MICRO 423 : ADVANCED ADDITIVE MANUFACTURING TECHNOLOGIES

3D printing using continuous wave light (single photon absorption)

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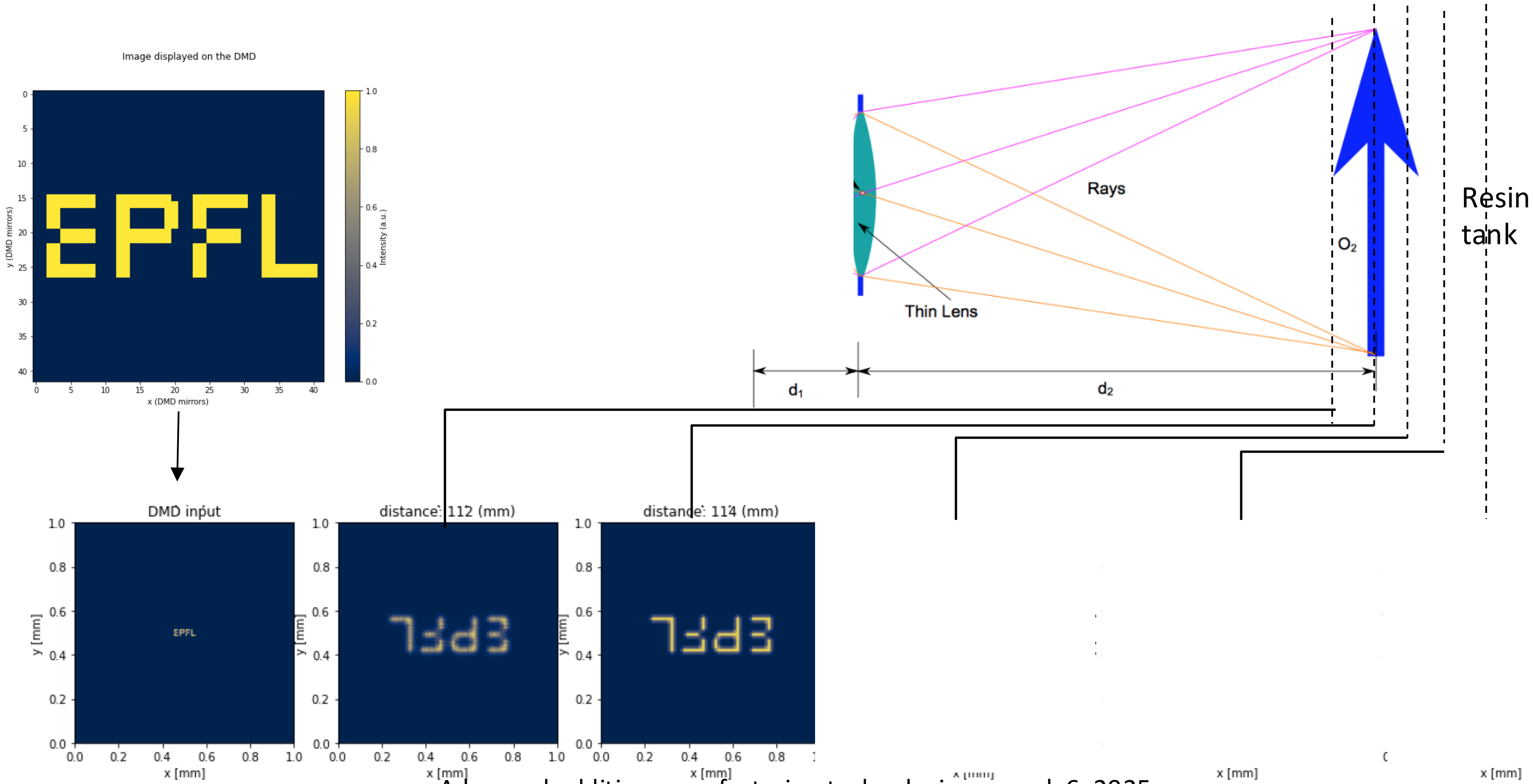
Modules of the 2025 course

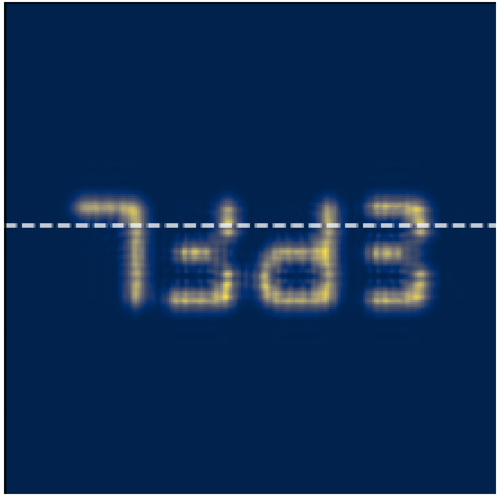
Topics covered	No	Lecture/Date
VAT Photo polymerization (history) – DLP printer – light engine – part I	5	20.03.2025
DLP printer – chemical components in a photoresin – role of oxygen – CLIP method– part II	6	27.03.2025
Tomographic Volumetric Additive Manufacturing (TVAM)	7	03.04.2025
Two photon Polymerization : nanoscale printing	8	10.04.2025
Two photon Polymerization : applications	9	17.04.2025
EASTER BREAK		22.04.2025
Prof. Paul Dalton, University of Oregon: Met Electro Writing (nanoscale)	10	1.05.2025
Gari Arutinov, Holst Center for AM: Mass transfer of microcomponents	11	08.05.2025
Julian Schneider: Scrona	12	15.05.2025
Patrizia Richner: Sonova (hearing aids). // **Design Competition**	13	22.05.2025

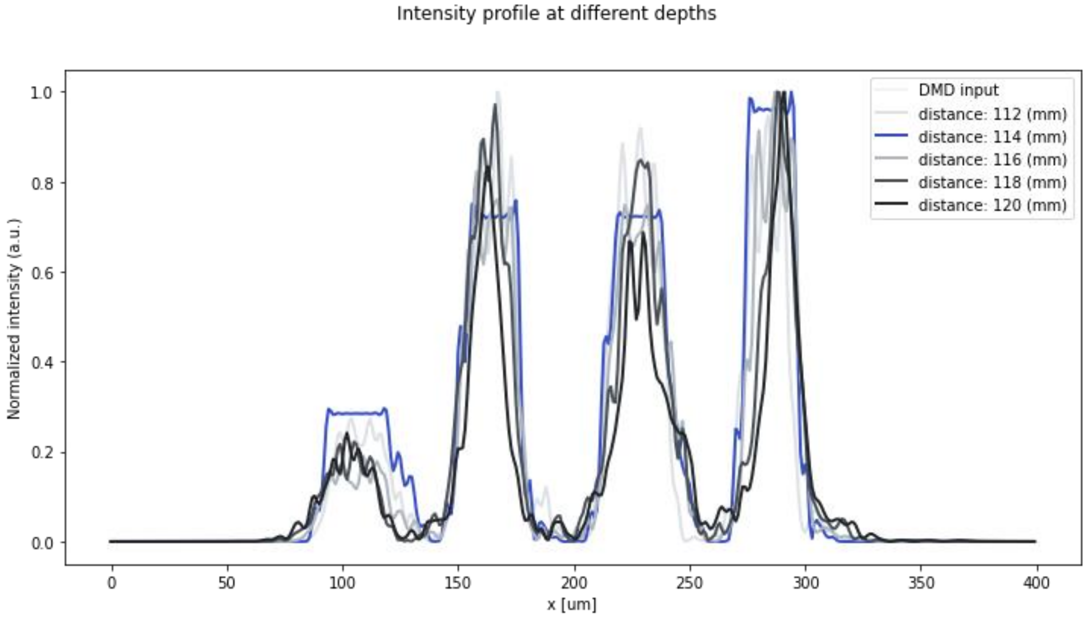
QUIZZ #2

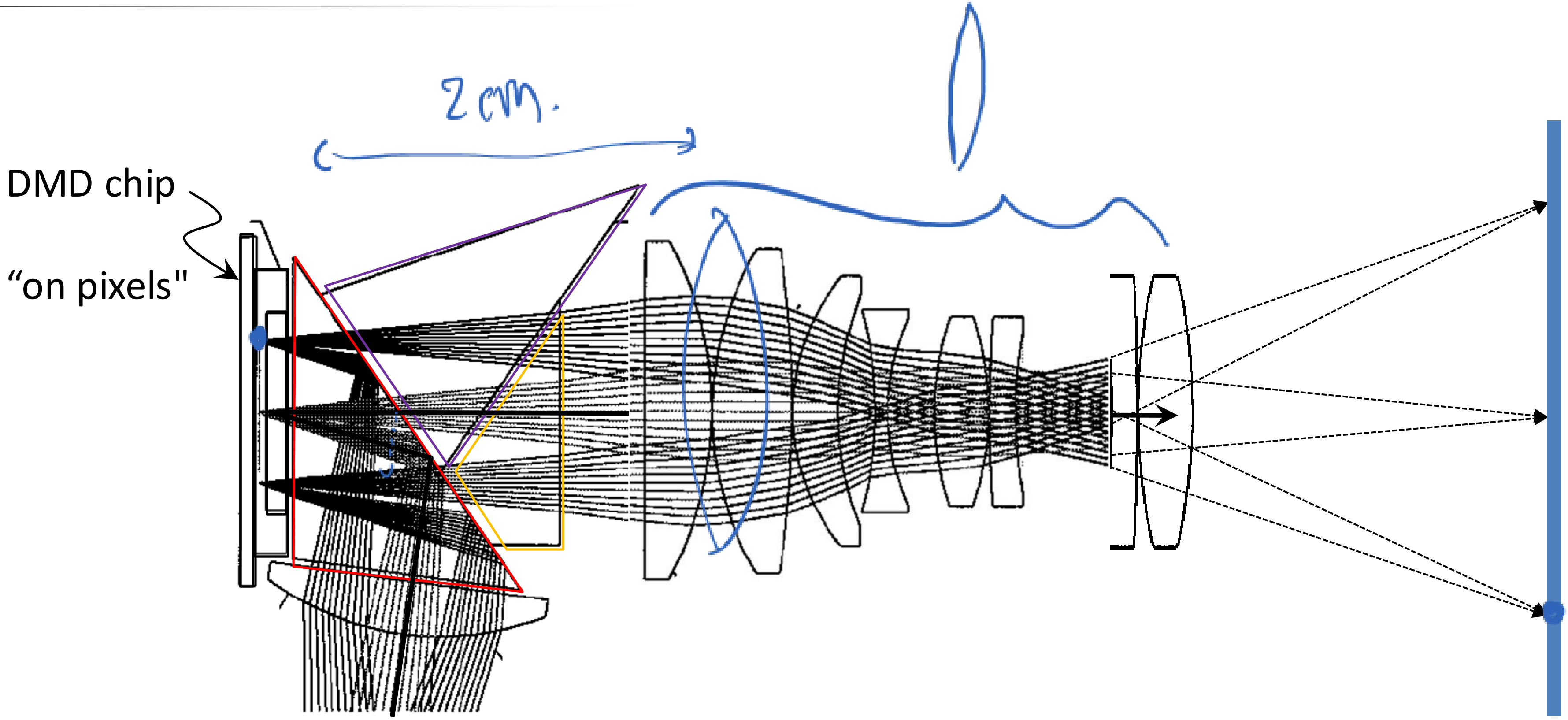
Review: Projection in a DLP printer



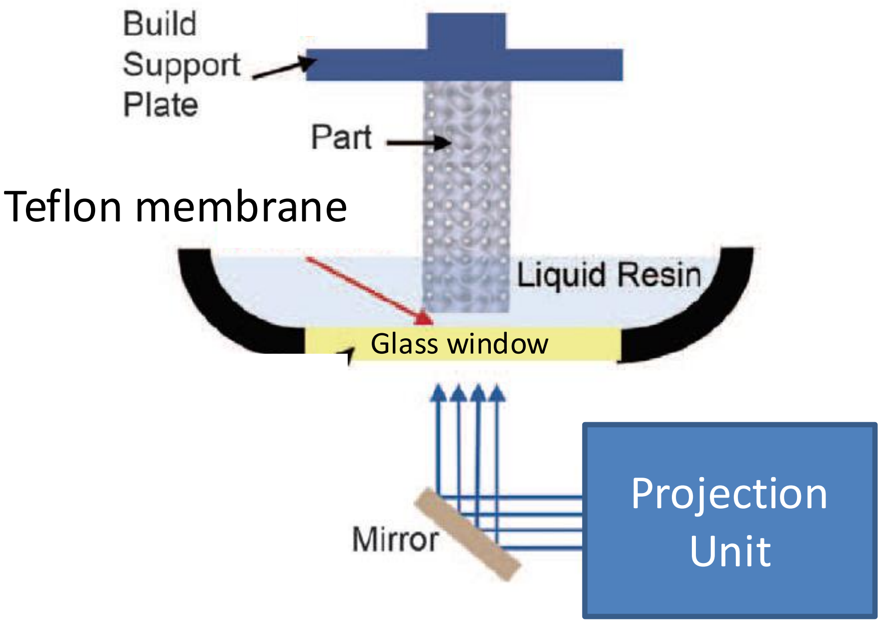
Projecting an image at the wrong plane compromises contrast

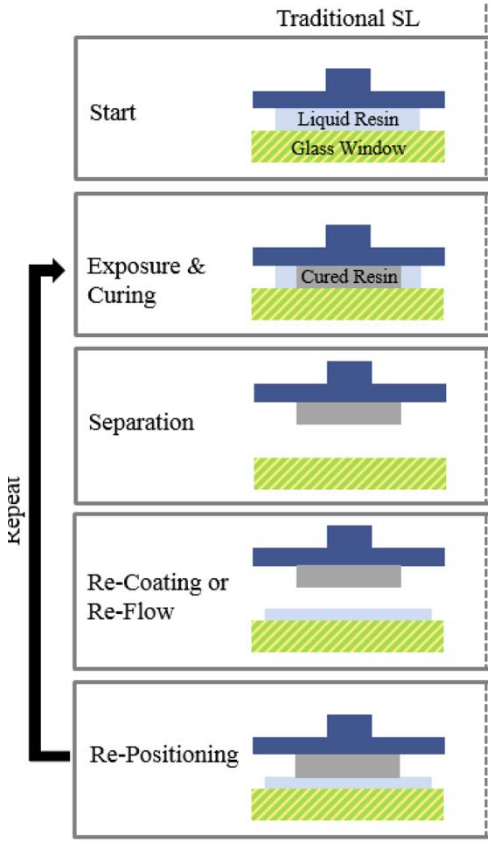




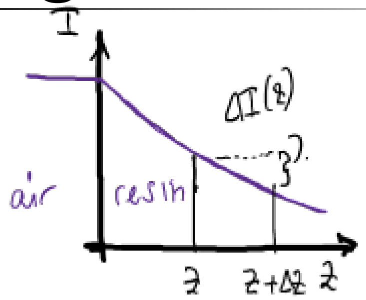

DMD chip
“on pixels"
2 cm.

Review: DLP 3D printing





Light absorption defines layer resolution



- $I(z) = I_0 e^{-\alpha z}$: intensity of light (Power / unit area) at depth z in resin
- $\Delta I(z) = I(z) - I(z+\Delta z)$ absorbed light intensity between z and z+Δz

$$= \left|\frac{dI}{dz}\right| \cdot \Delta z$$

$$= \alpha I_0 e^{-\alpha z} \cdot \Delta z$$

$$\alpha = \alpha_{PI} + \alpha_{dye}$$

- $\frac{\Delta I(z)}{\Delta z} = \alpha \cdot I_0 e^{-\alpha z}$ absorbed light intensity per unit depth

$D = \frac{\Delta I(z)}{\Delta z} \cdot t = \alpha \cdot t \cdot I_0 e^{-\alpha z}$ absorbed light dose (exposure) per unit depth

I want to cure (i.e. solidify) a thickness of depth z_{ct} (cure thickness)

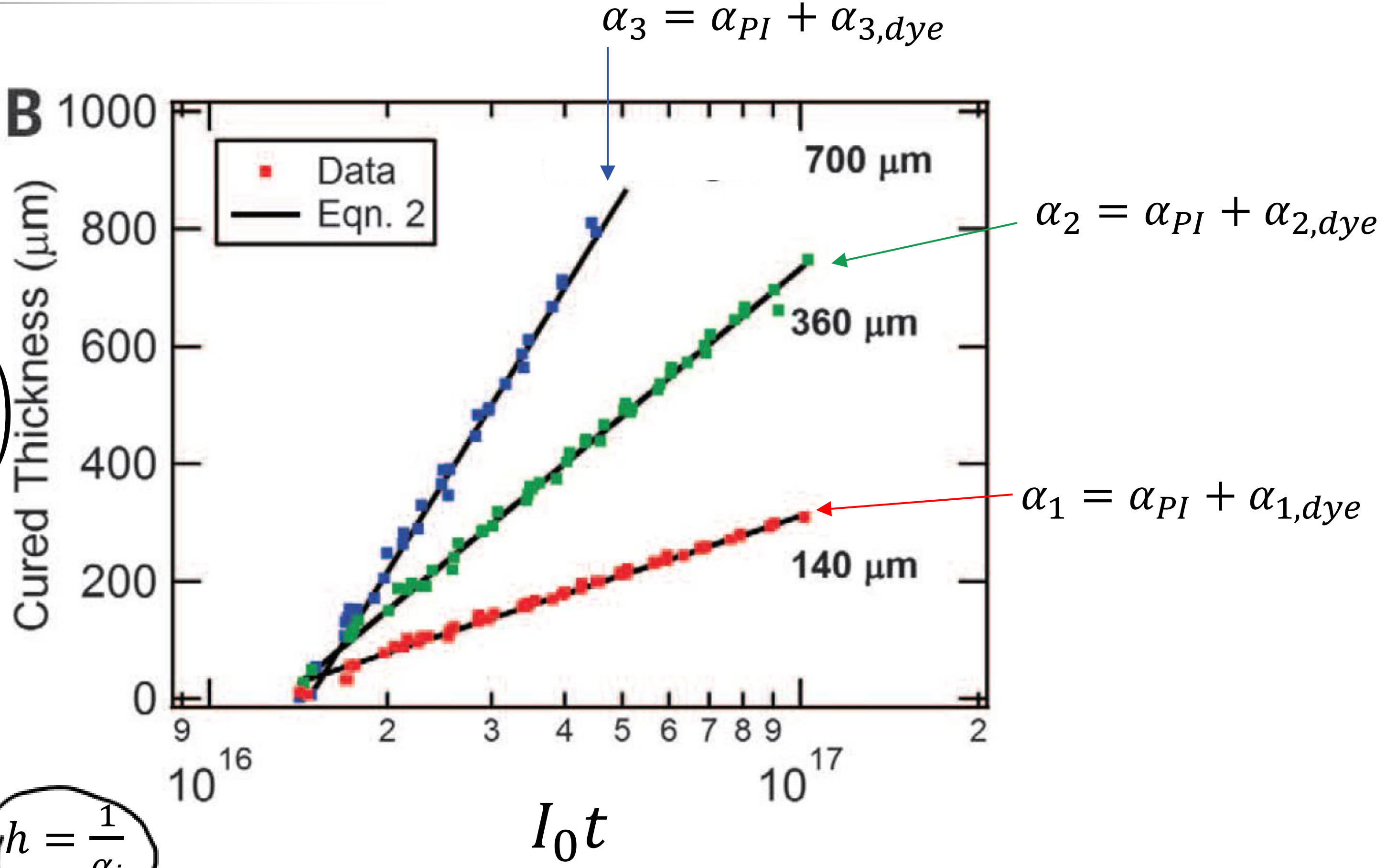
$D_c = \alpha t_c \cdot I_0 e^{-\alpha z_{ct}} \Rightarrow \frac{D_c}{\alpha t_c \cdot I_0} = e^{-\alpha z_{ct}} \Rightarrow \ln\left(\frac{D_c}{\alpha t_c \cdot I_0}\right) = -\alpha \cdot z_{ct}$

$\Rightarrow z_{ct} = -\frac{1}{\alpha} \ln\left(\frac{D_c}{\alpha t_c I_0}\right) = \frac{1}{\alpha} \cdot \ln\left(\frac{\alpha \cdot t_c \cdot I_0}{D_c}\right)$ (the usual critical dose in $mJ/cm^2 = E_c$

Review: Curing Depth

$$z_{ct} = \frac{1}{\alpha_i} ln\left(\frac{\alpha_i I_0 t}{D_c}\right)$$

Dose threshold for Polymerization



Penetration depth $h = \frac{1}{\alpha_i}$

RESIN PARAMETERS

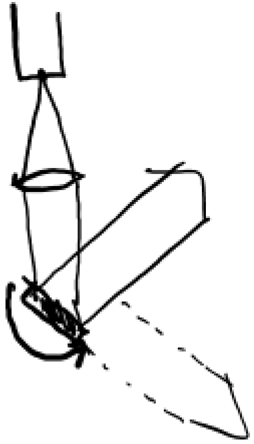
FH1100 STANDARD RESIN

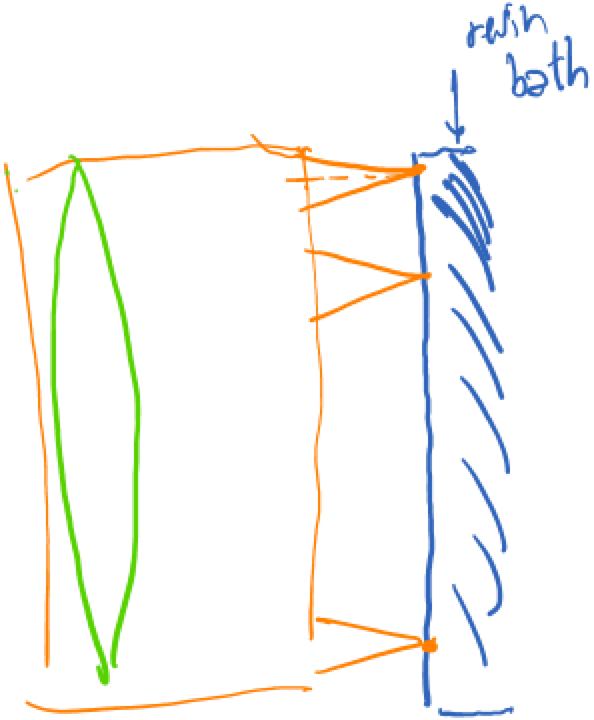
Appearance	Gray
Density (g/cm^3)	1.14
Viscosity (cps)	350 cps (25℃)
Critical Exposure Ec (mJ/cm^2)	12 mJ/cm^2
Penetration Depth (dp)	0.2 mm

As comparison
Water has a viscosity of 1 cps at 20ºC

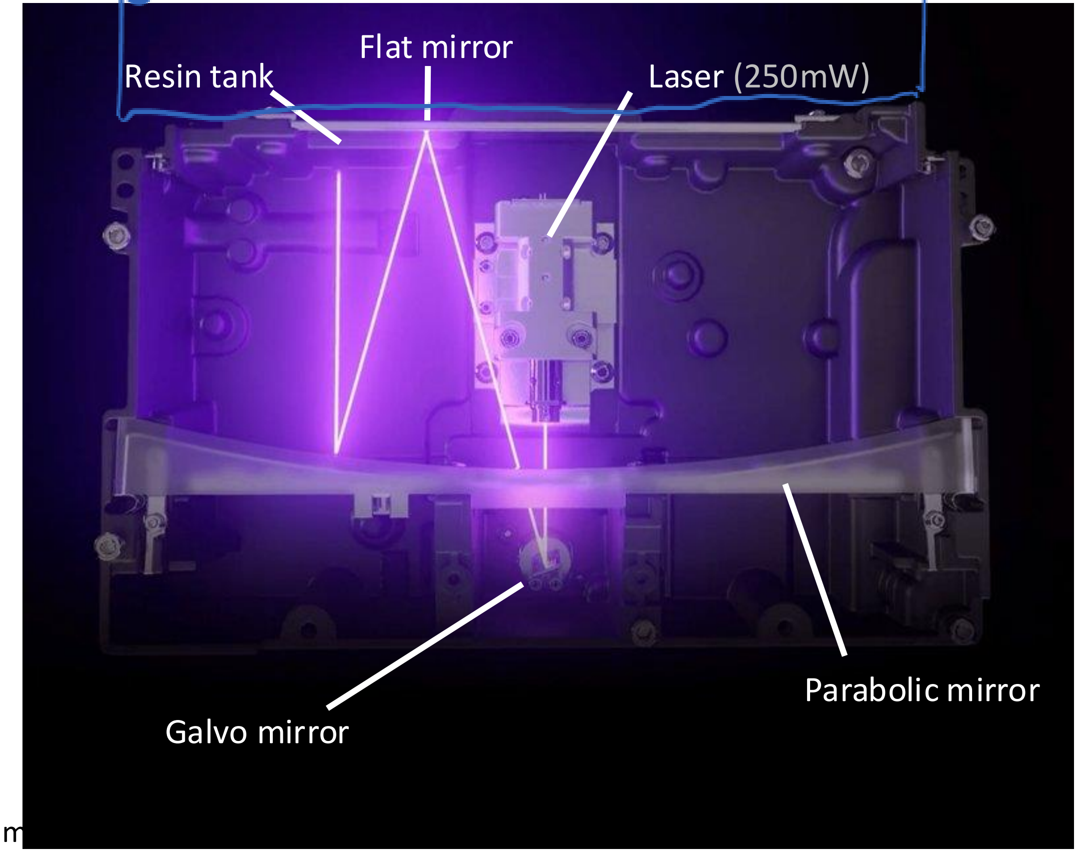
Formlabs 3 SLA printer

↑ stereo lithography.

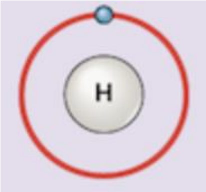


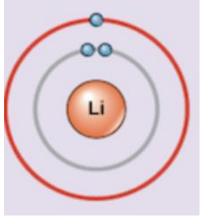


Formlabs 3 SLA printer

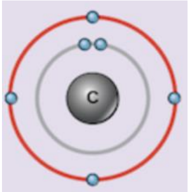


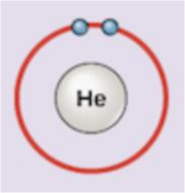
Organic chemistry basics

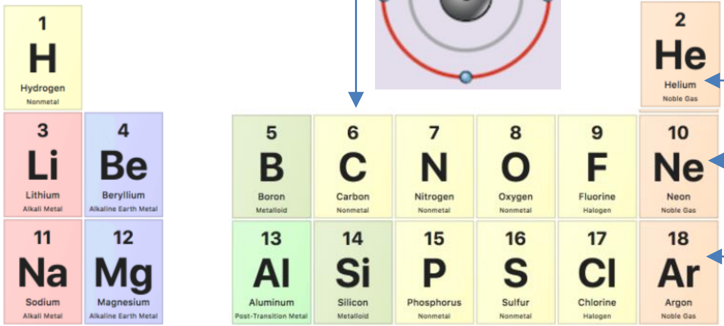




Same reactivity in each column



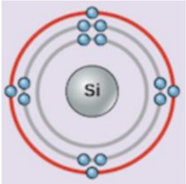


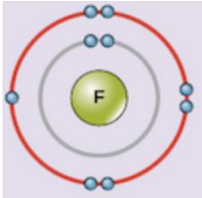


n=1 Filled with $2n^2=2$

n=2 Filled with $2n^2=8$

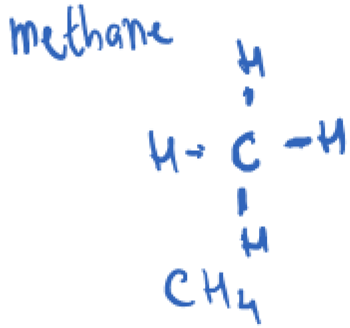
n=3 Filled with $2n^2=18$

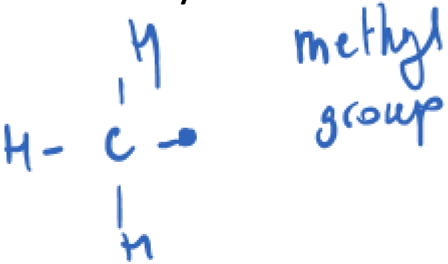


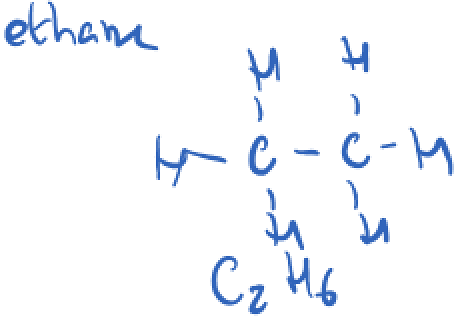


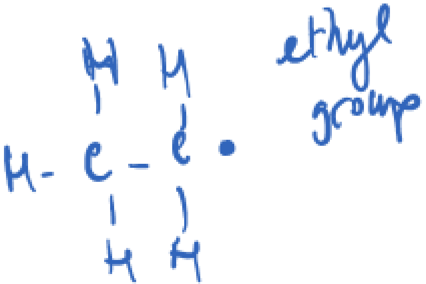
Single Carbon bonds

Alkane: → H removed → Alkyl:







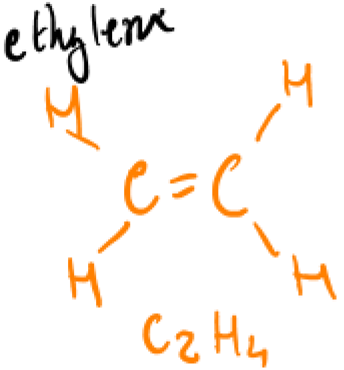


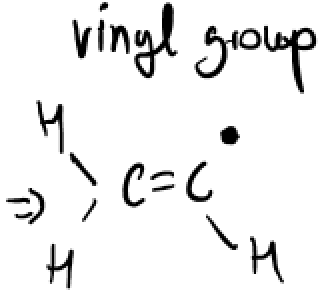
(propane) C_3H_8

Double Carbon bonds

Alkene:

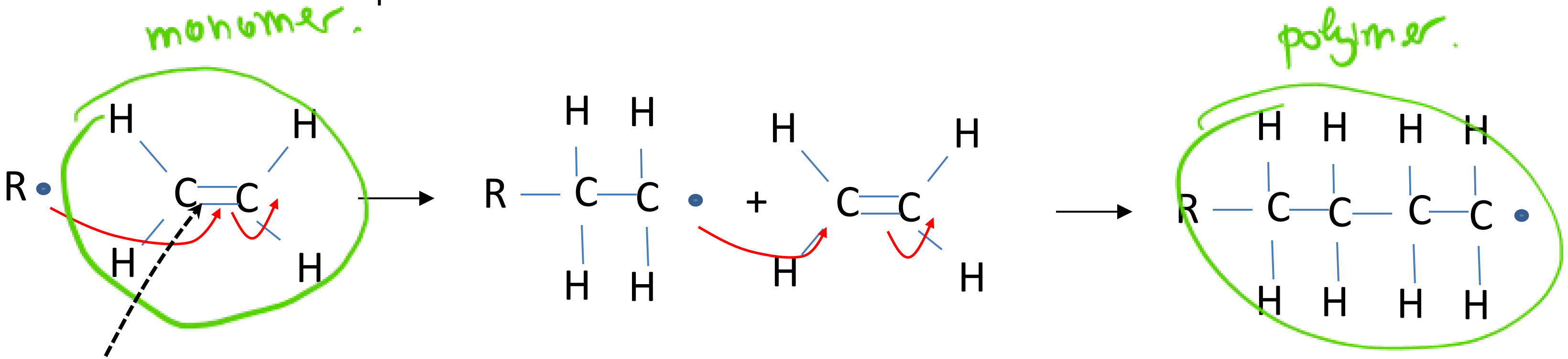
(ethene)





Radical chain Polymerization

R• Radical =molecule with unpaired electron



Ethylene molecule

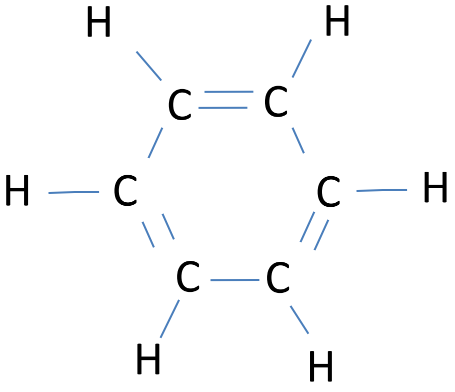
Polyethylene (PE)

polymer chains → thermoplastics

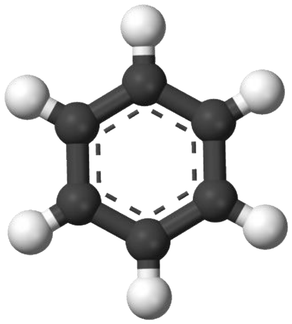
In a C=C double bond, one of the bond is weaker (260 kJ/mol vs 350 kJ/mol)

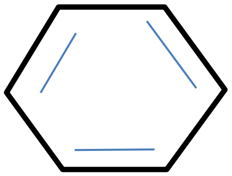
The Radical R* can be created by different energy sources: heat, light etc..

Radical chain Polymerization

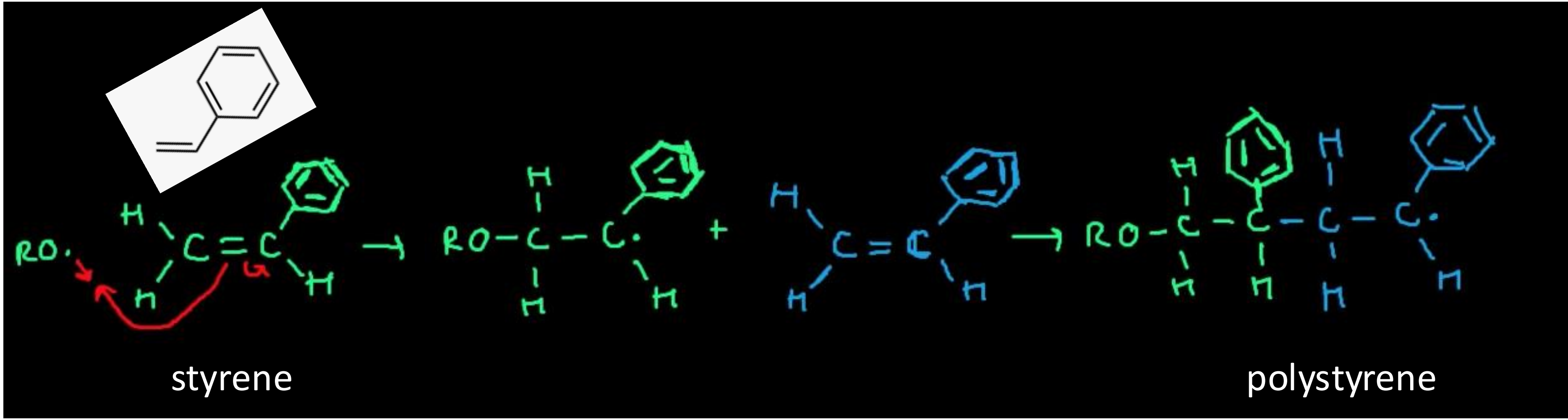


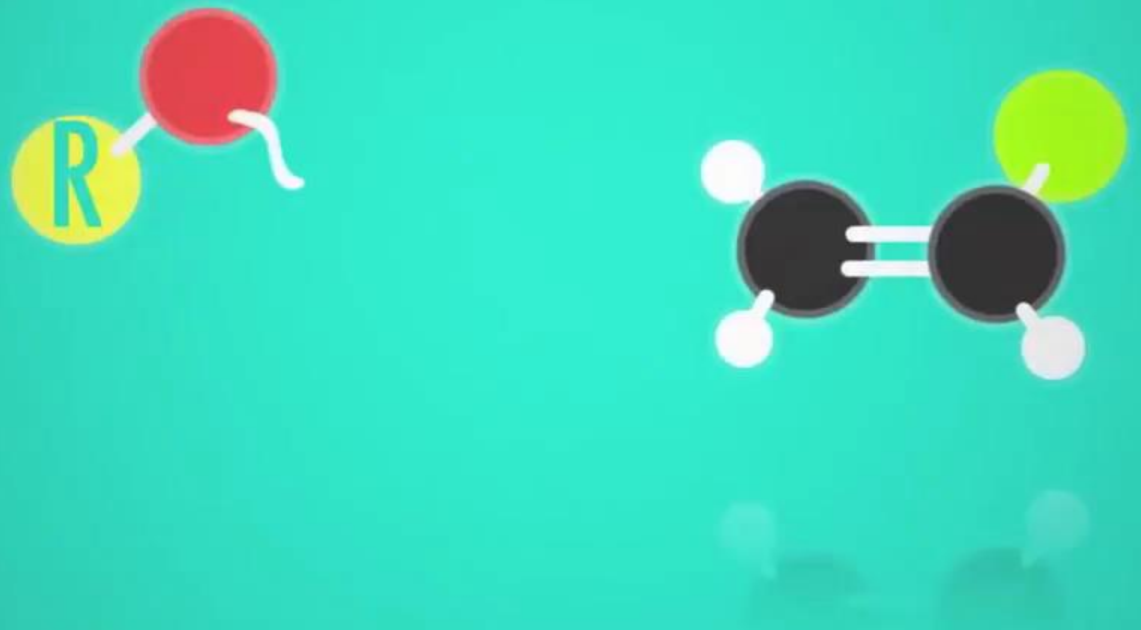
Benzene ring





Simplified representation




R

Chemical components in a resin for Stereolithography

Photoinitiator

Monomers for crosslinking, mechanical strength

Absorbing dye (penetration depth)

Inhibitor (stabilizer for shelf life)

Monomer to tune viscosity

Acrylate monomers:

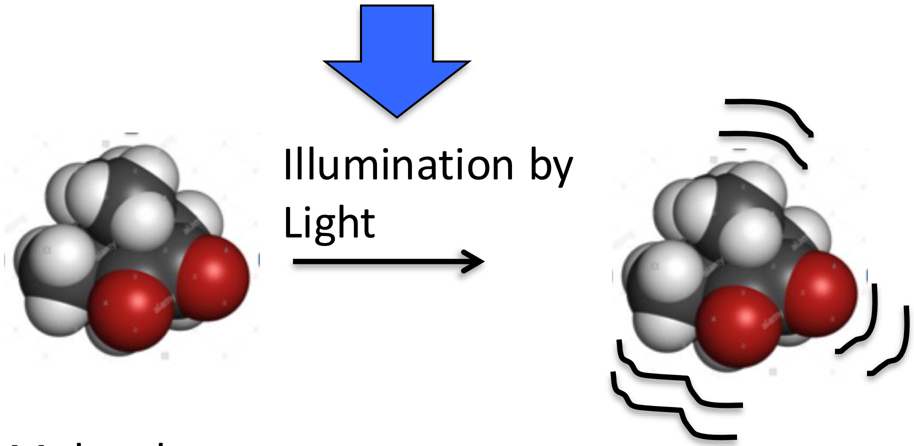
PEA: polyethylacrylate
TMPTA:
DPEPA:

IBOMA

Photoinitiator

Photo induced Radical **Polymerization**

The Photoinitiator ceases
to absorb light once it is “converted”
to a radical that induces polymerization



Molecule
(Photoinitiator or also
called Chromophore)

$R\cdot$

Excited State: **R**adical

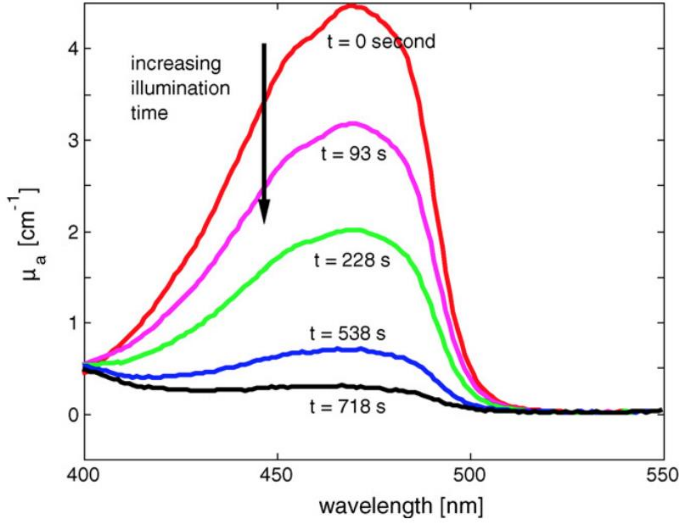
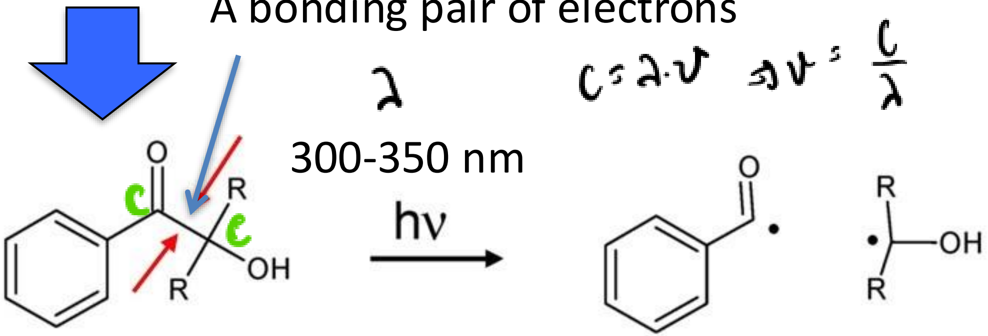


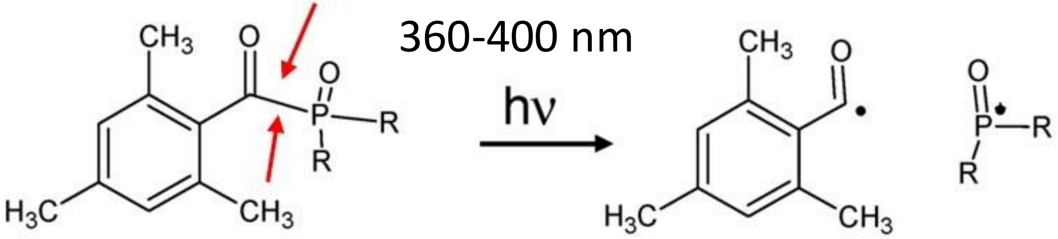
Fig. 6 – The absorption coefficient μ_a as a function of wavelength of resin with 0.7% CQ at five different illumination times for irradiance E_{total} = 160 mW/cm^2

Type I photoinitiators

Light energy is used to cleave
A bonding pair of electrons

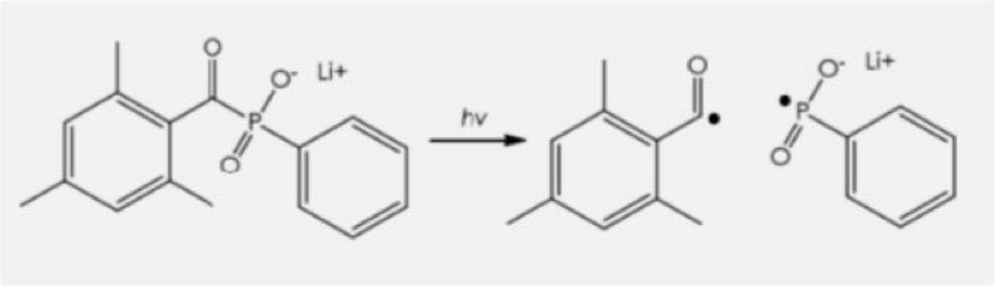


hydroxyacetophenone HAP



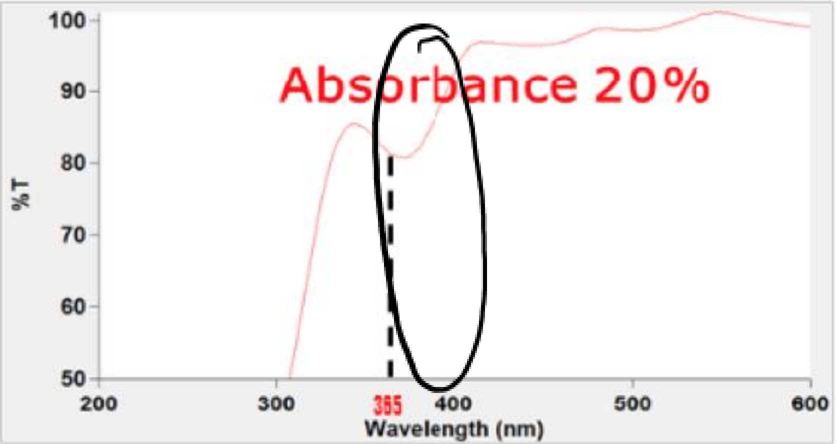
phosphineoxide TPO

Type I photoinitiators



Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP)

(popular PI for
Hydrogels – high solubility in
Water
30 g/liter compared to
3 mg/liter for TPO)

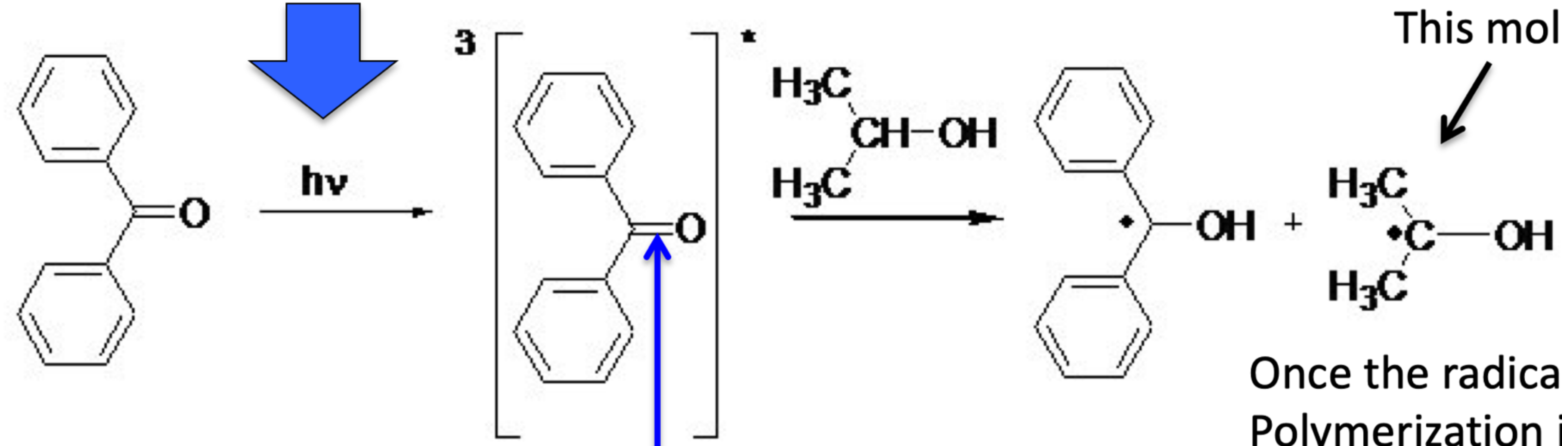


Type II photoinitiators

Less active than type I (one more step)

Need a co-initiator molecule to generate a Radical Reacting molecule

This molecule is active

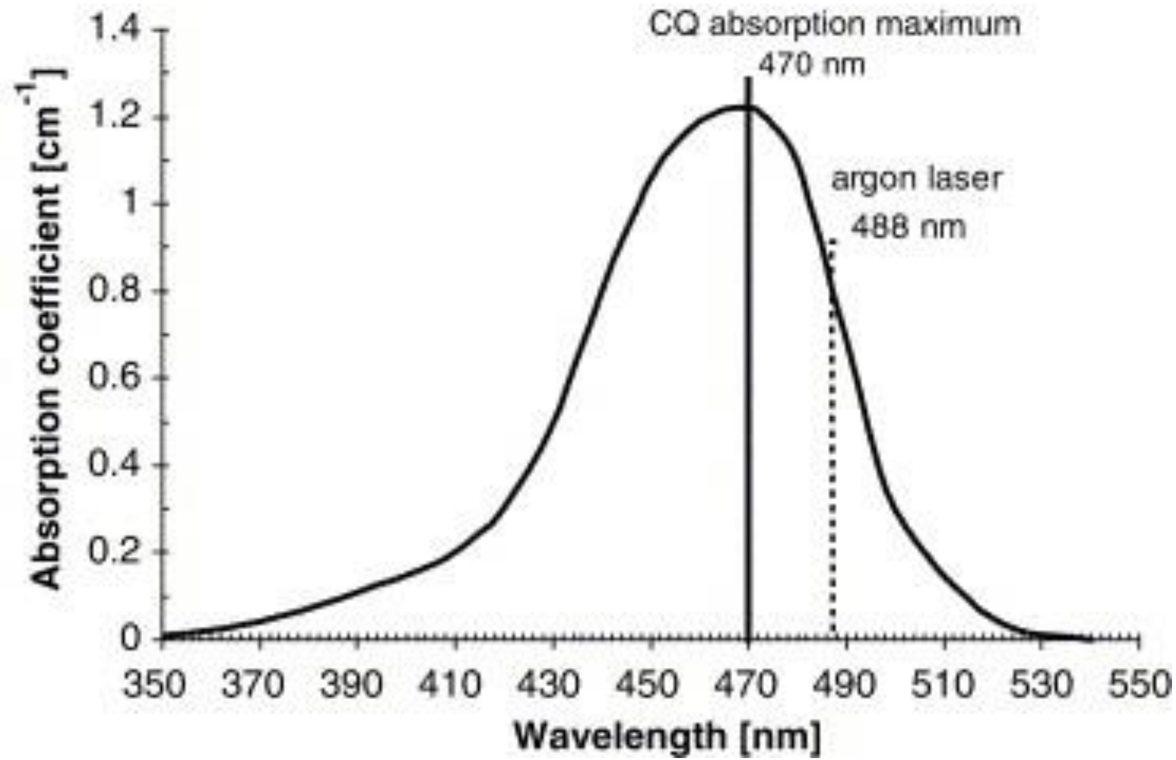


Benzophenone

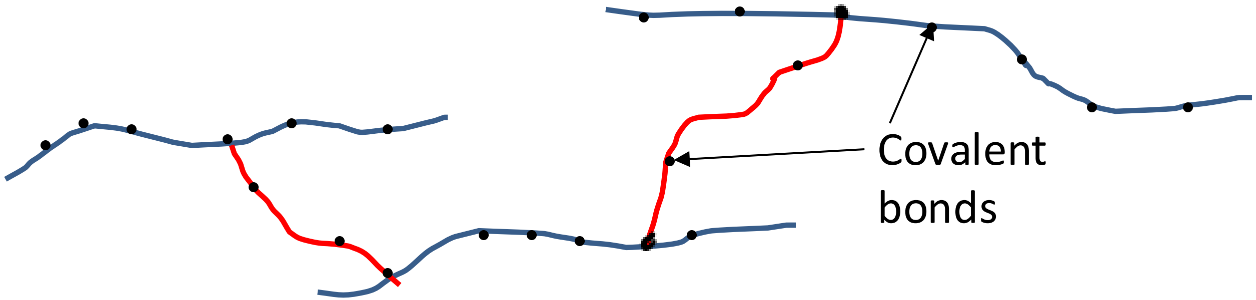
Excited electron in the double bond

Once the radical is generated, Polymerization is no different than any other free radical polymerization

The most widely used photoinitator in dentistry is Camphorquinone (CQ).
It is a type II Photoinitiator



Monomer



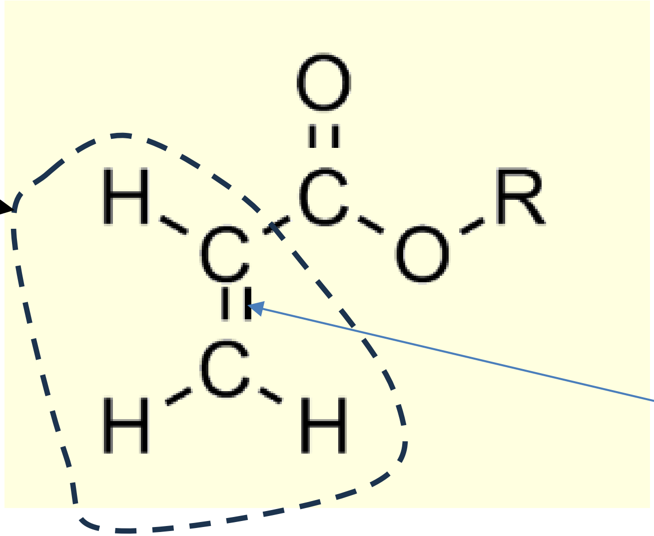
Need a monomer that can make chains via radical chain polymerization and link between chains (crosslinking) so that the curing is irreversible . The resin is called a thermoset.

It is not a thermoplastic (linear chains only, no cross linking), and thus there is no melting point for thermosets (only degradation with temperature)

Acrylate → important monomer in photopolymers

$$CH_2 = CH - COOR$$

Vinyl group



Acrylate molecule

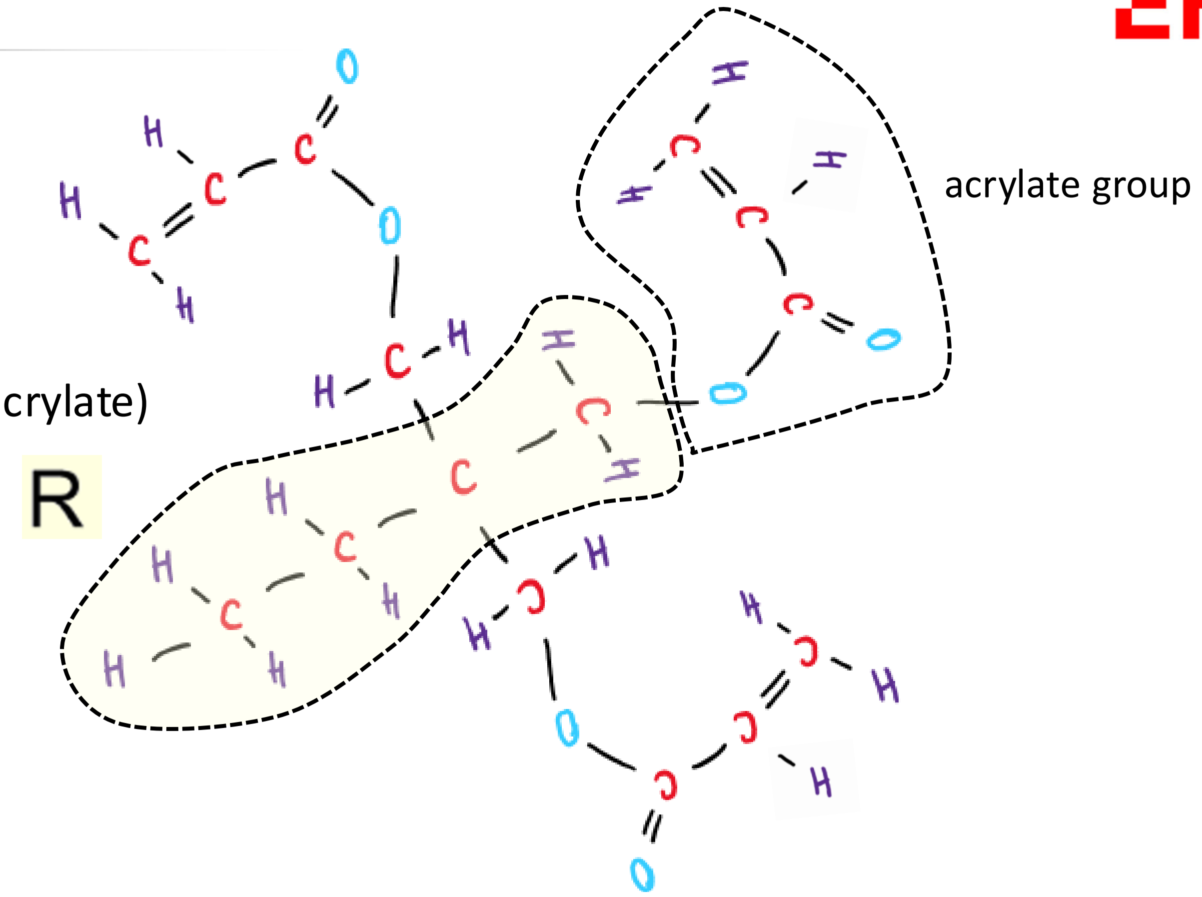
R :side chain (not a Radical !!)

Double bond used for radical polymerization

Example

Monomer Molecule
TMPTA
(Trimethylolpropane triacrylate)
$C_{15}H_{20}O_6$

3 branches for
Cross linking



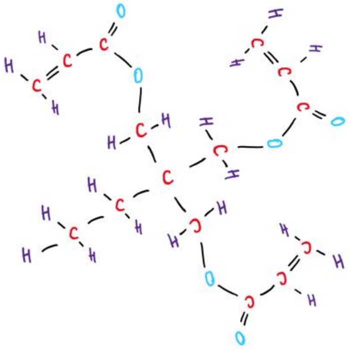
Criterion for gelation (liquid → solid)

Flory criterion for gelation: Fraction of reacted monomers $> \frac{1}{f-1} < 100\%$ → $f > 2$

f is called functionality

functionality = number of reactive groups per monomer molecule that can participate in the polymerization reaction.

Example: TMPTA

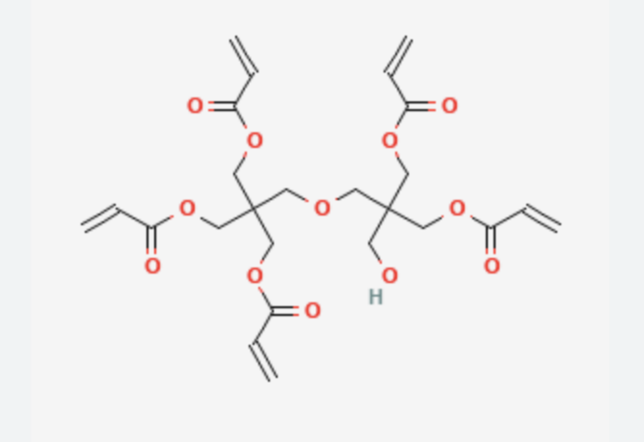


$f = 3$

Gelation threshold =Fraction of reacted monomers: $> \frac{1}{3-1} = 50\%$

Example

Dipentaerythritol pentaacrylate (DPEPA)



What is the gelation criterion ?

Gelation when fraction of reacted monomers $> \dfrac{1}{5-1} = 25\%$

"Tough 2000" resin from Formlabs

From safety data sheet:

Hazard-determining components of labeling:

- Urethane Dimethacrylate → $f = 2$
- Methacrylate Monomer → the functionality of the monomer is not mentioned
- Isobornyl methacrylate → $f = 1$
- Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide → Photoinitiator

When a resin is a mix of monomers with different functionalities, then the average functionality $\bar{f}$ is used in the Flory criterion:

$$\bar{f} = \frac{\sum_i x_i f_i}{\sum_i x_i}$$

x_i: fraction of component i

f_i: functionality of component i

for $\bar{f}$>2 , the functionality of the unknown monomer must be 3 or more

Role of oxygen

Photo-initiation

$$PI \xrightarrow{h\nu} 2R\bullet$$

Propagation
Polymer chain growth

$$R\bullet + M \rightarrow M\bullet$$

$$M_n\bullet + M \rightarrow M_{n+1}\bullet$$

Oxygen radical scavenging

$$R\bullet + O_2 \rightarrow R-O-O-$$

$$M_{n+1}\bullet\ O_2 \rightarrow \text{dead polymer}$$

Reaction kinetics

Photoinitiator molecule

$$In \xrightarrow{k_d} 2R\cdot$$

Kp: rate of decomposition

Photo initiator

Radical Chain Polymerization

$$R\cdot + DB \xrightarrow{k_p} R\cdot$$

Kp: rate of propagation

Radicals

$$R\cdot + R\cdot \xrightarrow{k_t} R_{dead}$$

Kt: rate of termination

Monomer Double bond

$$R\cdot + O_2 \xrightarrow{k_{t,O_2}} R_{dead}$$

Kt,o2: rate of termination

Oxygen

rate

$\frac{P}{area}$ → light intensity

$$\frac{d[In]}{dt} = -k_d \cdot I(z) \cdot [In]$$

generation

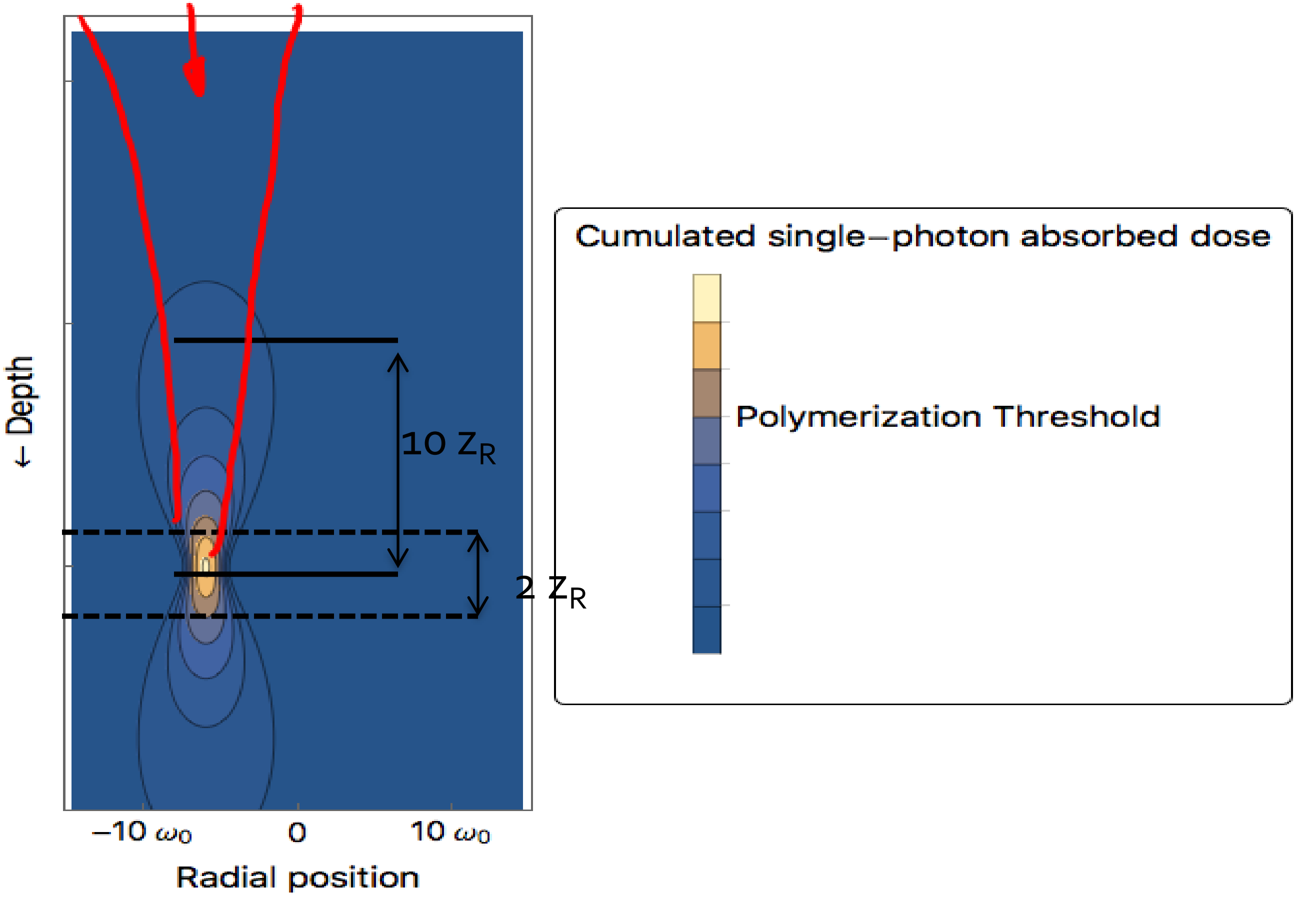
$$\frac{d[R\cdot]}{dt} = +2k_d I(z)[In] - [O_2][R\cdot] \cdot k_{O_2} - 2k_t[R\cdot]^2$$

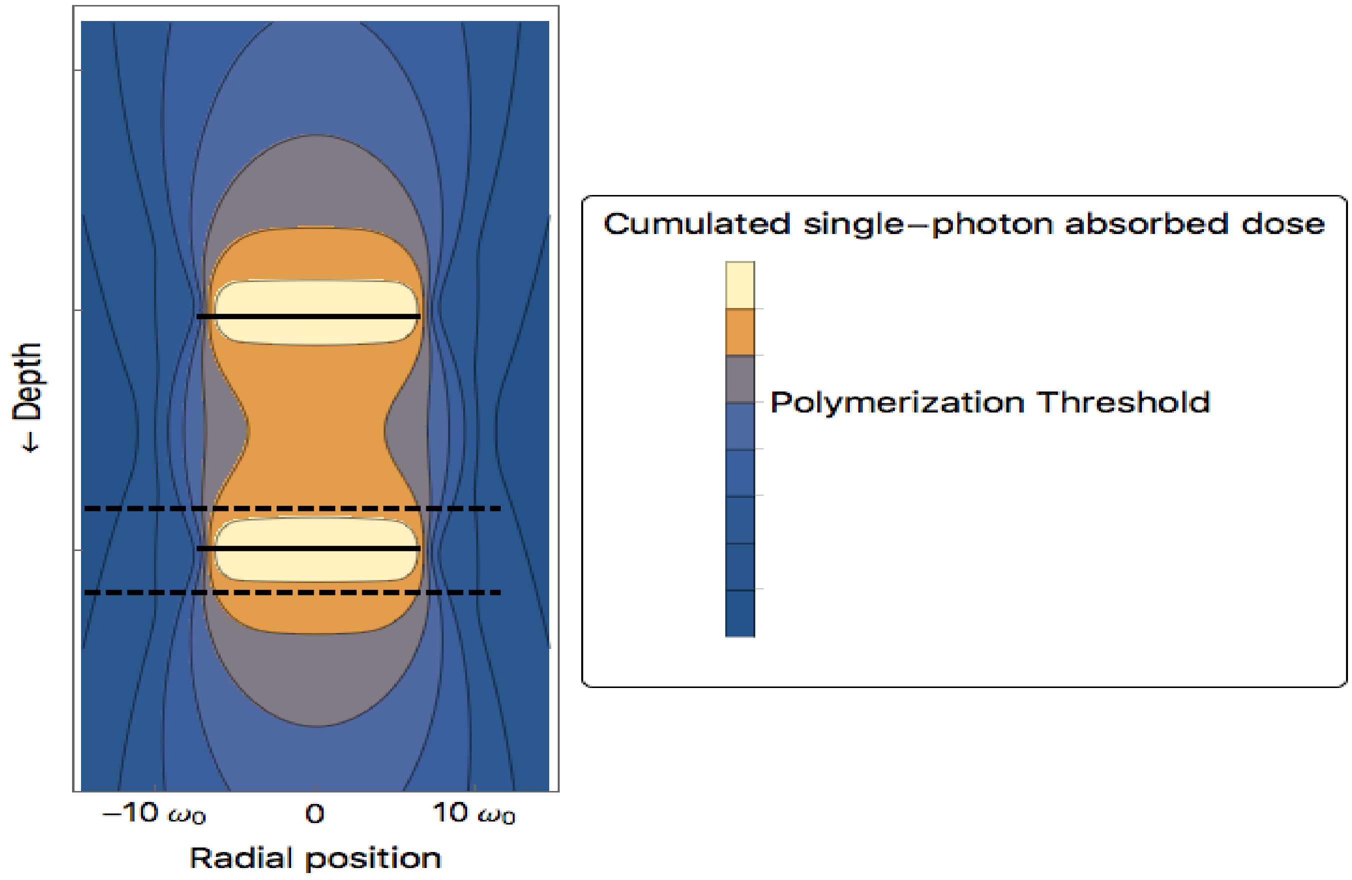
$$\frac{d[DB]}{dt} = -k_p [DB][R\cdot]$$

$$\frac{d[O_2]}{dt} = -k_{O_2}[R\cdot][O_2] + D_{O_2} \cdot \frac{\partial^2 [O_2]}{\partial z^2}$$

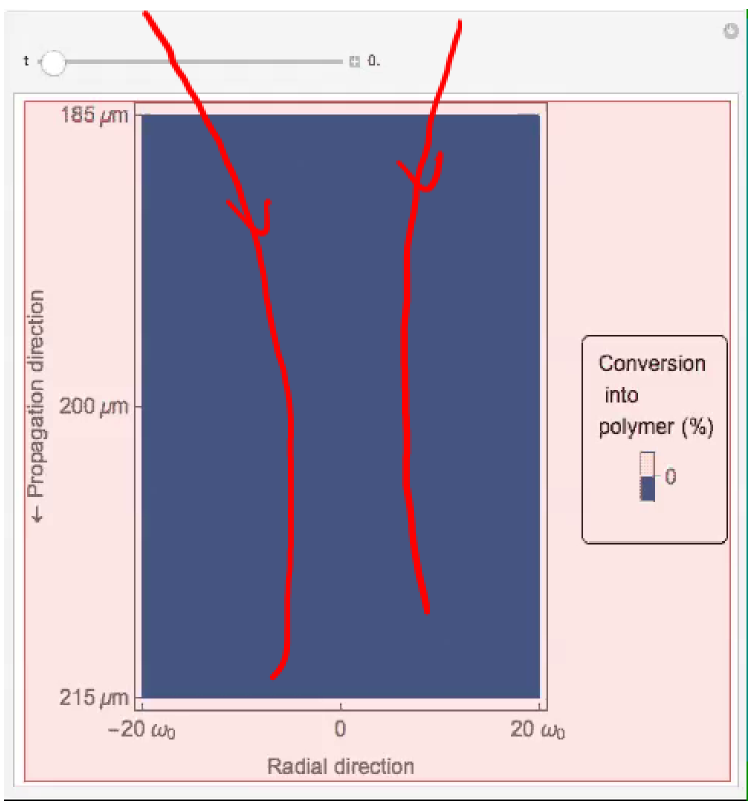
diffusion

Linear absorption and photopolymerization

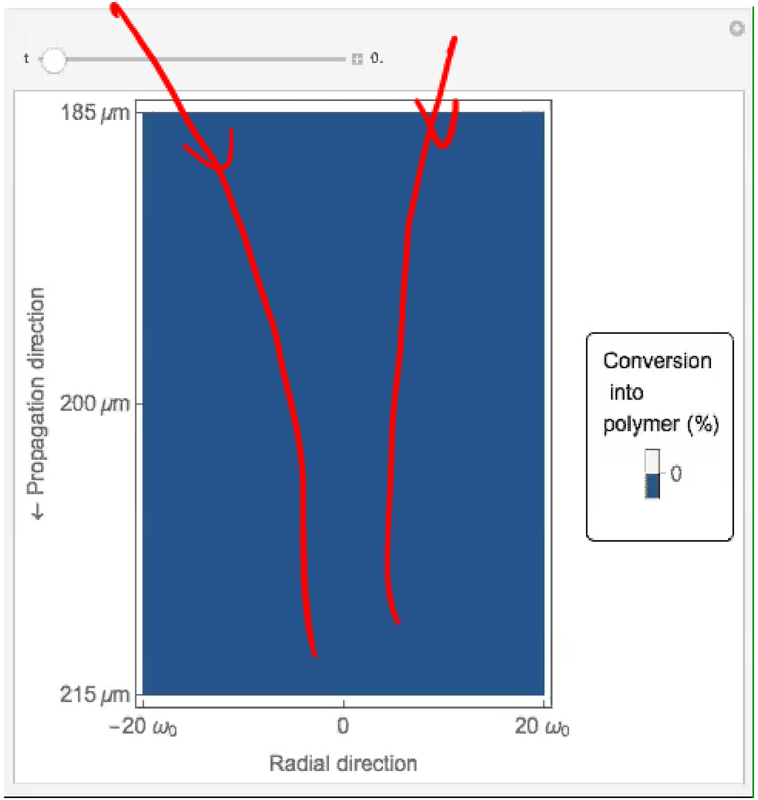



← Depth
−10 ω_0
0
10 ω_0
Radial position
Cumulated single−photon absorbed dose
Polymerization Threshold

Simulation without oxygen inhibition

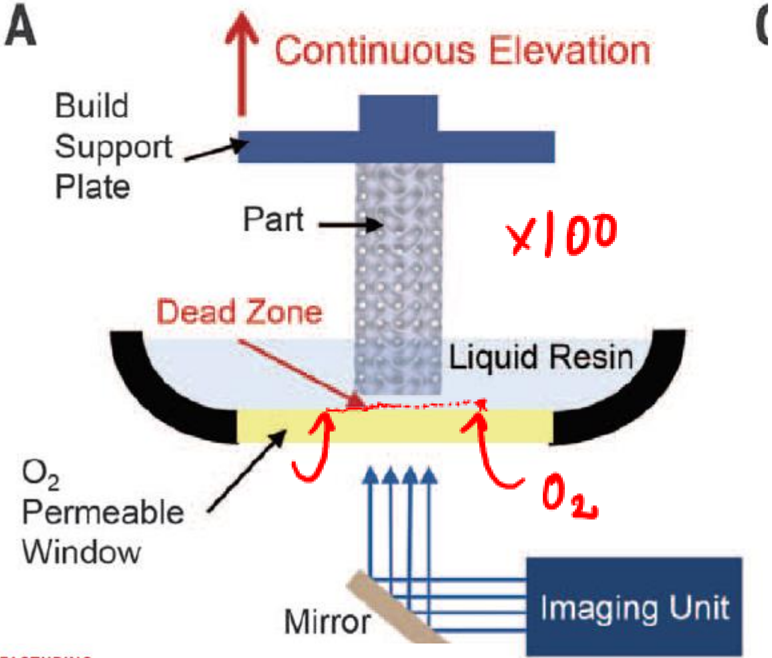


Simulation with oxygen inhibition



P = 250 nW, polymer: PEG-DA

Continuous liquid interface production (CLIP)

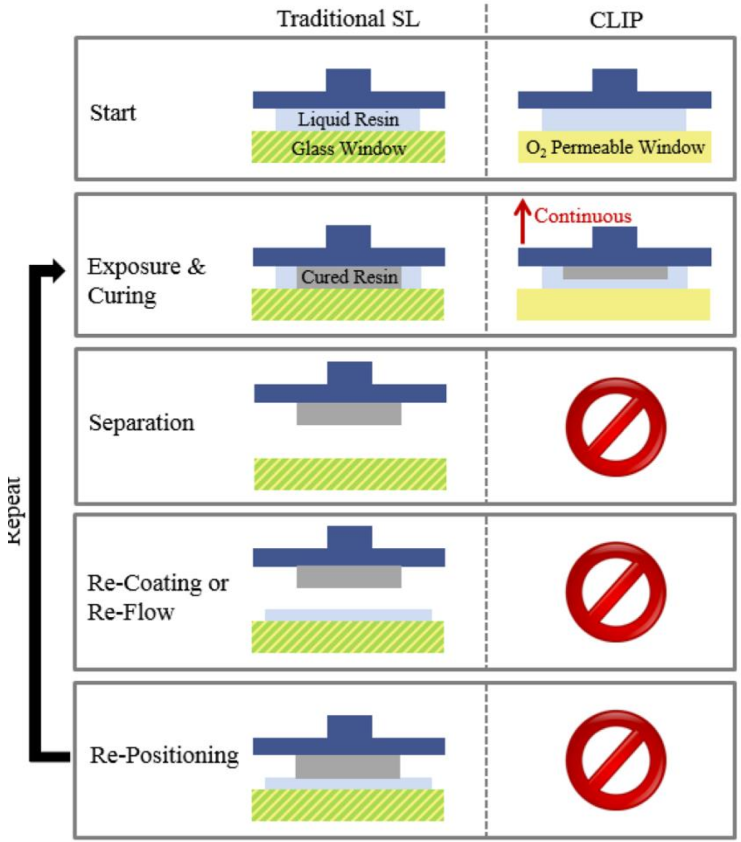


ADDITIVE MANUFACTURING

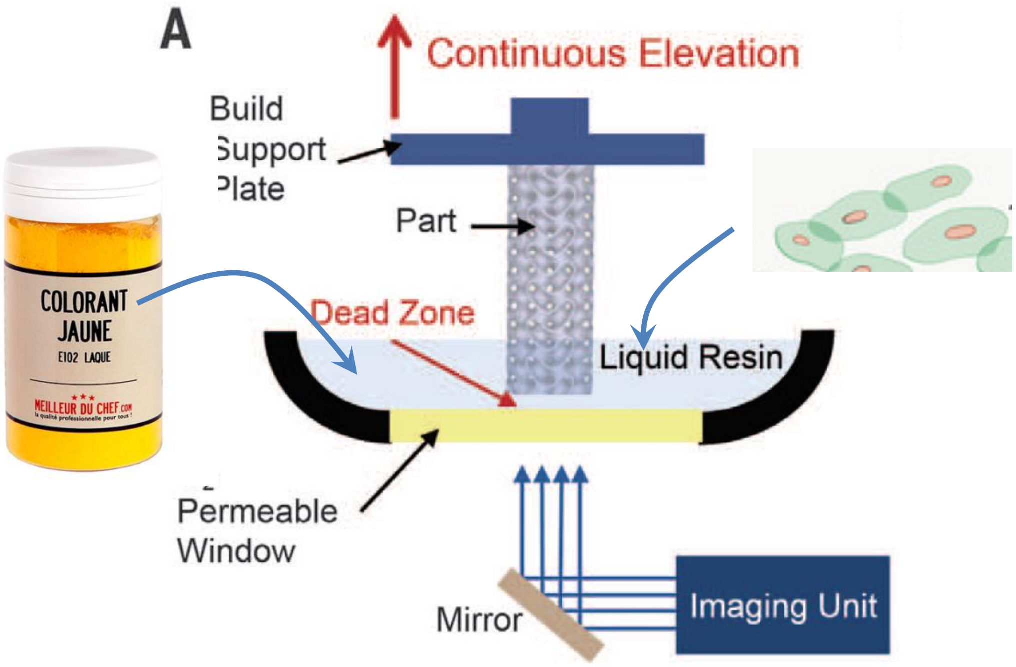
Continuous liquid interface production of 3D objects

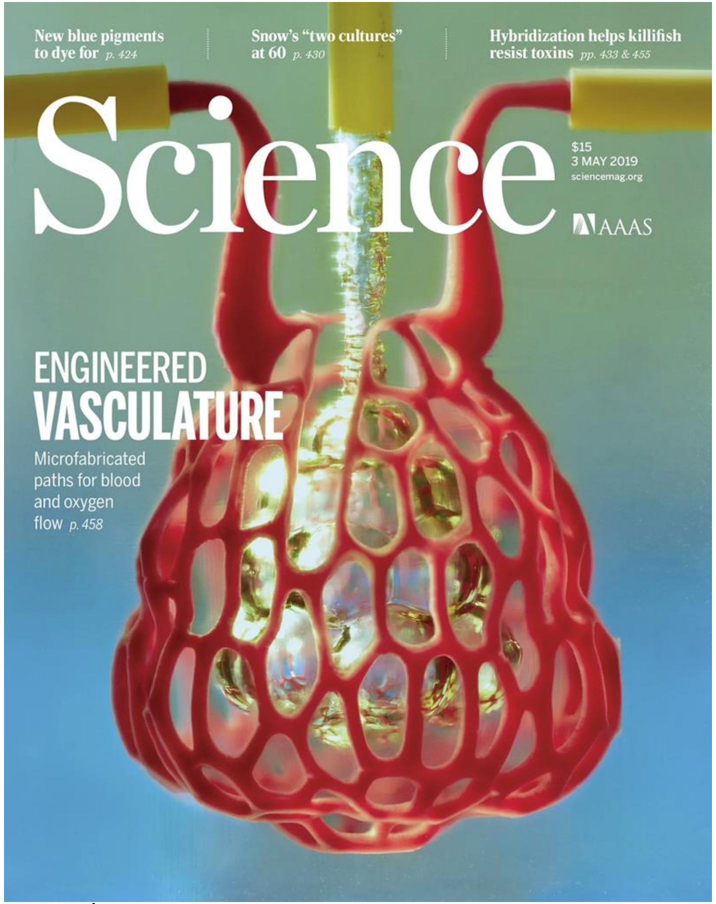
Science

John R. Tumbleston,[1] David Shirvanyants,[1] Nikita Ermoshkin,[1] Rima Janusziewicz,[2] Ashley R. Johnson,[3] David Kelly,[1] Kai Chen,[1] Robert Pinschmidt,[1] Jason P. Rolland,[1] Alexander Ermoshkin,[1*] Edward T. Samulski,[1,2*] Joseph M. DeSimone[1,2,4*]



https://www.carbon3d.com/our-technology/





Projection Stereolithography