High Efficiency Radical Photopolymerization Enhanced By Autonomous Dark Cure

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RadLaunch - March/10/2020

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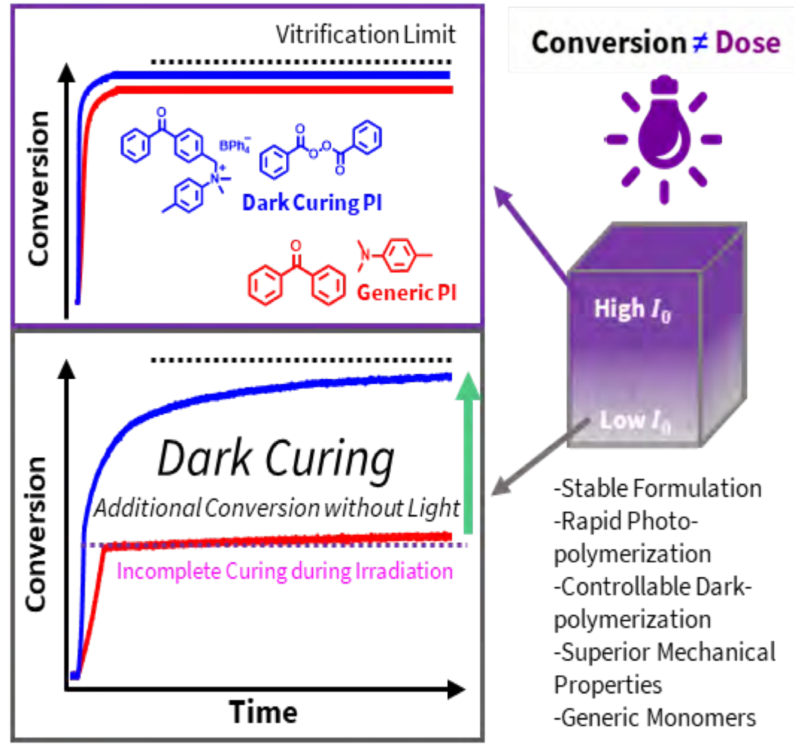


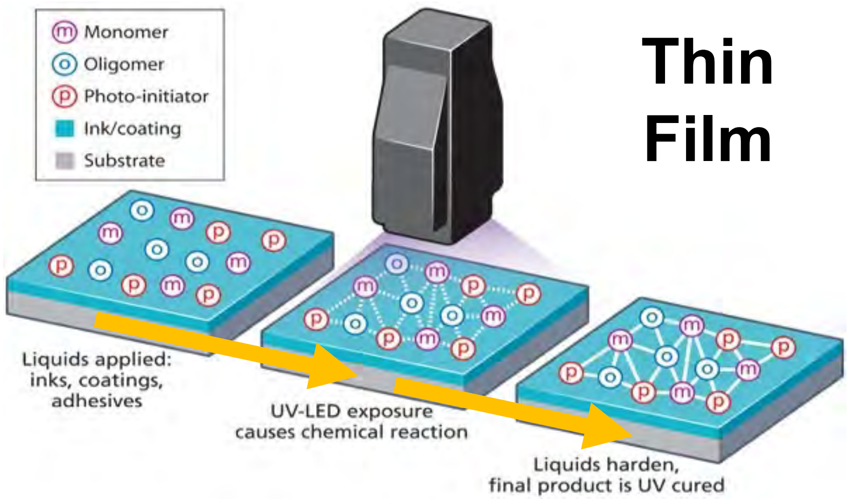
University of Colorado Boulder

Photopolymerizations Industry Center

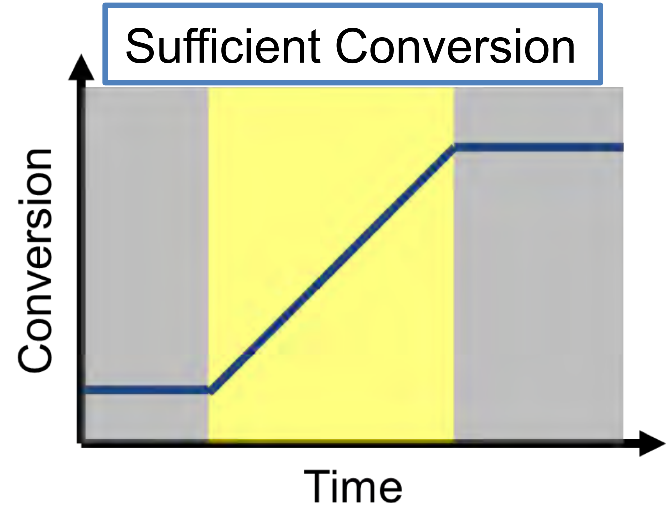
National Institute of Dental and Craniofacial Research

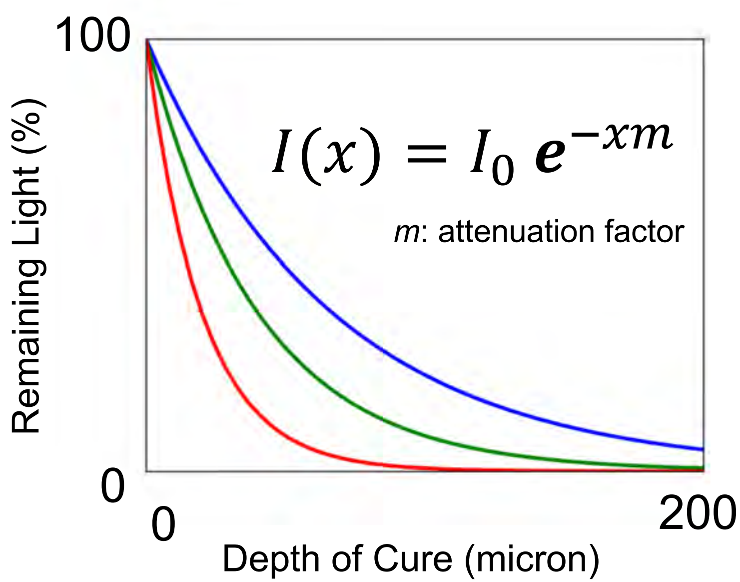
RADTECH UV+EB 2020

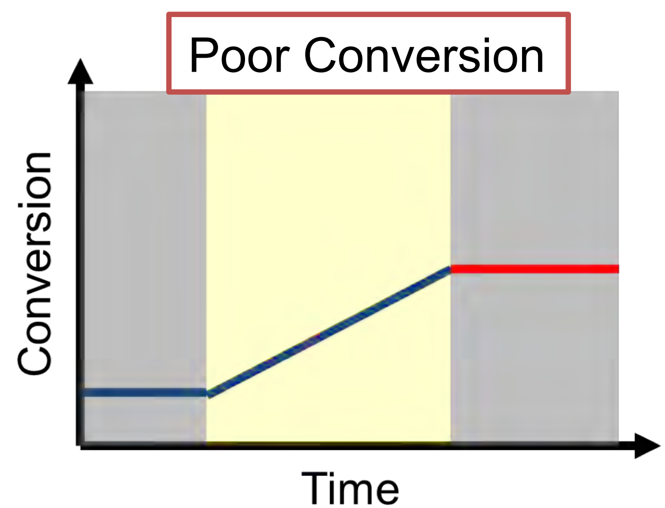
Conversion is determined by light dose



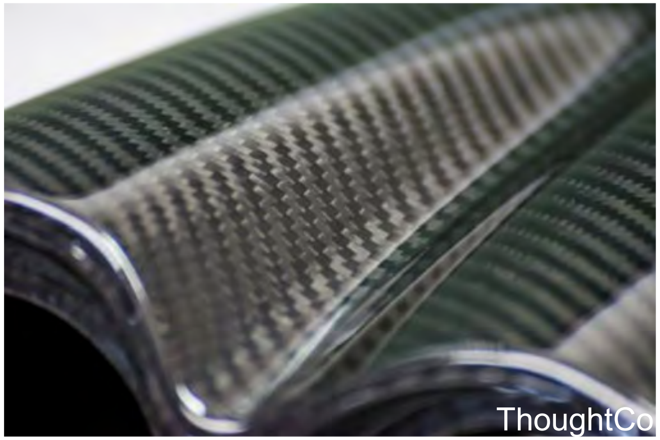
Thin Film







Photopolymer Applications are Expanding



Filled Resin (composite)

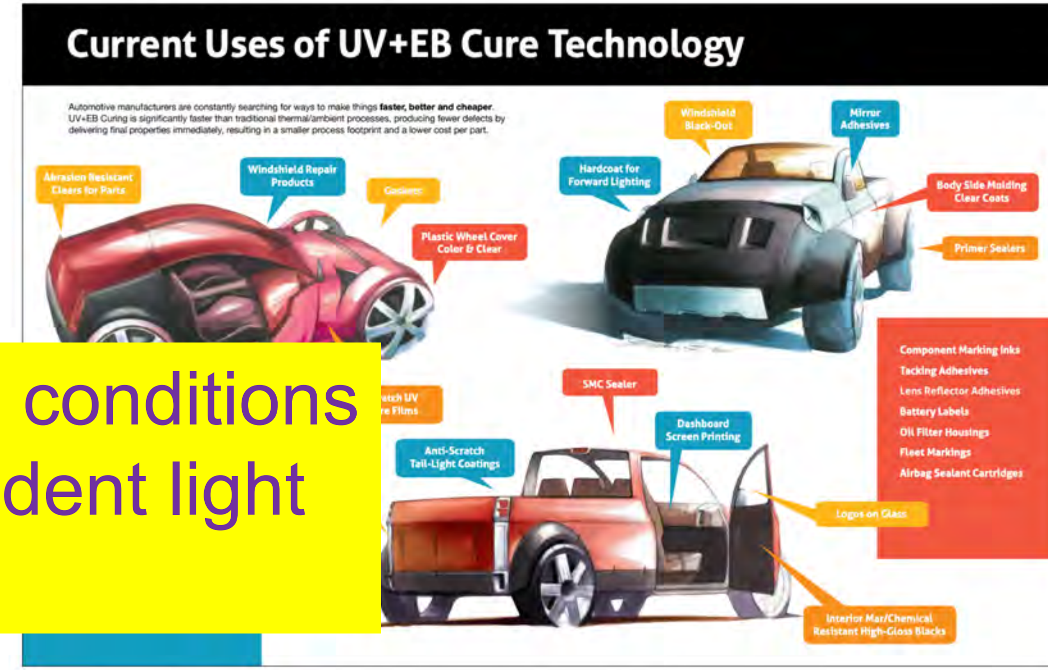
Pigmented Resin

Thick Resin

Non-ideal photocuring conditions due to light attenuation

Photopolymer Applications are Expanding

2017 Quarter 1
Vol. 3, No. 1
UV+EB TECHNOLOGY



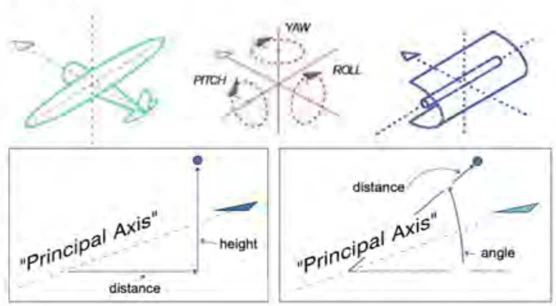
Non-ideal photocuring conditions due to geometry-depedent light exposure

Q. How Can the Orientation of UV Lamps in a 3D Curing System be Described?

A. There is a useful language.

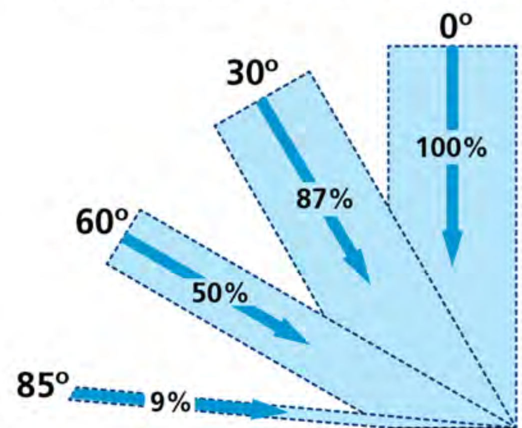
Life in the UV curing world was easier when UV lamps only stretched across a web or flat conveyor, and all we had to worry about was *width*, number of *rows* and *distance* from the work. But, as we move into 3D processing of complex shaped objects, lamps are located all over the curing zone. In fixed-lamp 3D configurations, each lamp has its own optimized position. Setting lamps in a large 3D installation falls somewhere between science and art.

Chain-on-edge systems and paint lines represent a whole family of problems in orienting the UV lamps. The line can be continually moving or intermittent.

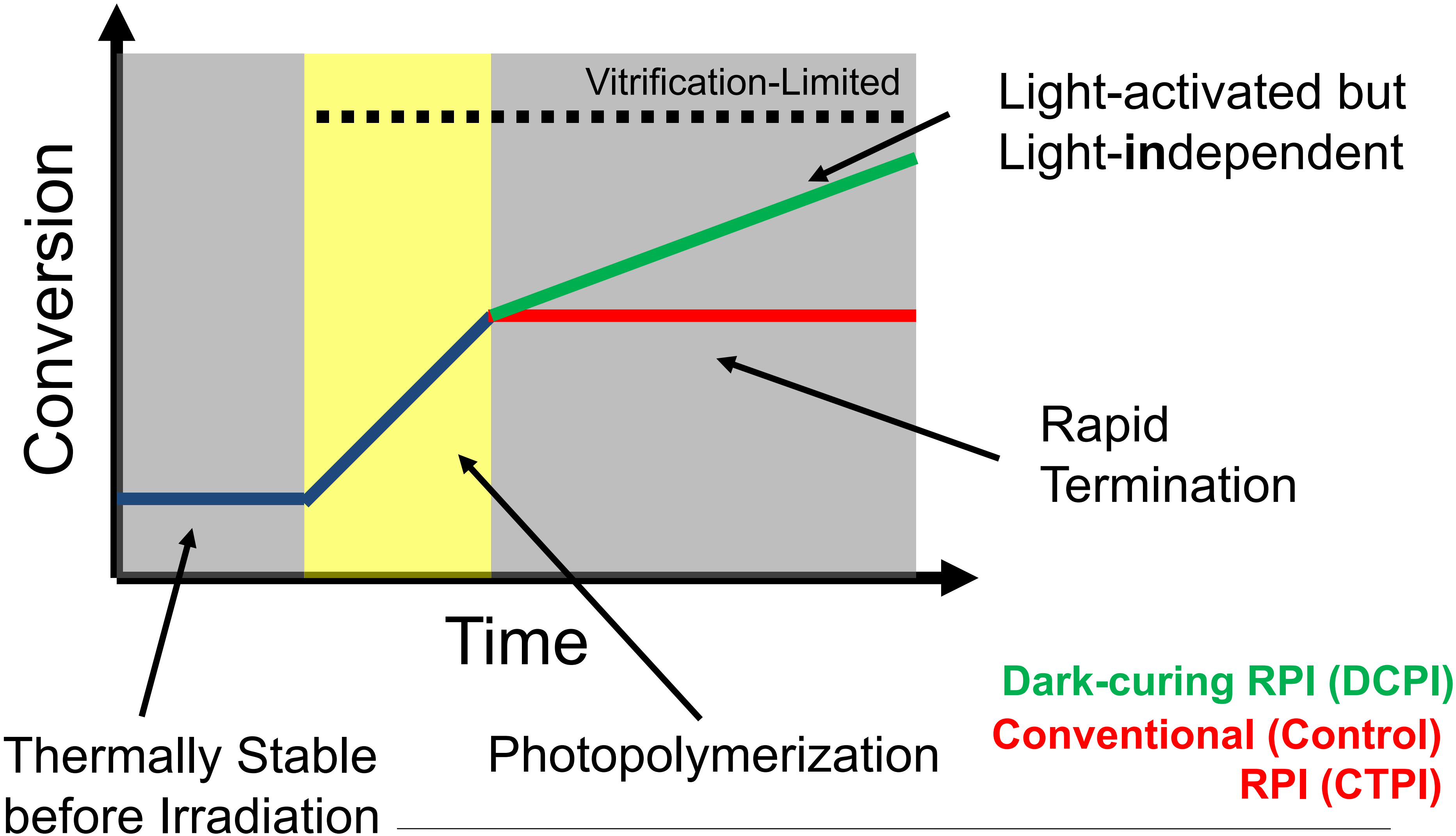


3D Objects and Their Surfaces

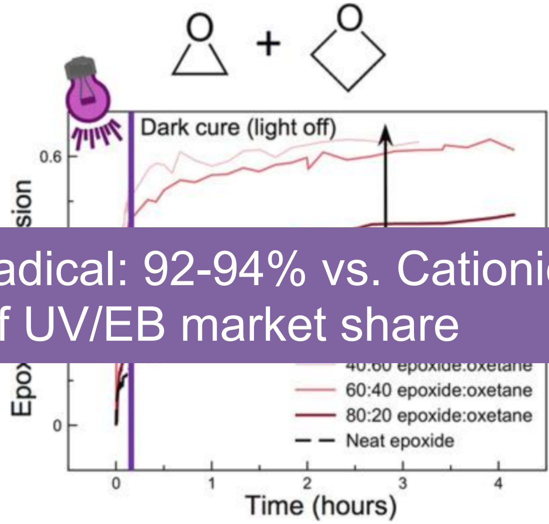
Cosine Law: $E_\theta = E * \cos(\theta)$



Dark-curing PI Overcomes Insufficient Dose

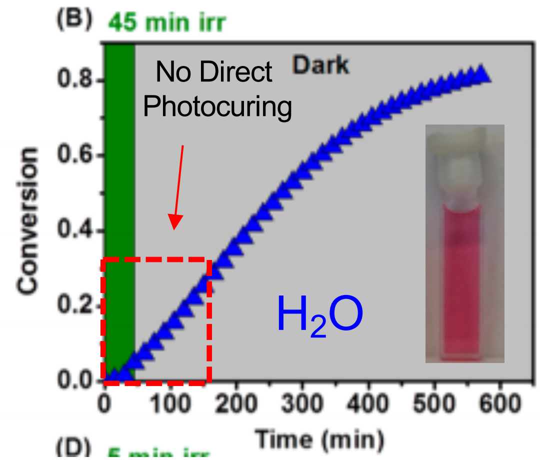


Previous Dark-curing is Limited

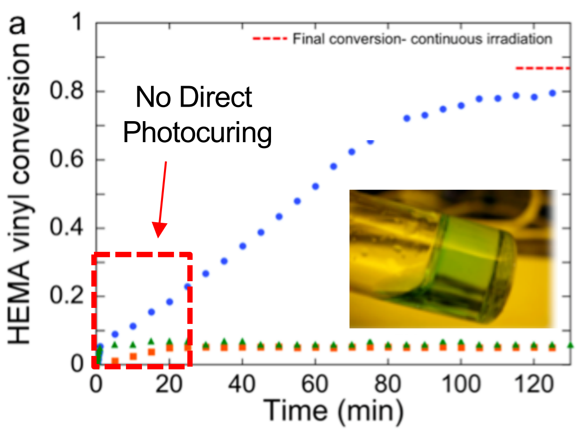


Radical: 92-94% vs. Cationic: 6-8% of UV/EB market share

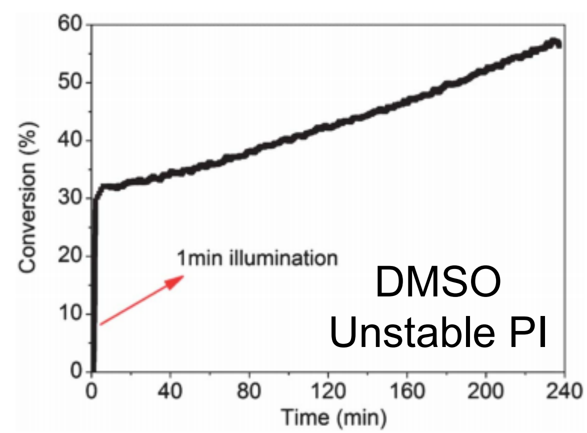
Kaalberg and Jessop



Shanmugam, Xu, Boyer



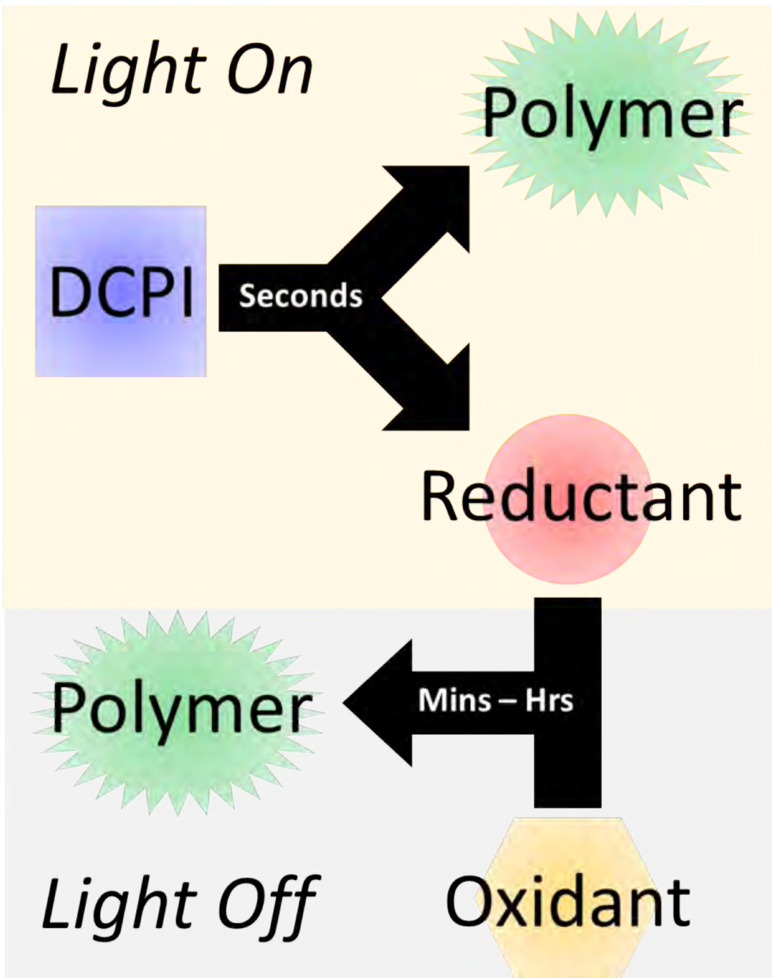
Aguirre-Soto, Musgrave, Stansbury

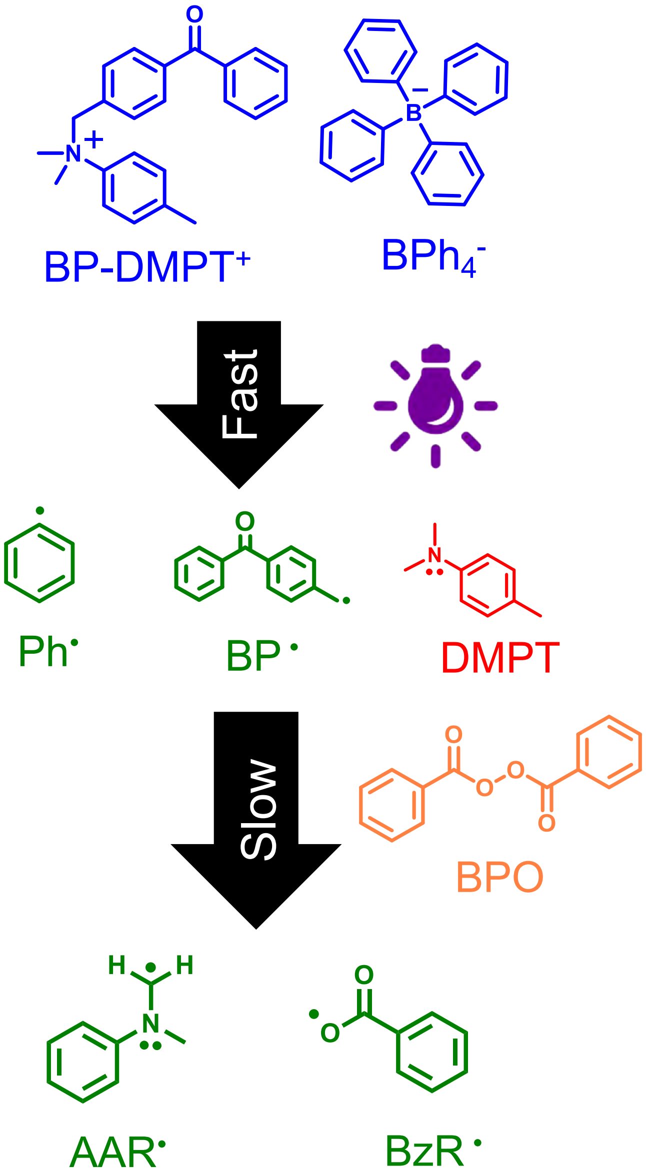


He, Yang

Kaalberg and Jessop, *J. Polym. Sci., Part A: Polym. Chem*. **2018**, 56, 1436-1445
Aguirre-Soto, et al. *J. Am. Chem. Soc.* **2014**, 136, 7418-7427
Shanmugam, et al. *Macromolecules*, **2018**, 50, 1832-1846
He et al. *Polym. Chem.* **2014**, 5, 2951-2960

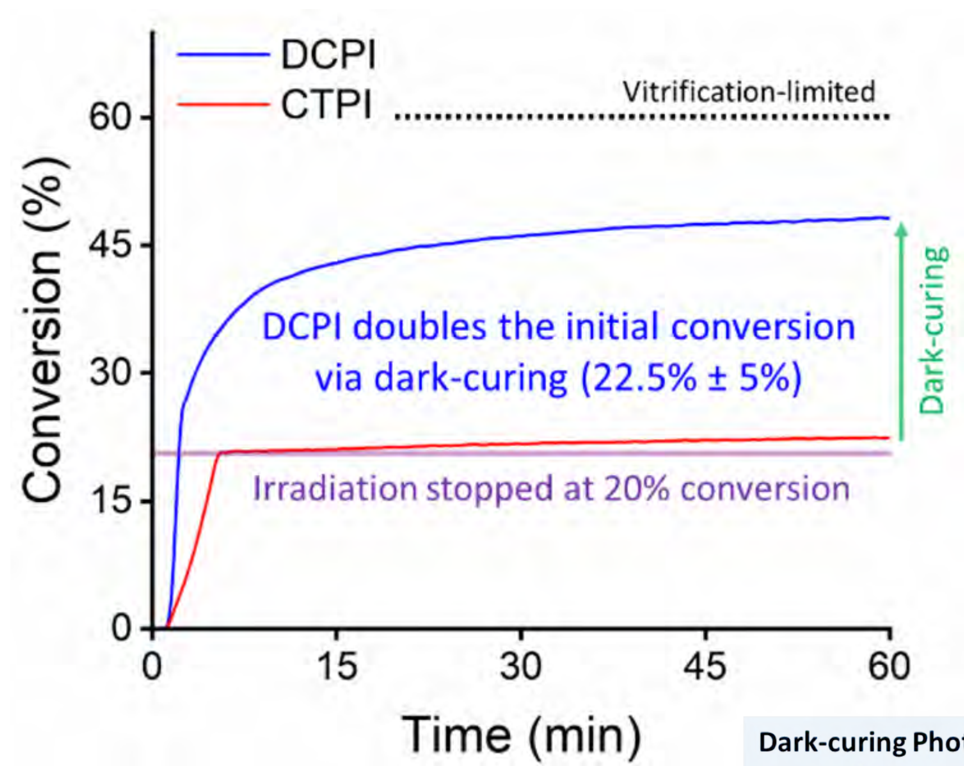
New Radical Dark-curing Initiator (DCPI)

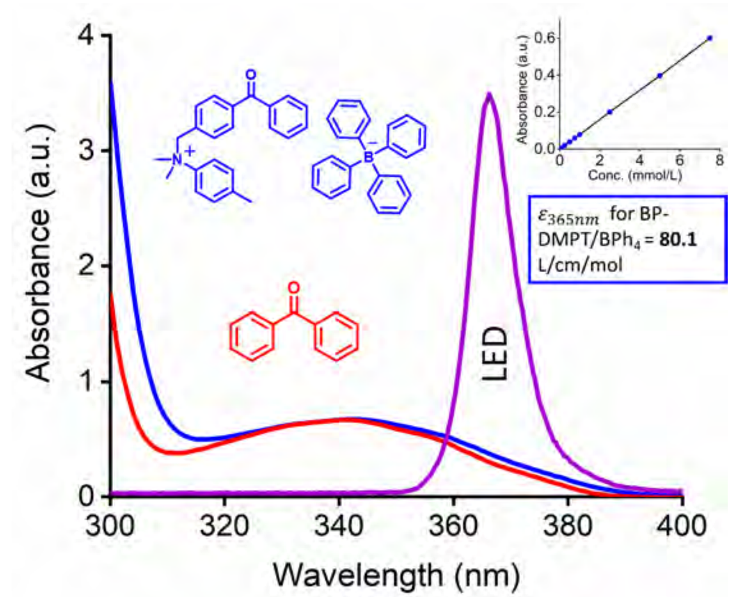


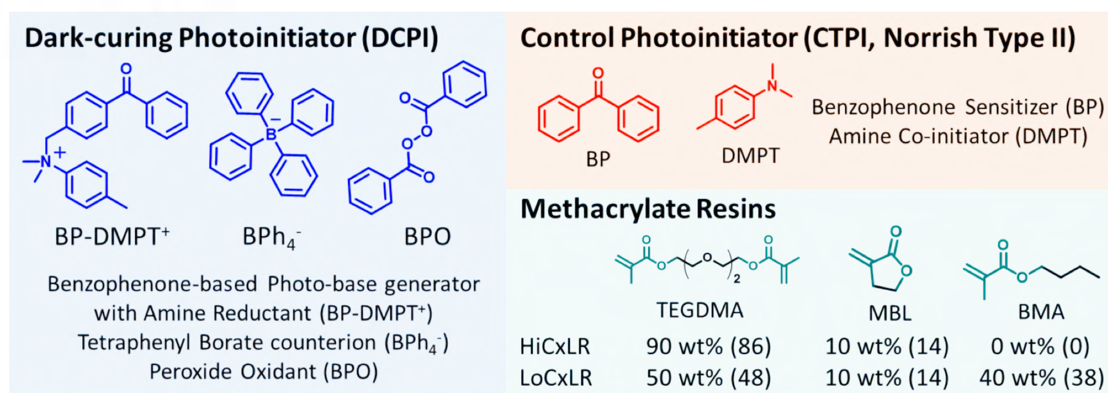


Kangmin Kim et al. J. Am. Chem. Soc., **2019**, 141, 15, 6279-6291
Kangmin Kim et al. Submitted, **2020**

DCPI Guarantees Additional Conversion



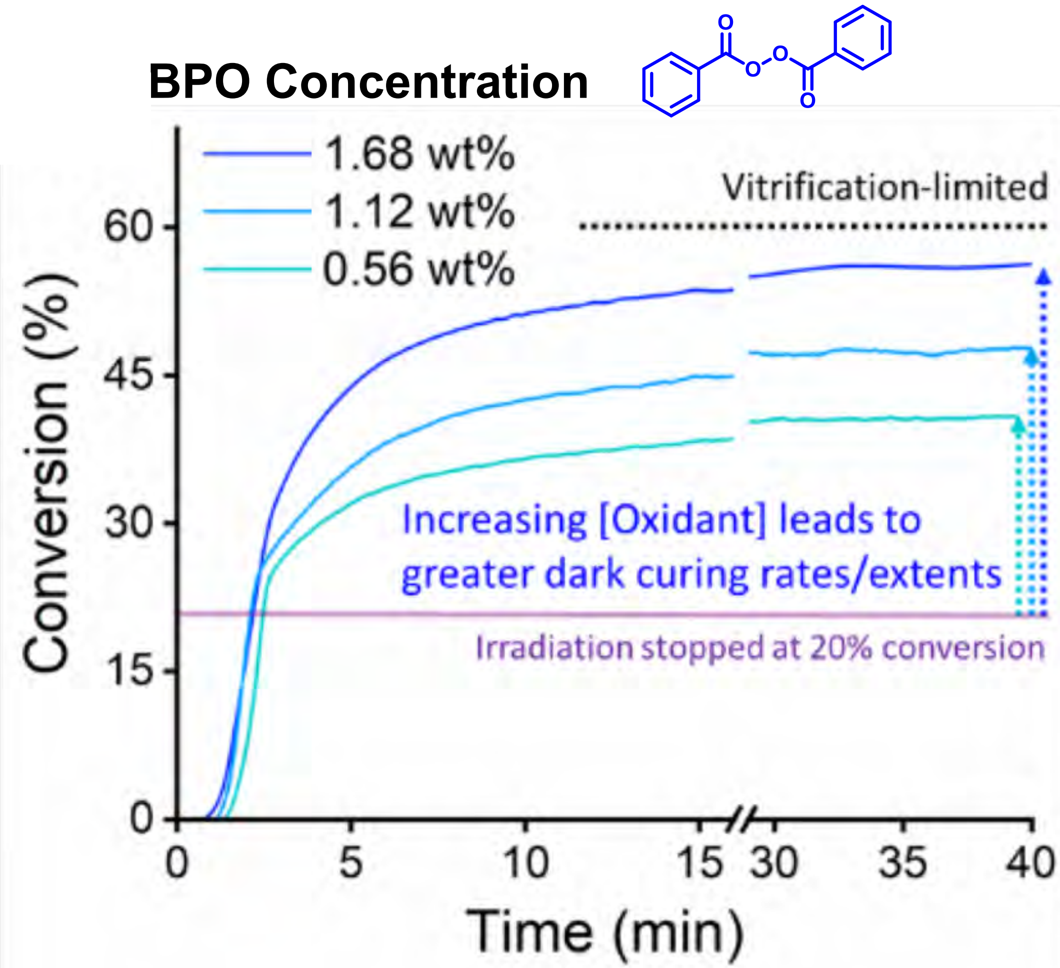


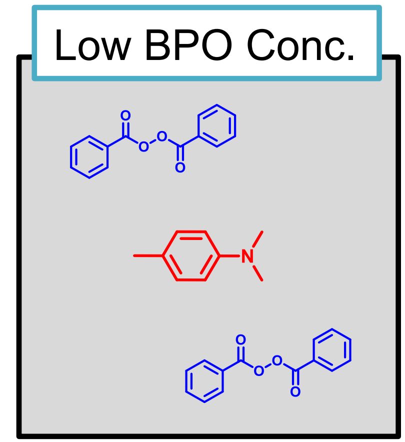


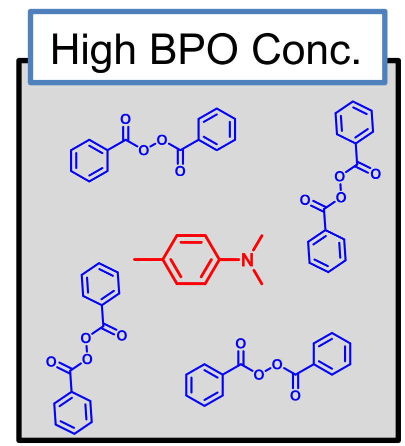
0.5 wt% [DCPI];
30mW/cm^2 365 nm LED

Kangmin Kim et al. Submitted, **2020**

Easy Modulation of Dark-curing Rates







High Encounter Rate
= High Dark-curing Rate

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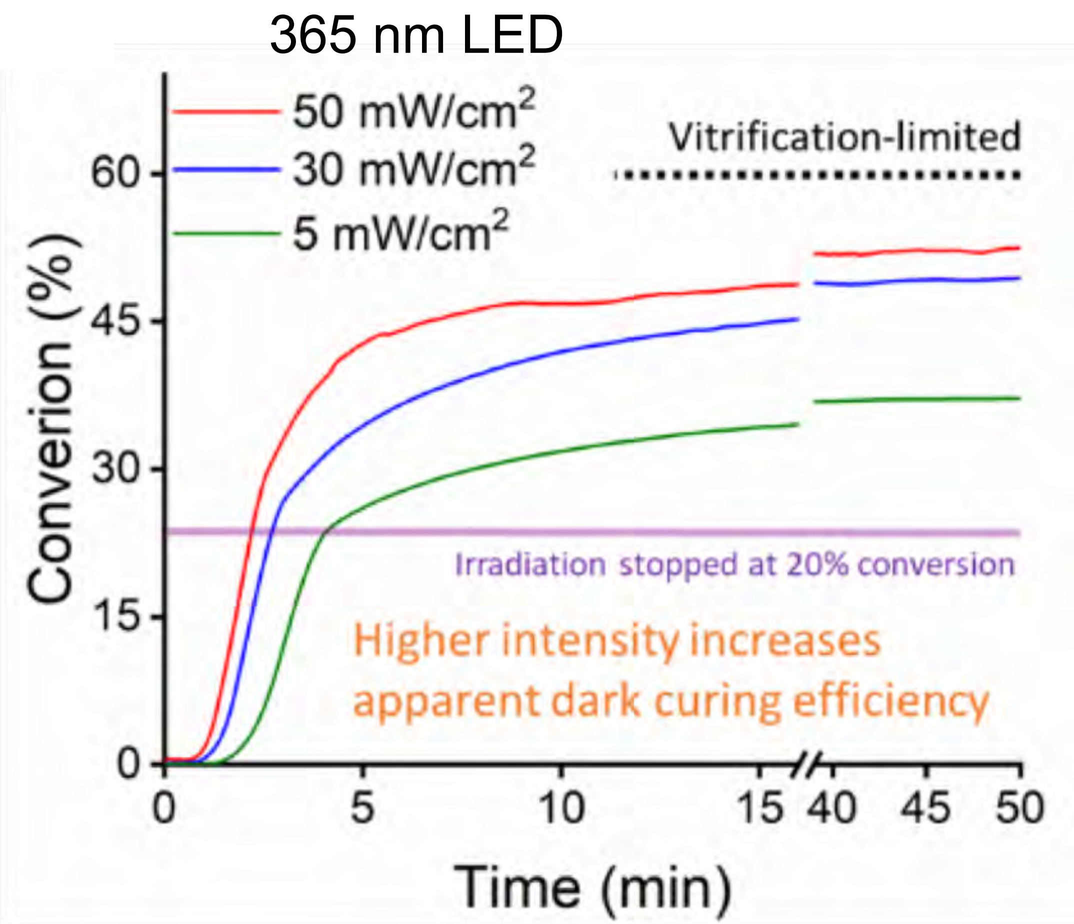
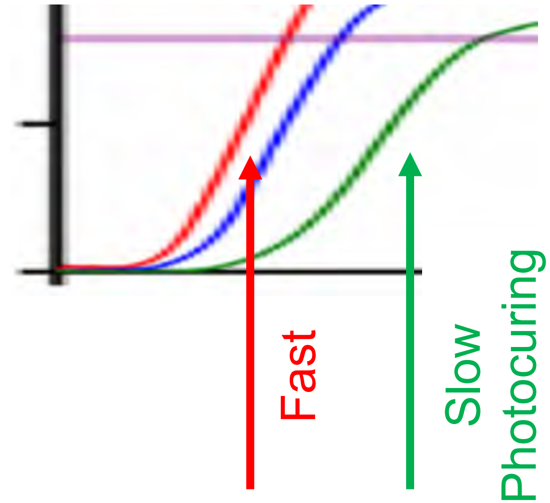
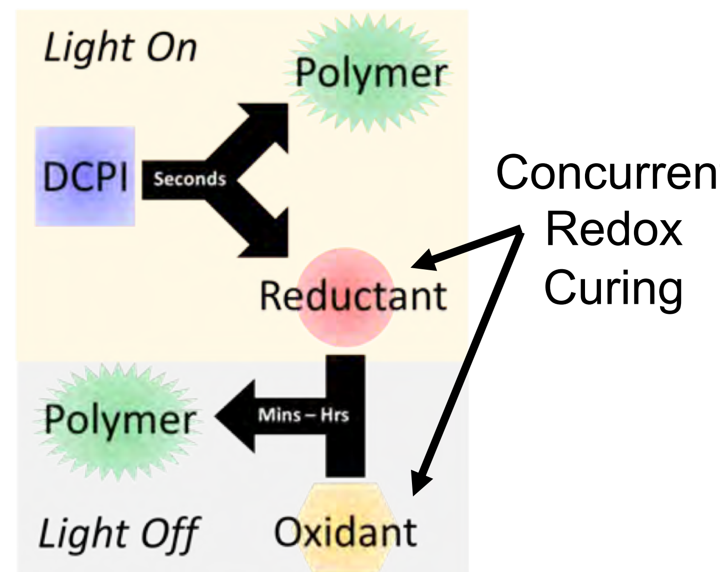
Kangmin Kim et al. Submitted, **2020**

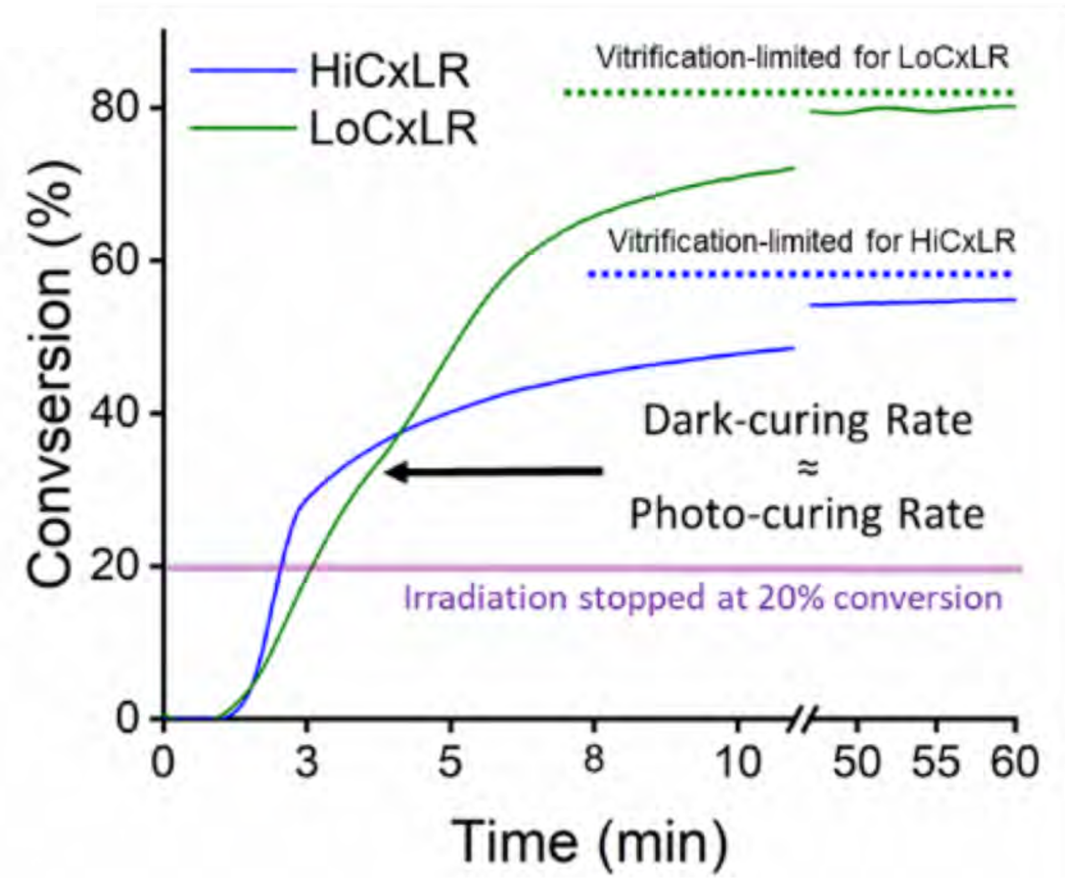
Higher Intensity = Better Dark-curing



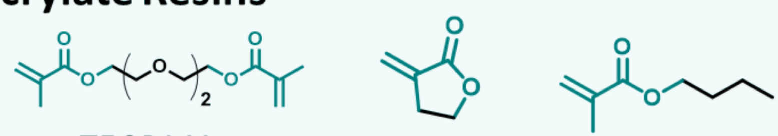




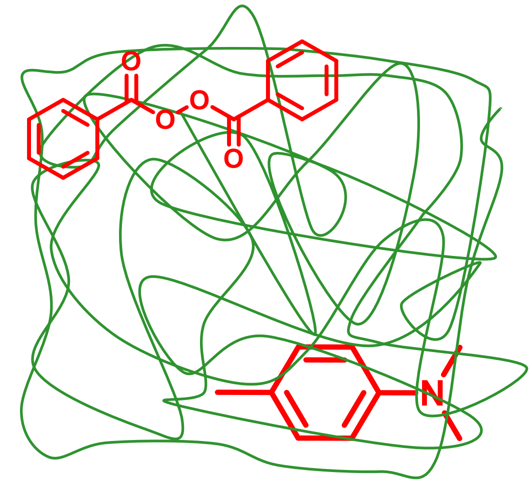
Resin Conditions Change the DCPI Results



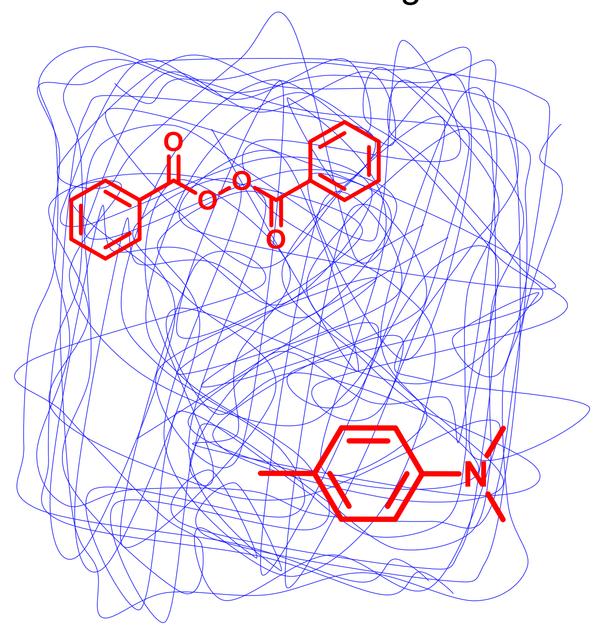
Methacrylate Resins



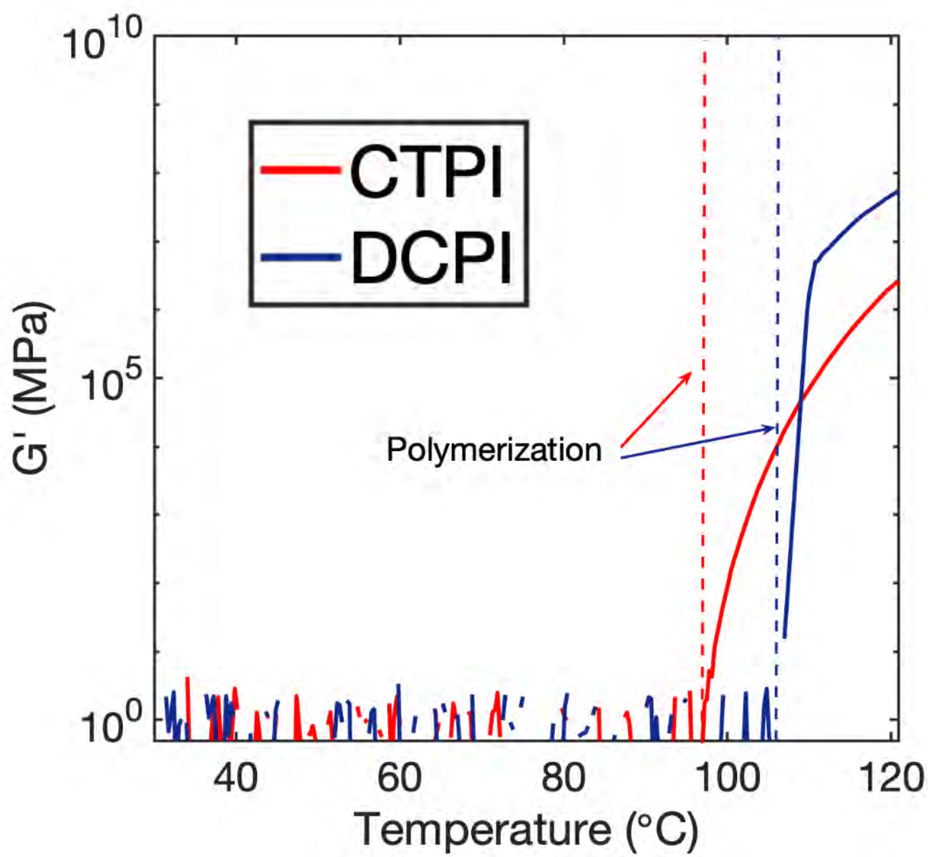
	TEGDMA	MBL	BMA
HiCxLR	90 wt% (86)	10 wt% (14)	0 wt% (0)
LoCxLR	50 wt% (48)	10 wt% (14)	40 wt% (38)



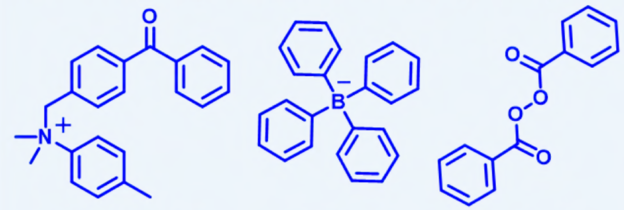
High Diffusion Rate +
High Vitrification Conversion
= Greater Dark-curing Extent



DCPI formulation is as Stable as CTPI formulation



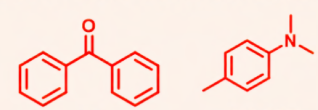
Dark-curing Photoinitiator (DCPI)



BP-DMPT$^+$ BPh$_4^-$ BPO

Benzophenone-based Photo-base generator with Amine Reductant (BP-DMPT$^+$)
Tetraphenyl Borate counterion (BPh$_4^-$)
Peroxide Oxidant (BPO)

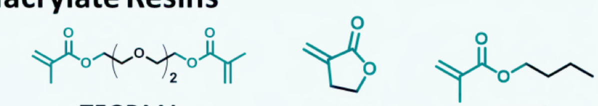
Control Photoinitiator (CTPI, Norrish Type II)



BP DMPT

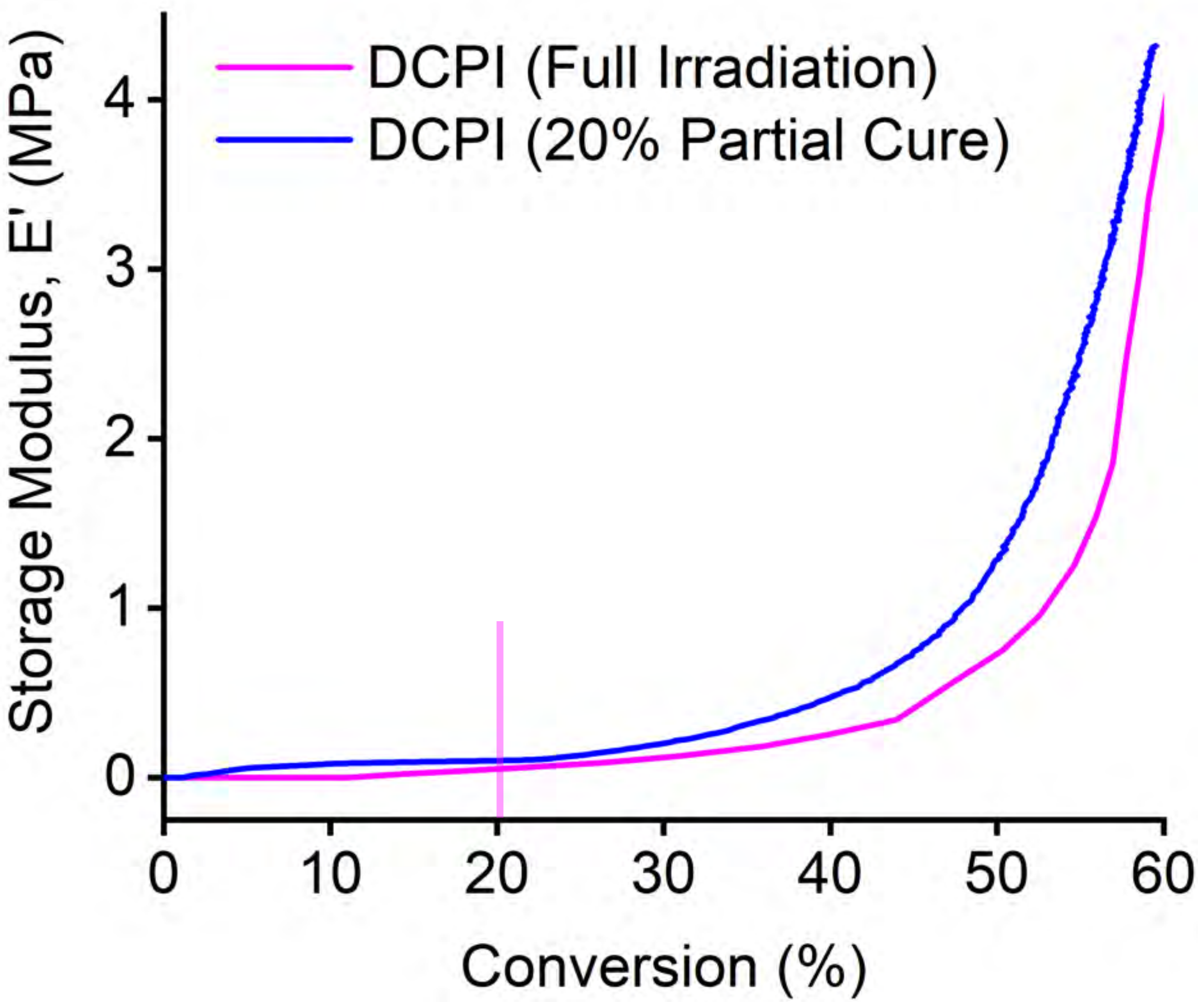
Benzophenone Sensitizer (BP)
Amine Co-initiator (DMPT)

Methacrylate Resins



	TEGDMA	MBL	BMA
HiCxLR	90 wt% (86)	10 wt% (14)	0 wt% (0)

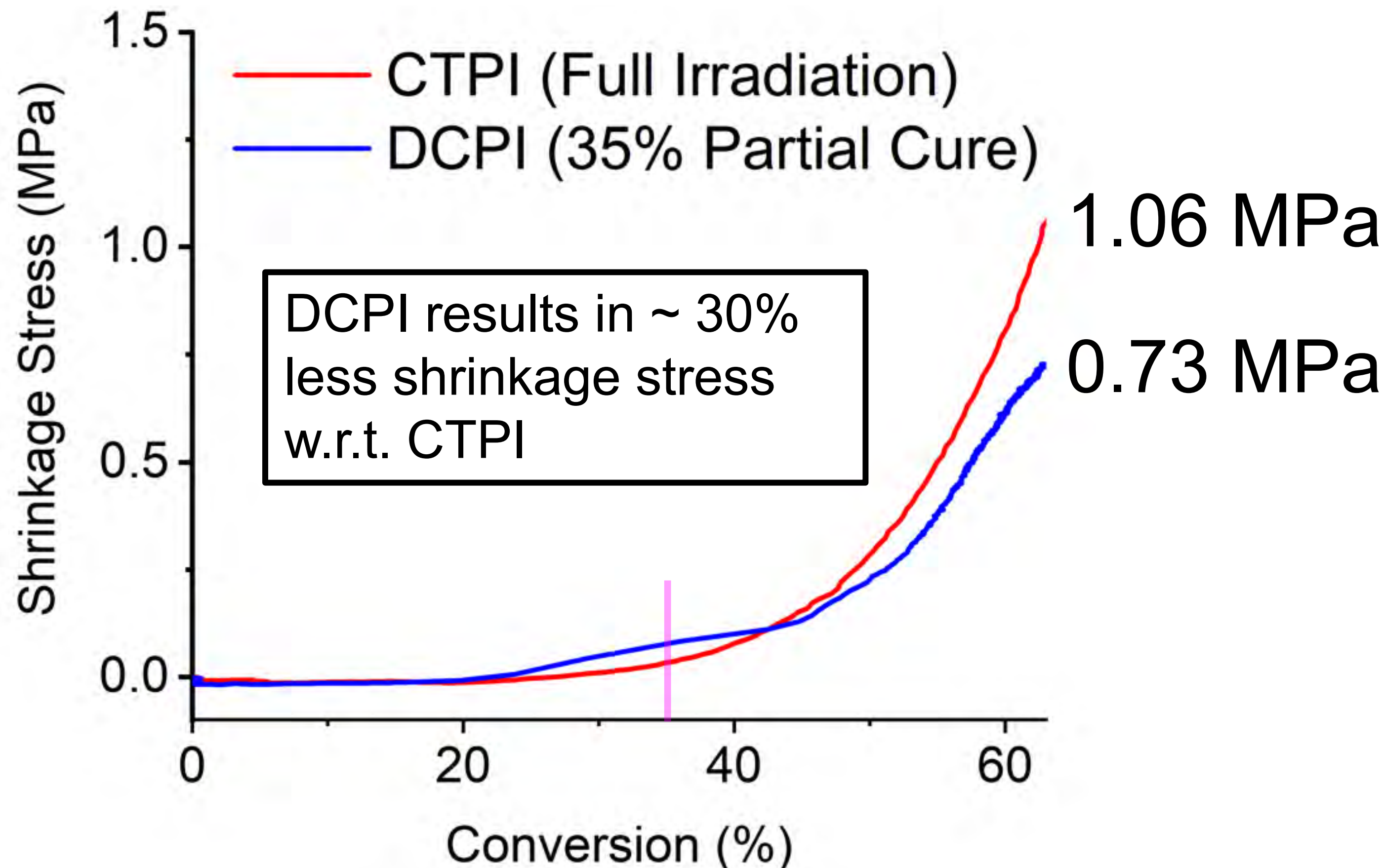
Mechanical Property of DC polymer is Robust



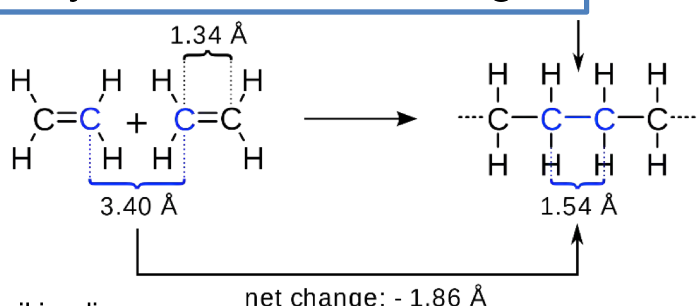
Dark-curing develops E' from 0.1 MPa at 20% to 4.3 MPa at 60%

E' of dark-cured polymer is comparable to E' of photo-cured one

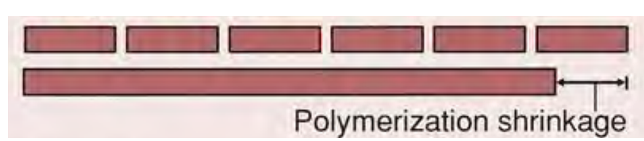
DC Polymer may even be Better (Lower Shrinkage)



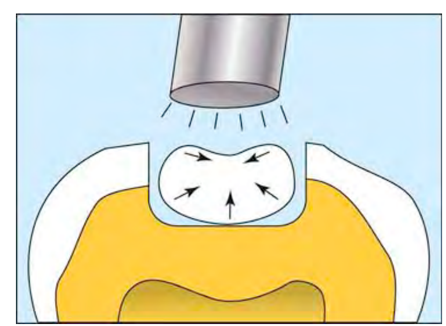
Polymerization Shrinkage



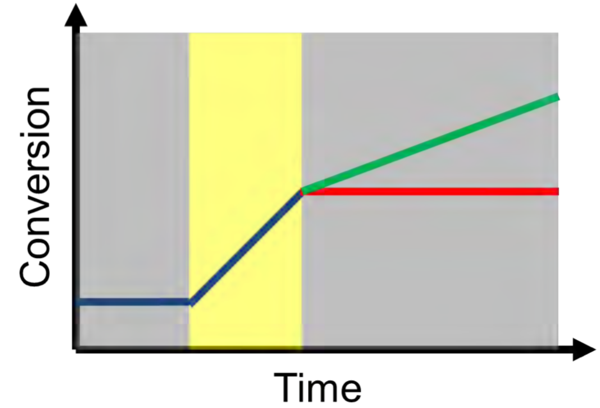
wikipedia



pocketdentistry

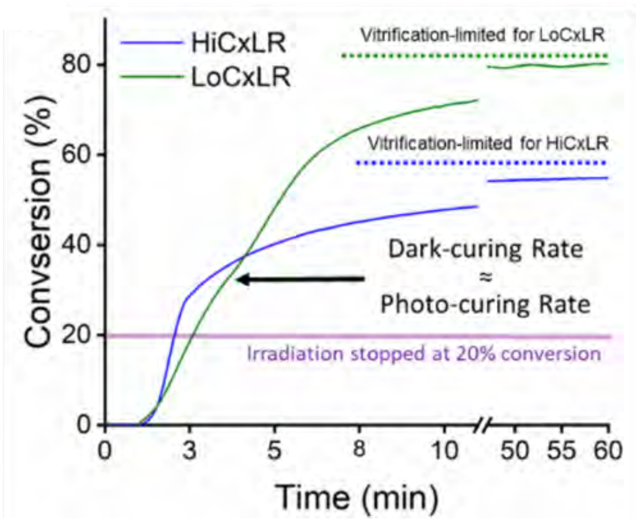


Objective: developing a photoinitiator that continues polymerization after Irradiation is interrupted

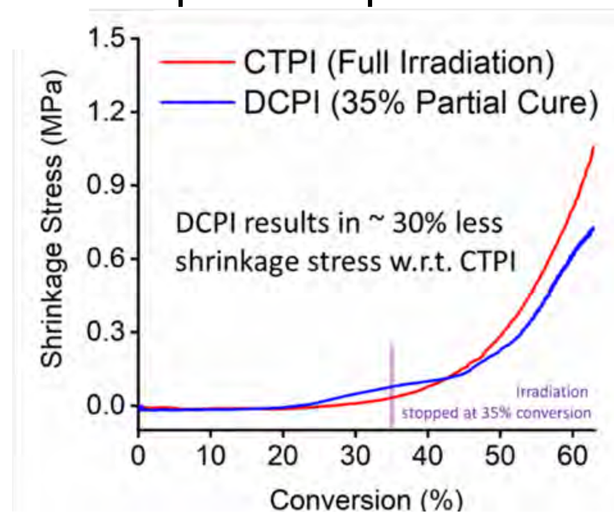


Result:

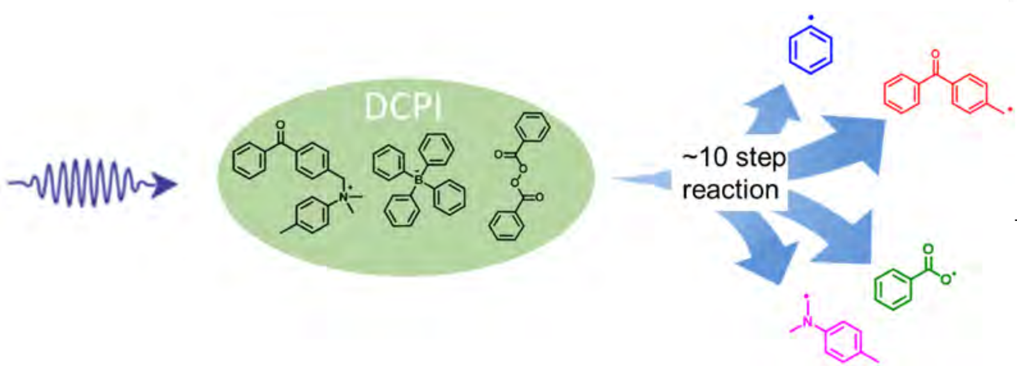
1. Additional 25-60% post-conversion is observed.



2. Dark-cured polymer is comparable/superior to photo-cured polymer

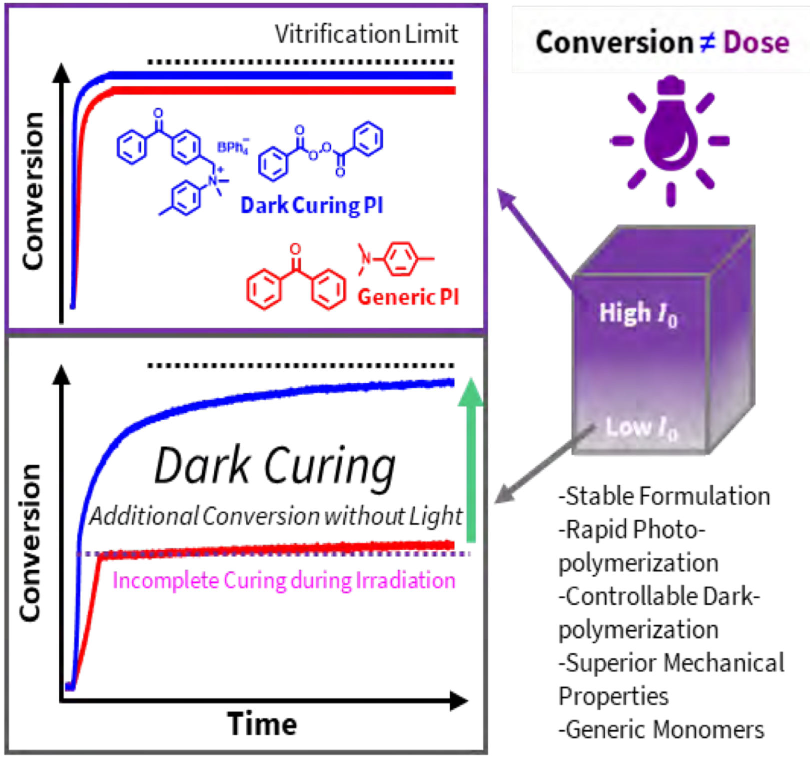


3. PI with the highest photon-efficiency to date



Complementary Presentation on Wed, PM 1:15

Paradigm-Shifting Technology: Conversion is not determined by light dose



Impacts

1. Increases the reliability of photocuring process while minimizing user errors by automatically correcting initially under-cured regions

2. Enables new applications by promoting curing of light-attenuating samples or complex geometries

3. Improves manufacturing throughput while saving energy

Complementary Presentation on Wed, PM 1:15

Thank you for listening

Questions?

Complementary Presentation
on Wed, PM 1:15

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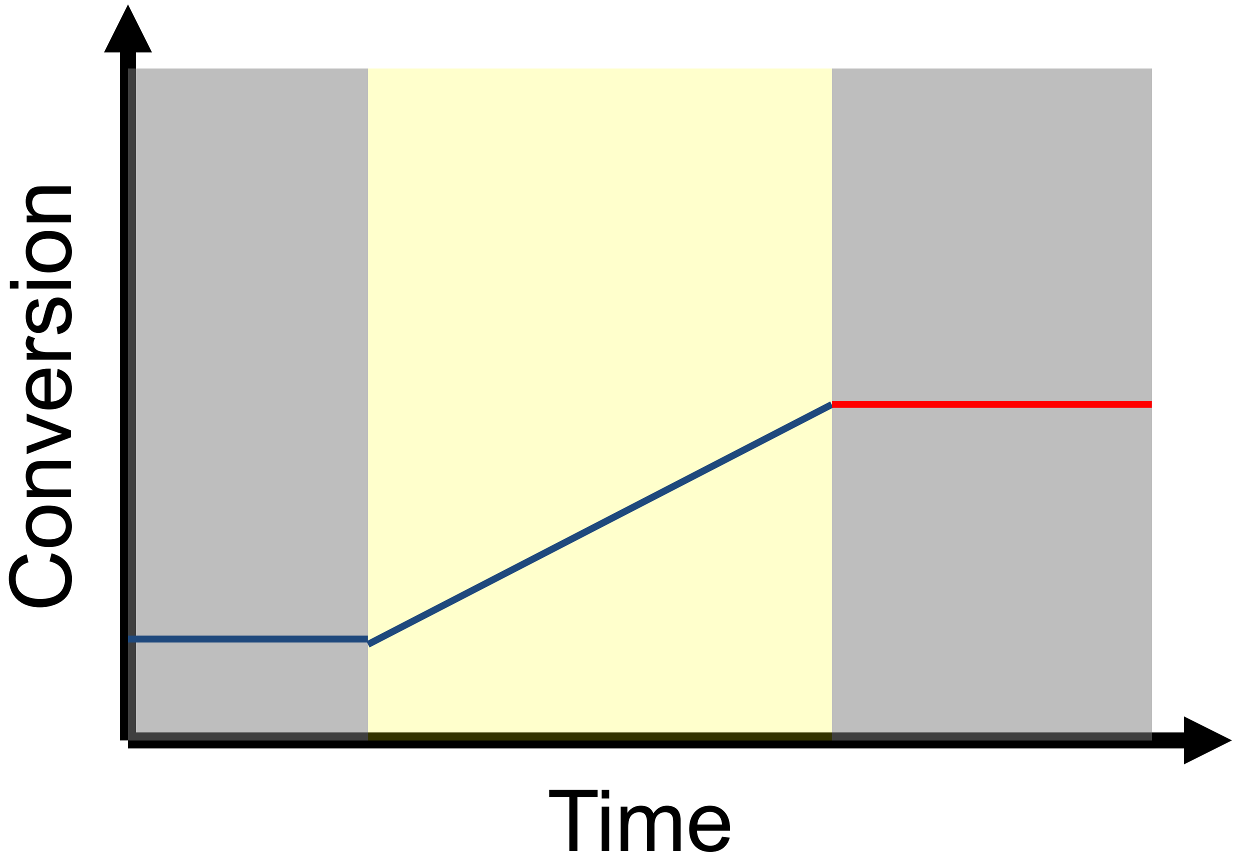
Dark-curing PI Overcomes Insufficient Exposure



Dark-curing RPI (DCPI)
Conventional RPI (CTPI)

Thermally Stable before Irradiation

Photopolymerization