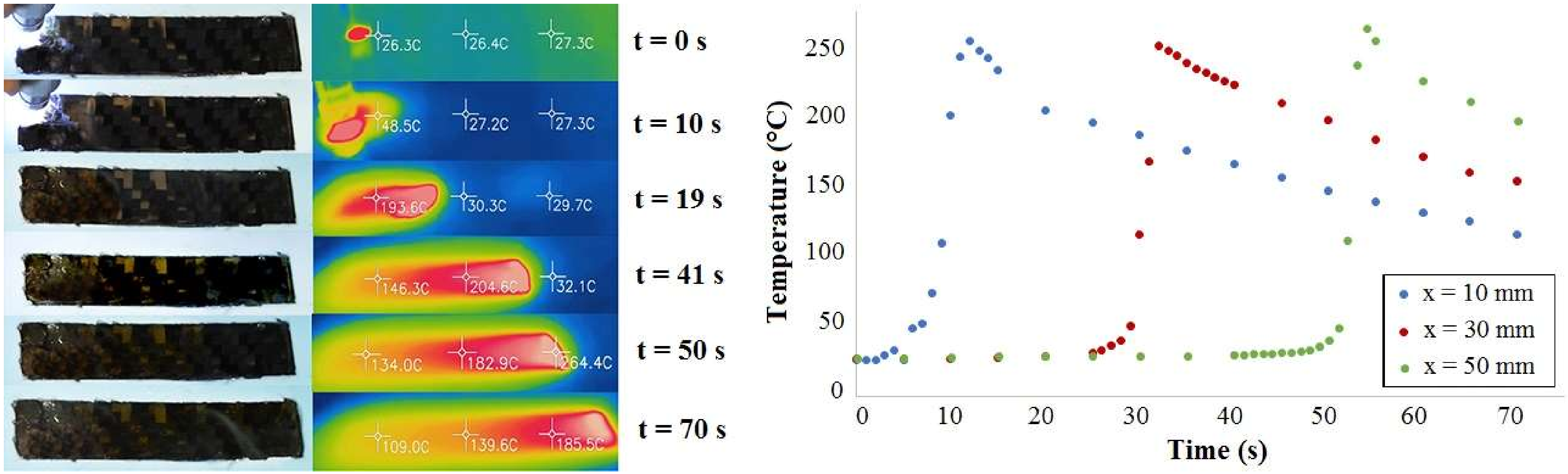
M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

Frontal Photopolymerization



M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

Thermal front: composite



By reporting the distance of the front as a function of the highest temperature reached in the sample, it should be possible to obtain the front advancement along the axial direction. Indeed, **the polymerization front propagates at constant speed**, and this linear behaviour is strongly supporting the suggested front propagation mechanism

M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

POLITECNICO
DI TORINO

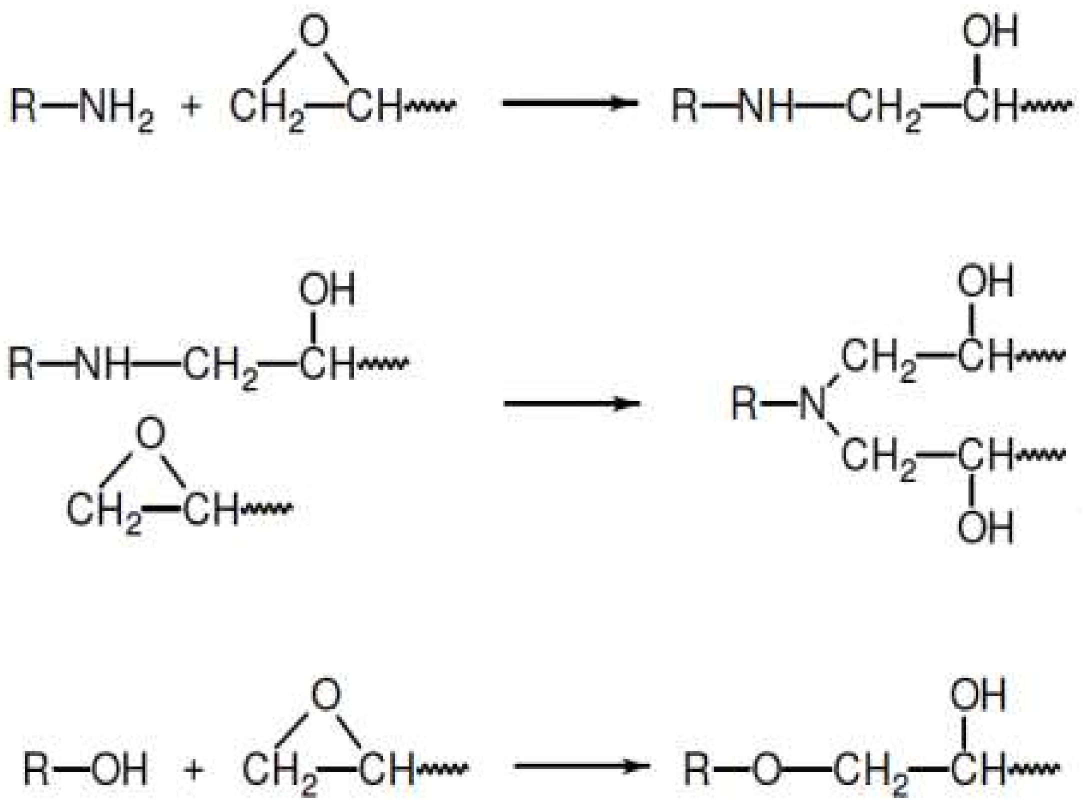
Formulations

Sample	PI	TPED	Rate	T massima
	$\%_{wt}$	$\%_{wt}$	cm/min	°C
Resin	1,5	1,5	4,0	262,8
Composite	1,5	1,5	5,1	264,4

A higher front velocity and a slightly higher maximum temperature reached was measured for the composite's samples. This was attributed to the good thermal conductivity of the carbon fiber which facilitate the thermal front propagation.

M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

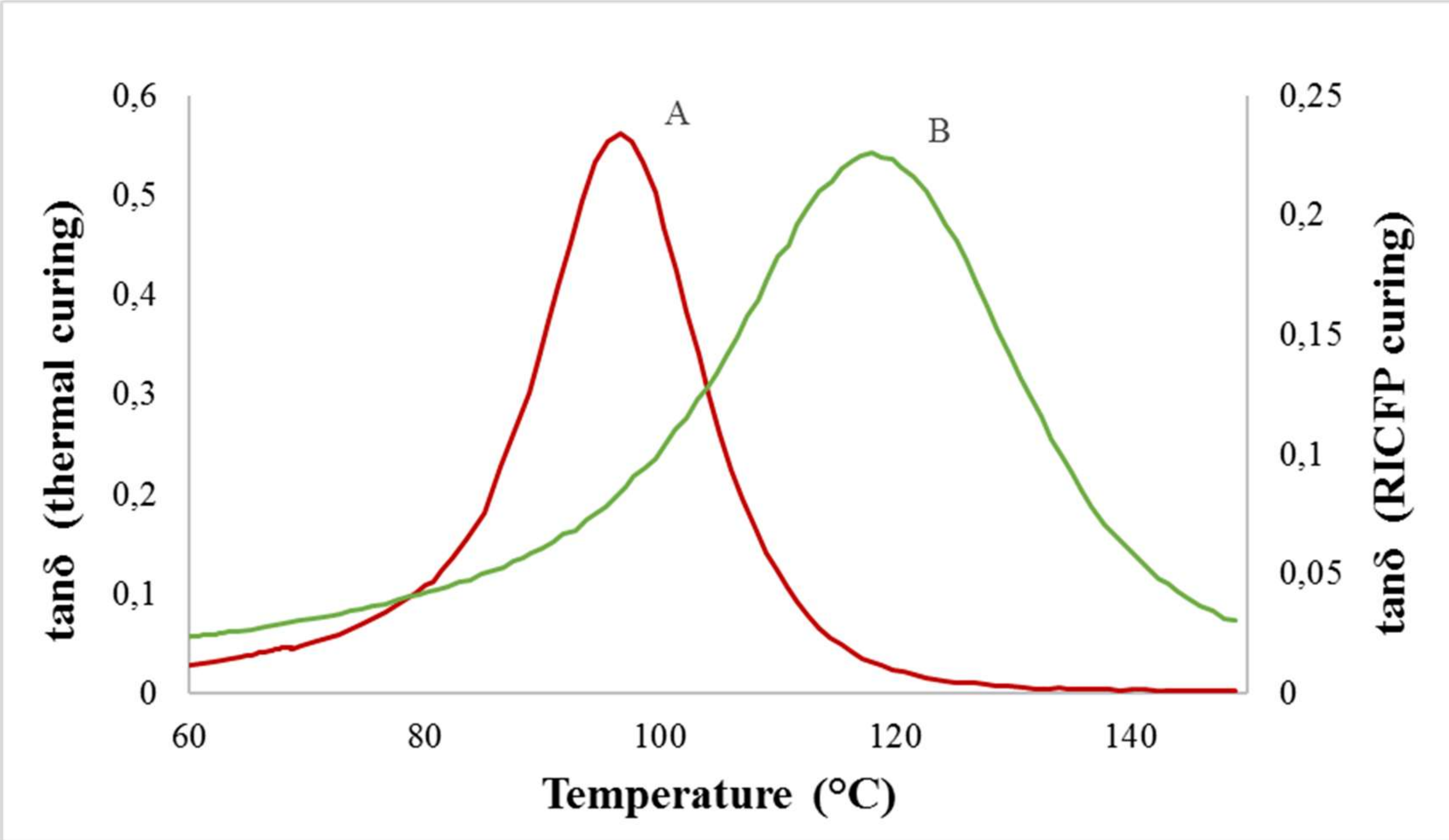
Thermal carbon composites



M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

POLITECNICO DI TORINO

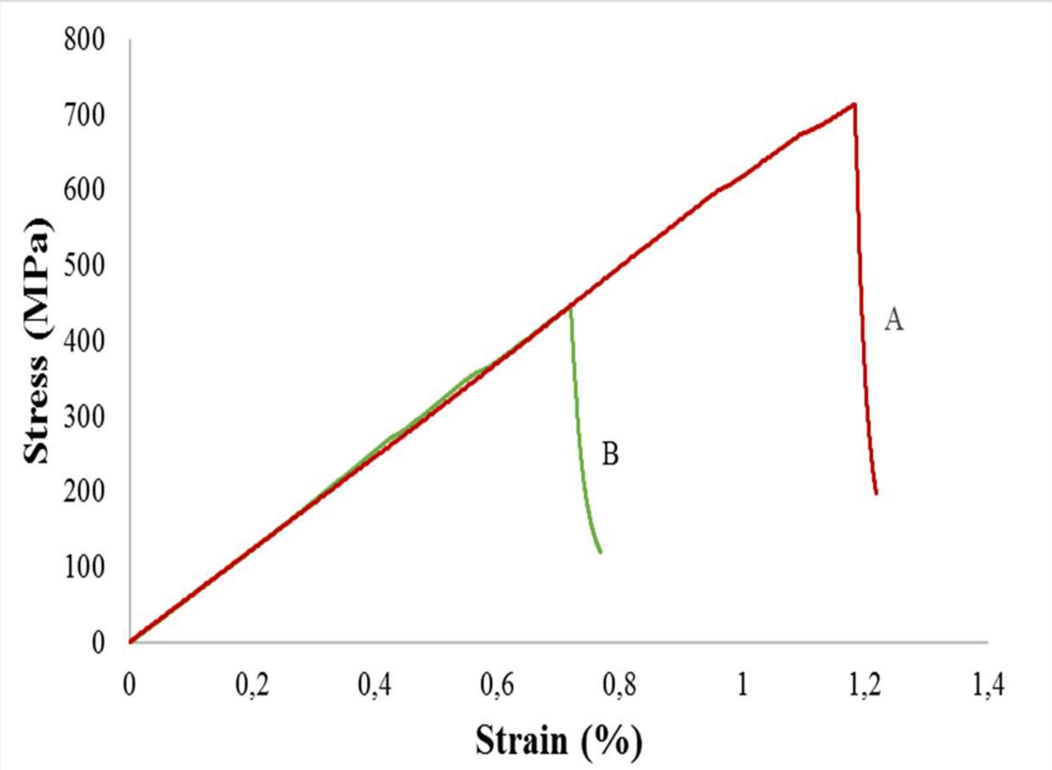
DMTA



Tanδ curve obtained by DMTA analysis of the crosslinked epoxy-carbon fiber composites obtained via **thermal curing** (curve **A**) and via **RICFP** (curve **B**).

M. Sangermano. I. Antonazzo, L. Sisca, M. Carello, Polymer International, **in press**

Stress-Strain Curves



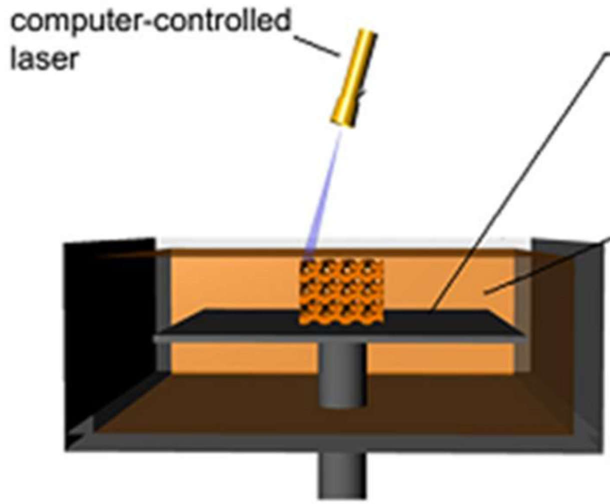
Sample	E (GPa)	σ_f (MPa)
Thermal Cured Composites	61±5	715±54
Frontal Cured Composites	61±4	447±81

Stress-strain average curves of the crosslinked epoxy-carbon fiber composites obtained via **thermal curing** (curve **A**) and via **RICFP** (curve **B**).

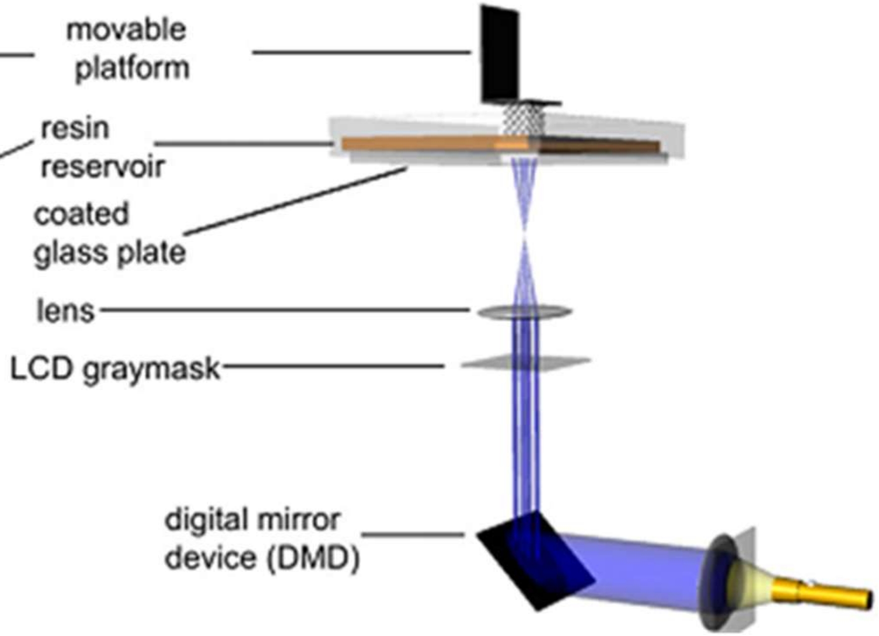
3D-Printing

The two main AM techniques that are based on photopolymerization are: SL-Stereolithography and DLP- Digital Light Processing.

SL-Stereolithography

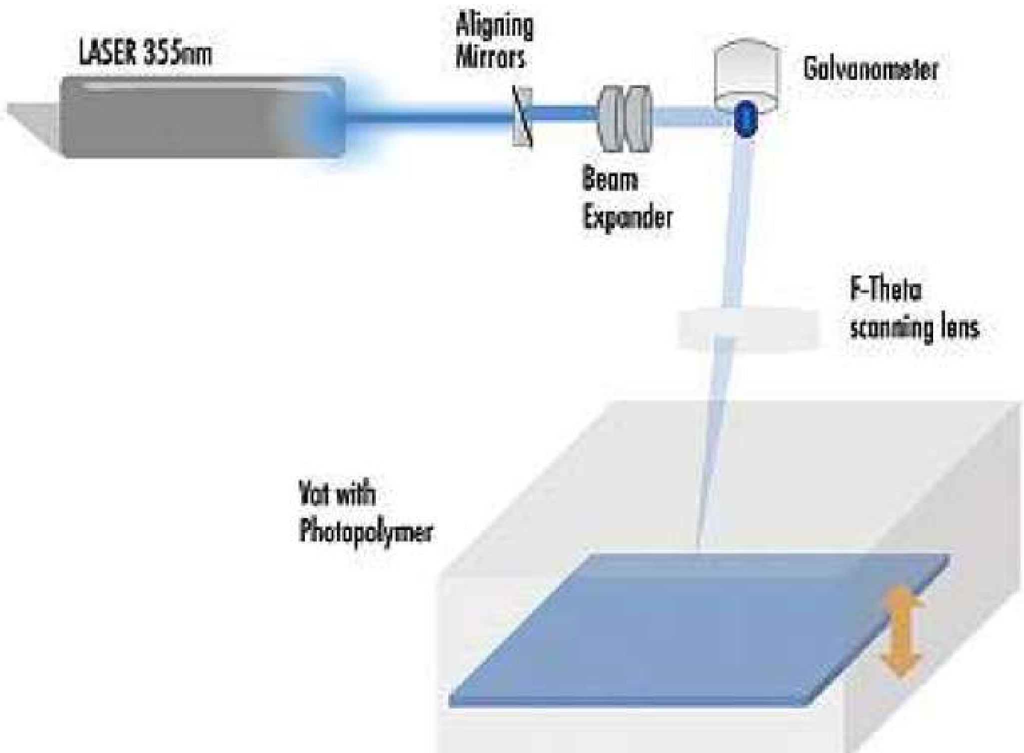


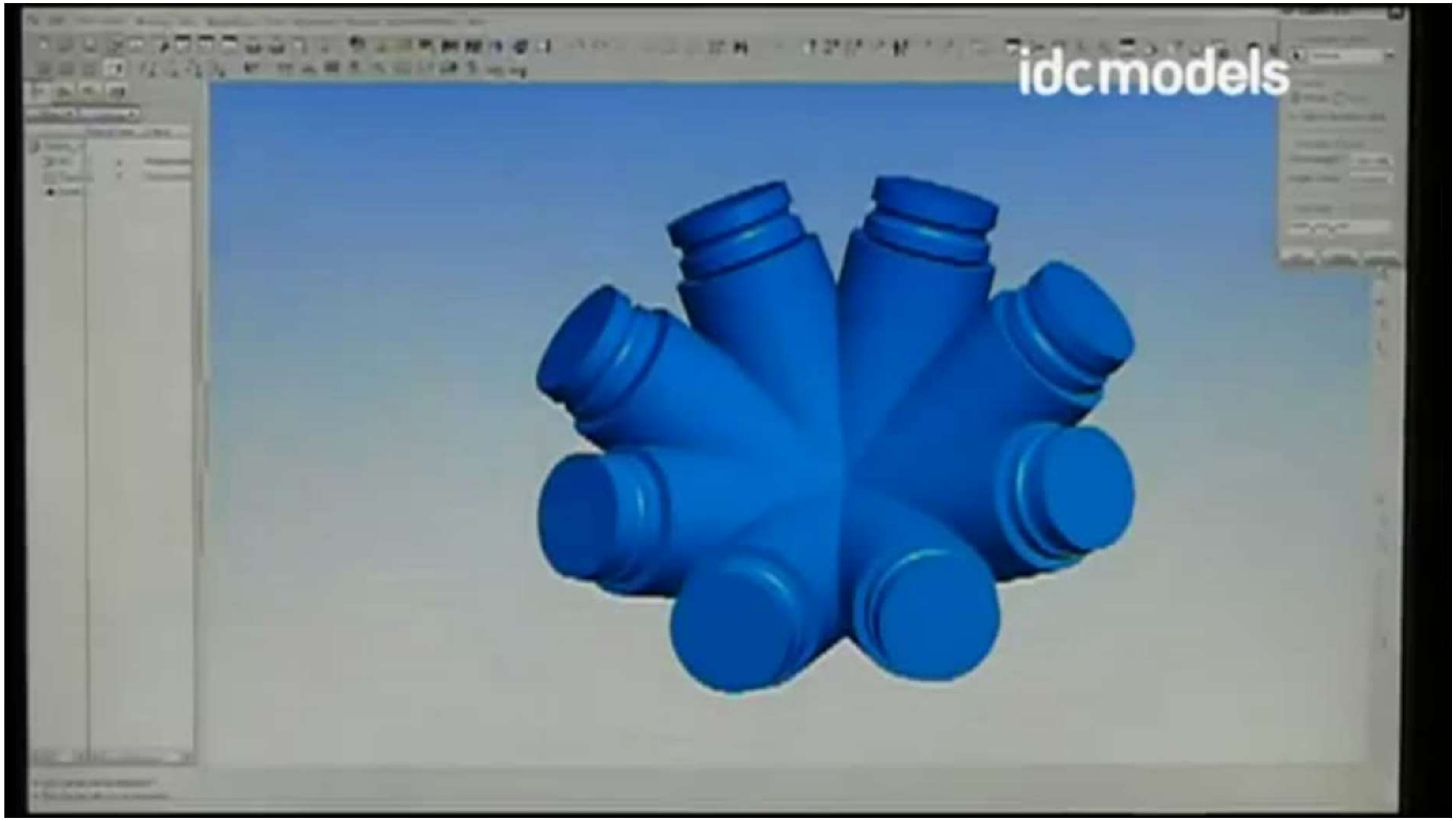
DLP-Digital Light Processing



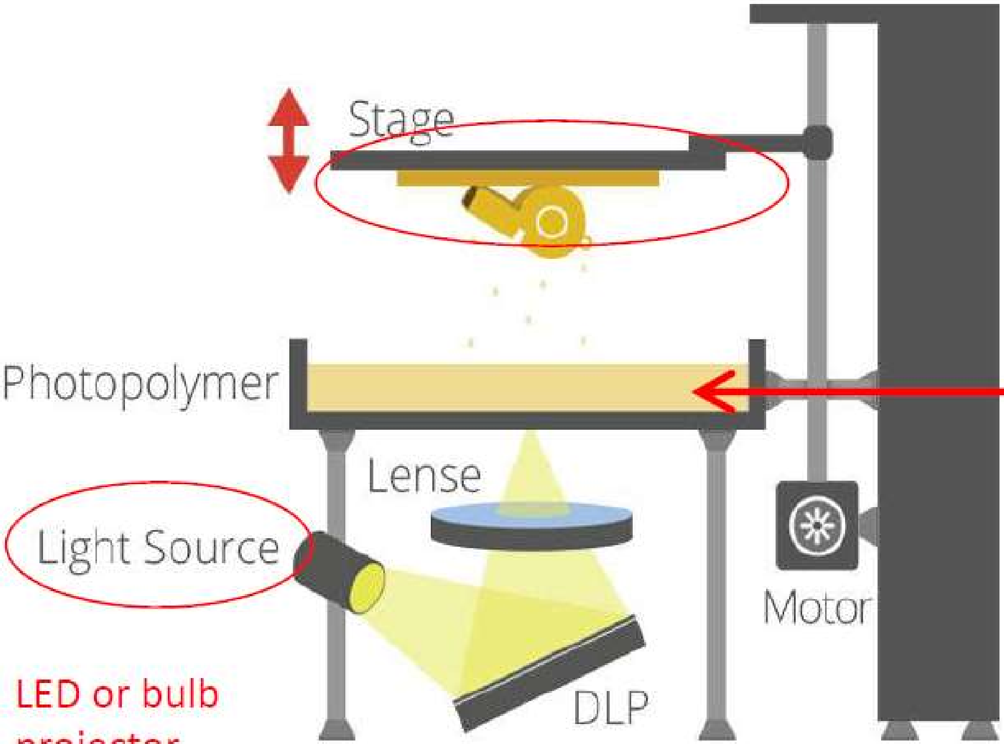
Stereolitography (SLA)

Point by point laser-induced curing of a photocurable resin.
Usually the building platform is fixed and the laser scans the surface.



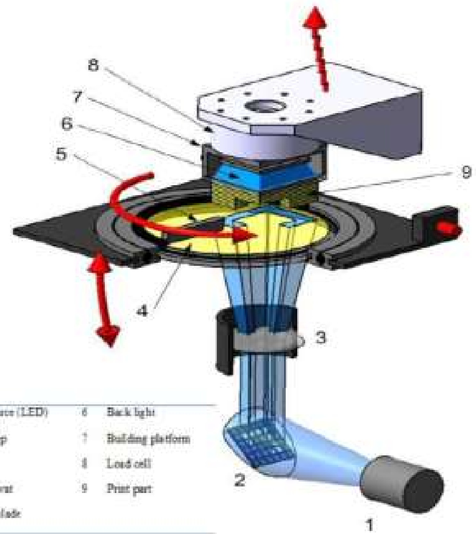

idcmodels

DLP (Digital light processing)



Vat with transparent bottom

LED or bulb projector



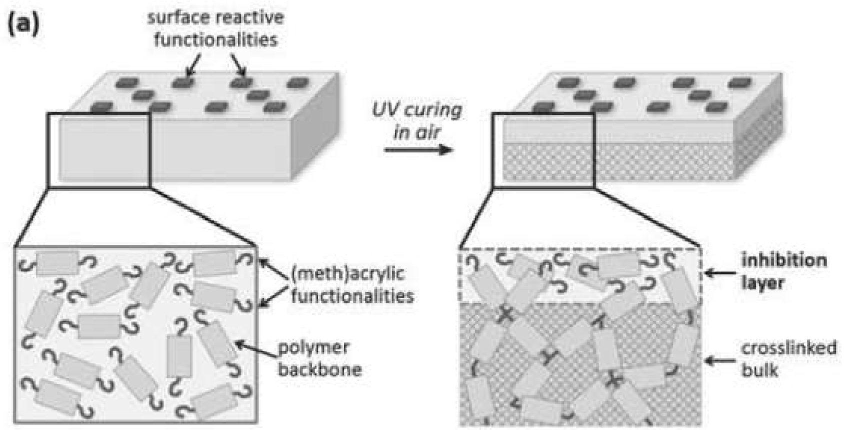
1	Light source (LED)	6	Back light
2	DMD chip	7	Building platform
3	Optics	8	Load cell
4	Material vat	9	Print part
5	Coating blade		


DLP Projector
Sterolithography
3D Printer

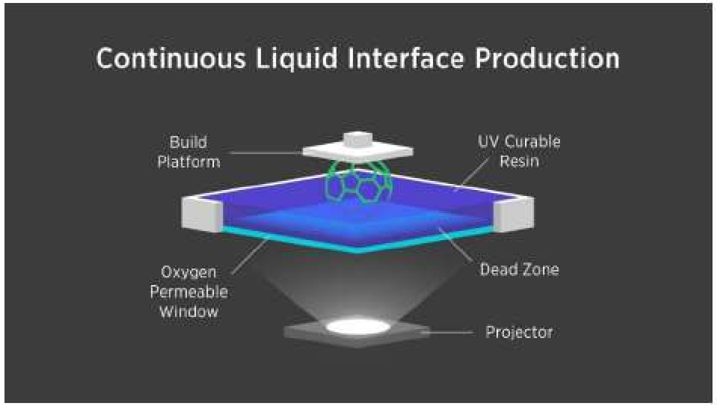
[redacted]

Stereolithography (SLA) and **Digital Light Processing** (DLP)

Oxygen Inhibition

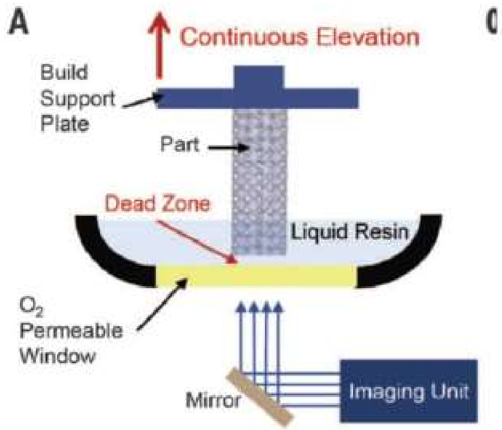


Usually it's a problem but in this case….

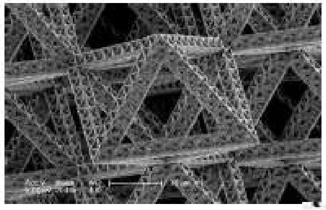


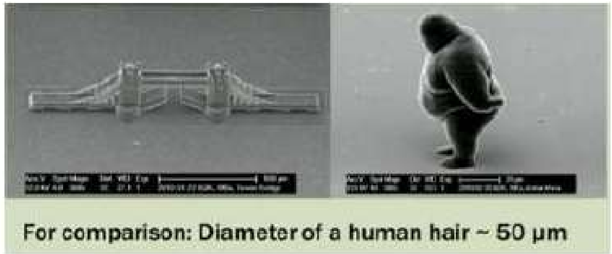
CLIP

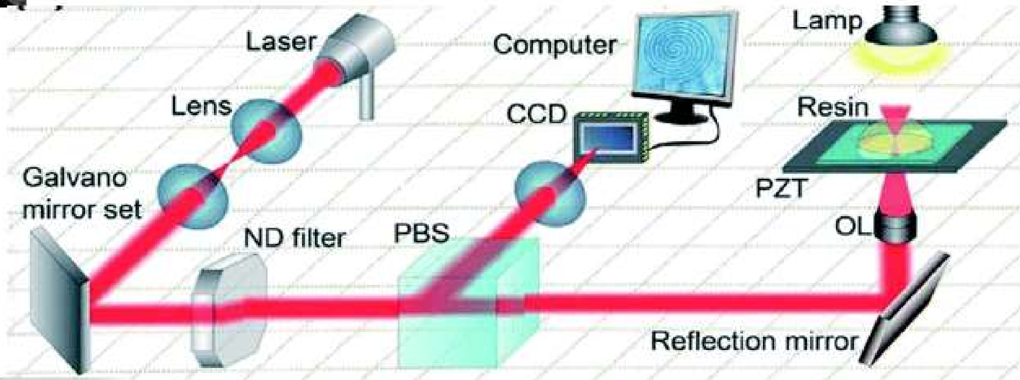
Continuous liquid interface production of 3D objects



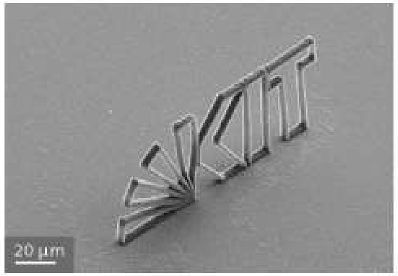
2PP



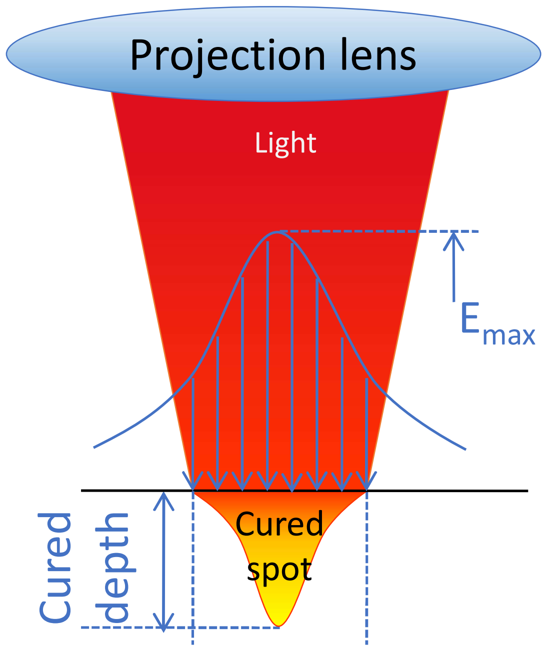

For comparison: Diameter of a human hair ~ 50 µm


Laser
Computer
Lamp
Lens
CCD
Resin
Galvano
mirror set
PZT
ND filter
PBS
OL
Reflection mirror


200 µm


20 µm

- In the processes the control of the thickness of the layer that is cured is extremely important for assure the dimension accurancy of the part.
- For a given resin, the cure depth is determined by the energy of the light to which the resin is exposed.

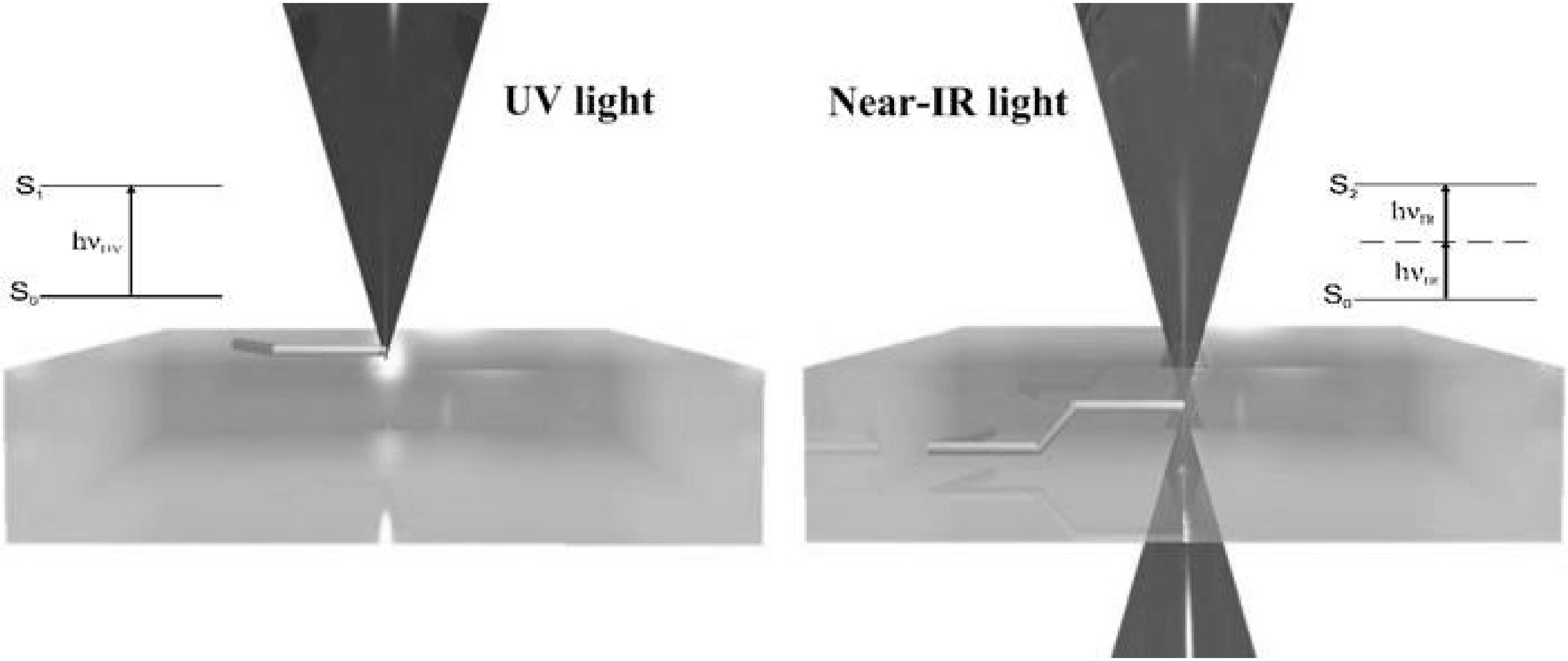


- Where Ec is the critical energy Ec (mJ/cm2) and Dp (mm) the penetration depth Dp (mm).
- The critical energy Ec is the energy required to reach the gel point, i.e the point where the solidification begins. As the applied irradiation dose (E) exceeds the critical energy (Ec), a solidified layer is formed from the resin surface.

Multi-photon absorption was demonstrated with the help of lasers, since the intensities much higher than provided by other light sources could be achieved. It was demonstrated that an atom can absorb two or more photons simultaneously, thus allowing electron transition to the states that can not be reached with a single photon absorption. Two-photon absorption (TPA) is mediated by a virtual state which has an extremely short lifetime (several femtoseconds). Thus, TPA is only possible if a second photon is absorbed before the decay of this virtual state. Note that excited energy levels S_1 and S_2, shown below are not exactly the same, since the selection rules for single photon and two-photon absorption are different. The main advantages of multi-photon microscopy are high spatial resolution and the ability to selectively excite specific molecules.

The **two-photon polymerization** (**2PP**) technique is based on the interaction of femtosecond laser radiation which induces a highly localised chemical reaction leading to polymerization of the photosensitive material with current resolution down to 100 nm.

In stereolithography, a UV laser, applied to scan the surface of the photosensitive material, is producing 2D patterns of polymerized material. The UV laser radiation induces photopolymerization through single photon absorption at the surface of the material. Therefore, with stereolithography it is only possible to fabricate 3D structures using a layer-by-layer approach. Since photosensitive materials are usually transparent in the infrared and highly absorptive in the UV range, one can initiate two-photon polymerization with IR laser pulses **within** the small volume of the material by precisely focused near-infrared femtosecond laser pulses.



UV light
Near-IR light
S1
hvUV
S0
S2
hvIR
hvIR
S0

A promising three-dimensional microfabrication method that has recently attracted considerable attention is based on two-photon polymerization with ultrashort laser pulses.[1-5] When focused into the volume of a photosensitive material (or photoresist), the pulses initiate **two-photon polymerization** via two-photon absorption and subsequent polymerization. After illumination of the desired structures inside the photoresist volume and subsequent development — e.g., washing out the nonilluminated regions — the polymerized material remains in the prescribed 3-D form. This allows fabrication of any computer-generated 3-D structure by direct laser "recording" into the volume of a photosensitive material .

Three-dimensional microstructuring of photosensitive materials by two-photon polymerization is effective for the fabrication of 3-D structures having a resolution of 100 nm or better.