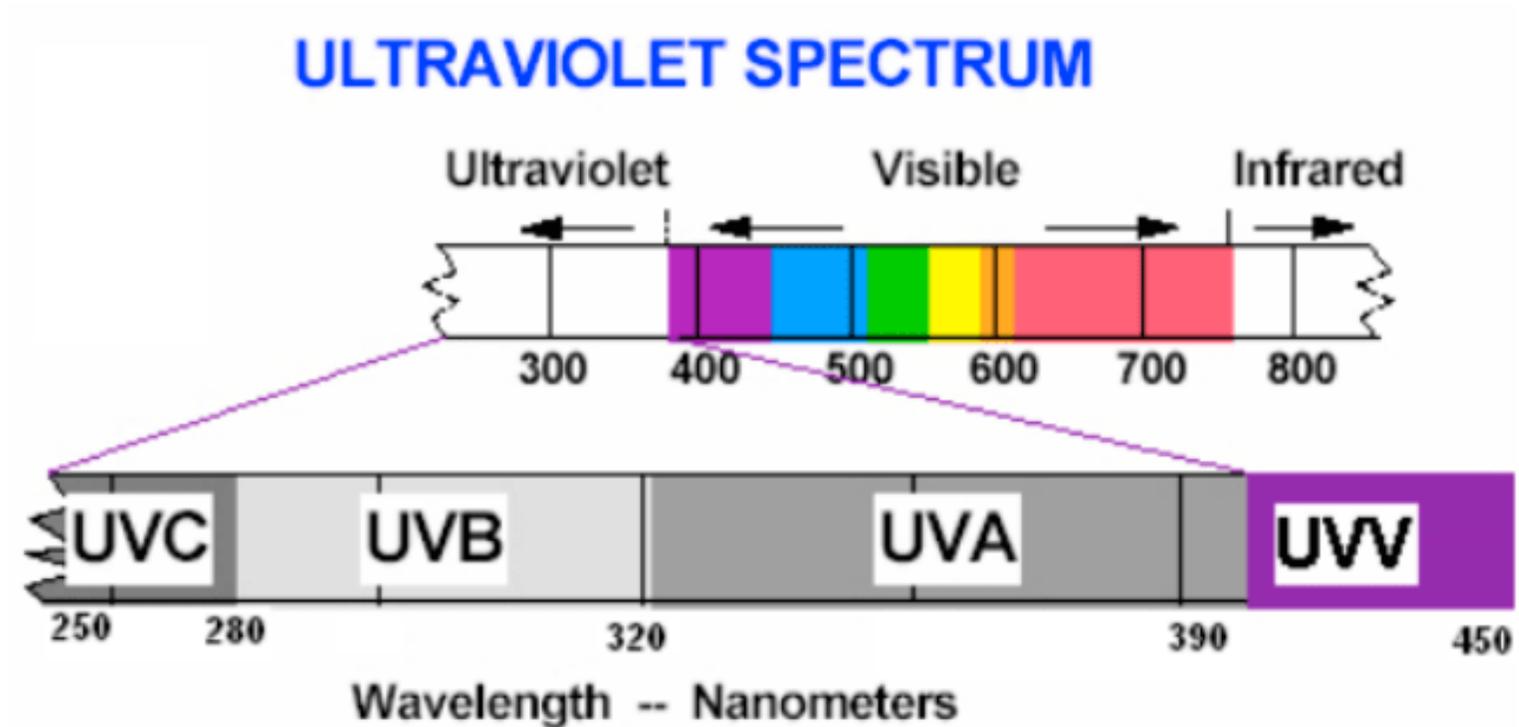




Jeremy Yatvin Ph.D.
Applications Chemist



extinction coefficient	How strongly a given molecule absorbs light at a particular wavelength
λ_{max} (pronounced "lambda max")	The wavelength at which a molecule absorbs the most energy; also known as peak absorbance
absorbance	The amount of light a material takes in as opposed to reflecting or transmitting it $A = -\log_{10}(\%T)$
polymerization	The reaction by which monomers (and oligomers) are converted to high molecular weight materials (polymers)
cure	The conversion of unreacted material to reacted material; transformation of monomers and oligomers to a polymer network; in practical terms, usually the point at which the wet material reaches a mar free state (or any other property of interest)
photons	A quantum of light; a packet of light energy
radical	AKA free radical, a molecule fragment with 1 unpaired electron. Not an ion (has no charge). Highly reactive.
homolysis	A bond cleavage event that results in two unpaired electrons



- UVC 200-280 nm
- UVB 280-320 nm
- UVA 320-400 nm
- UVV 400-450 nm

UV mercury lamps

Mercury lamps emit light corresponding to the emission spectrum of mercury or various doped mercury amalgams



Mercury,
general
purpose

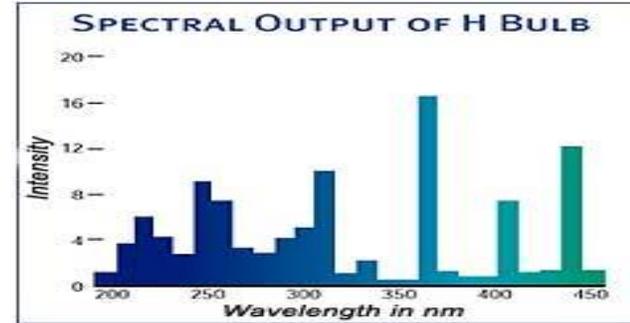


FIGURE A

Gallium doped,
UVA and V
enriched

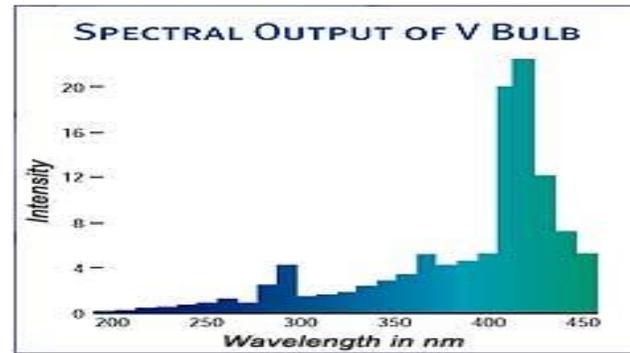


FIGURE B

Iron doped,
UVA enriched

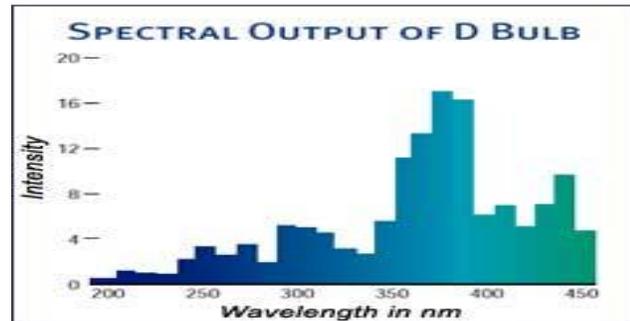
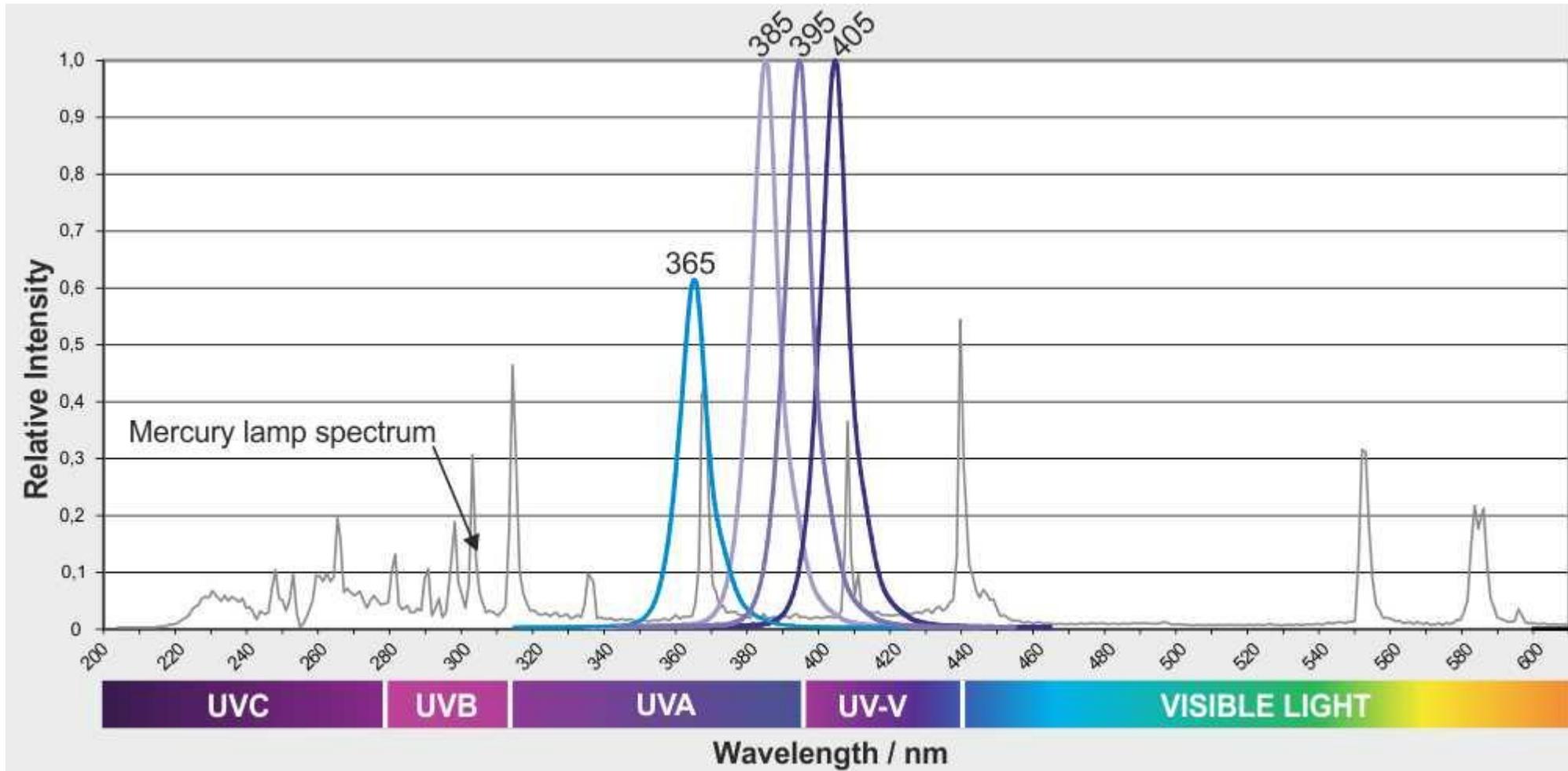


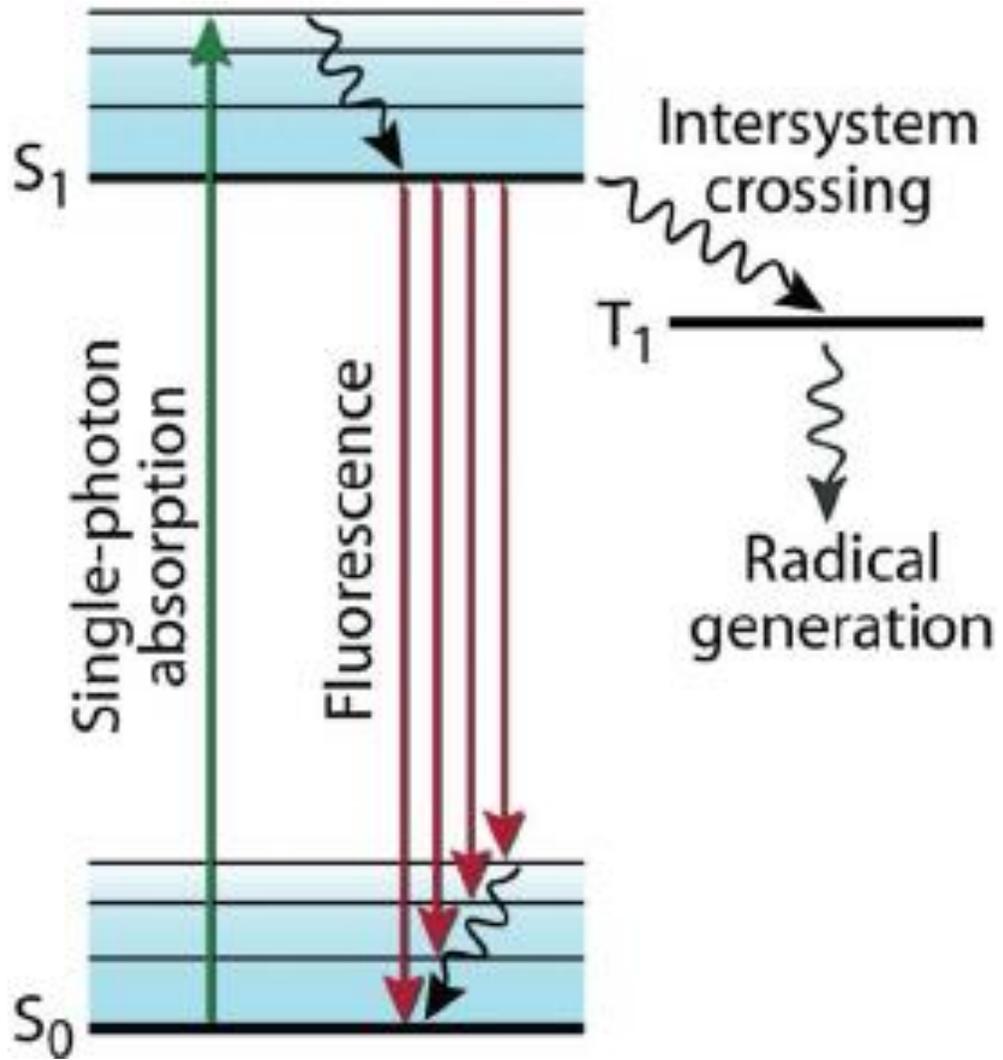
FIGURE C

UV LED lamps

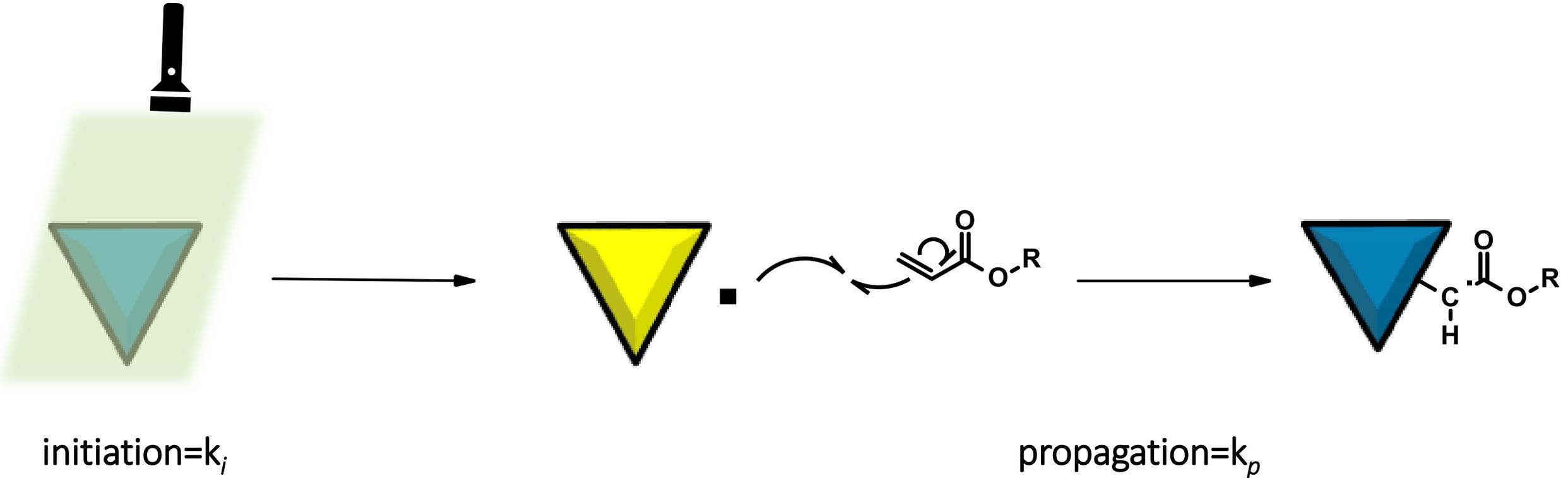


LEDs emit light associated with band gap of a semiconductor

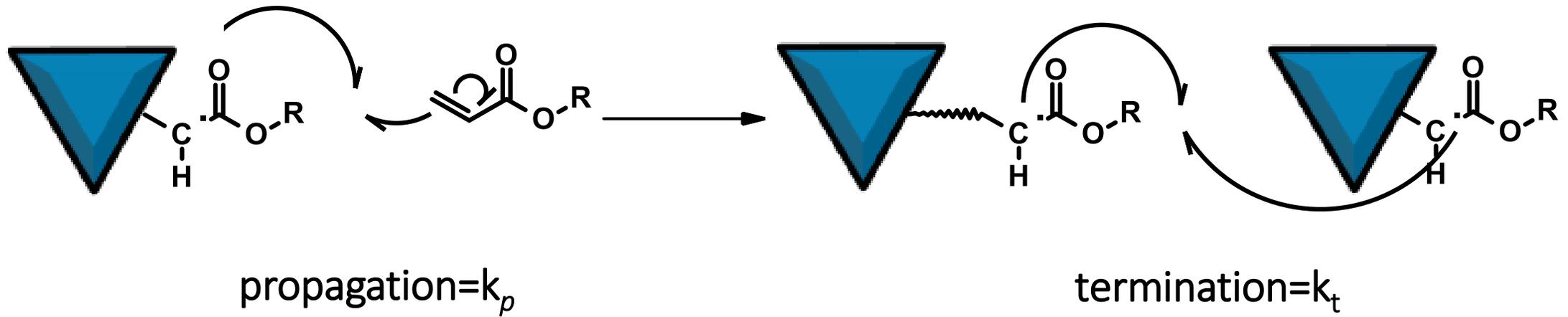
Photoinitiators



UV initiated photopolymerization



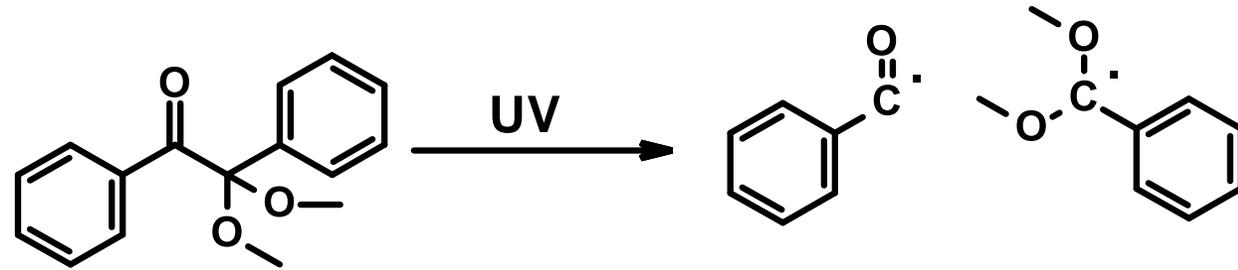
UV initiation photopolymerization



$$k_t \gg k_i \gg k_p$$

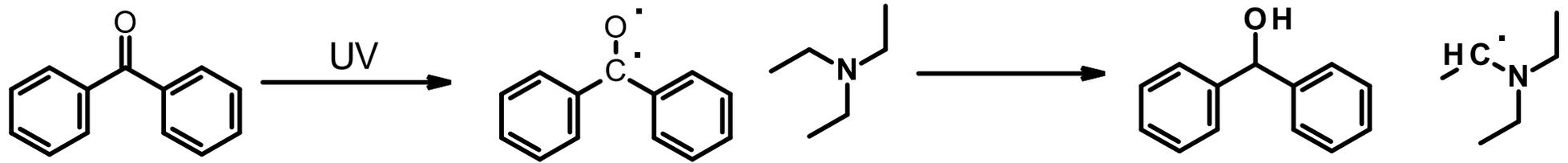
Photoinitiators

Norrish type I



monoaryl ketone

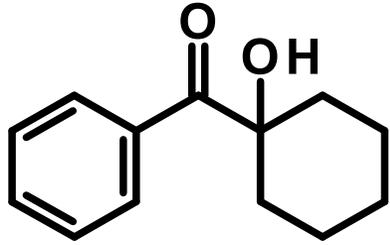
Norrish type II



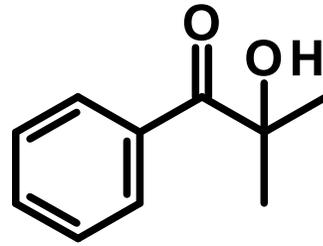
diaryl ketone

synergist

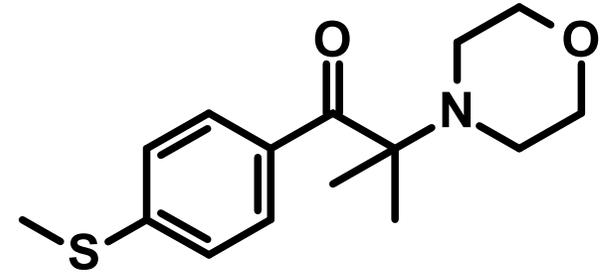
Typical type I photoinitiators



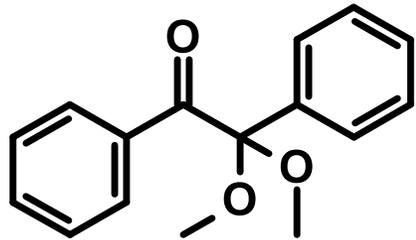
CPK



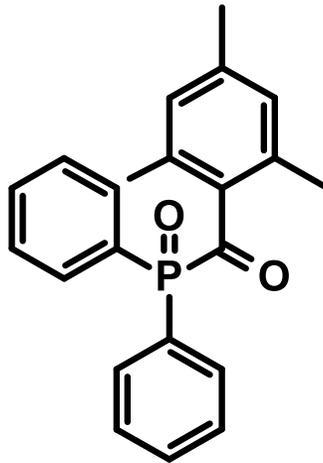
HDMAP



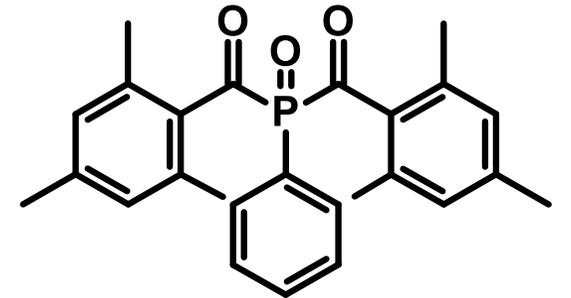
DMMTA



BKL/BDK

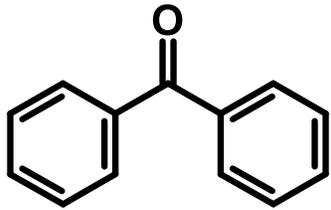


TPO

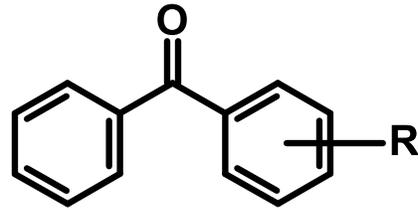


BAPO

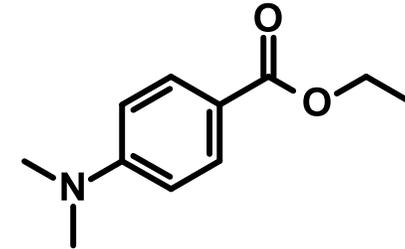
Typical type II photoinitiators and synergists



Benzophenone (BP)



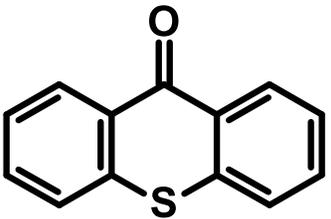
Various alkylated BPs



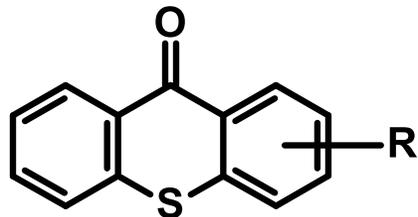
EDB



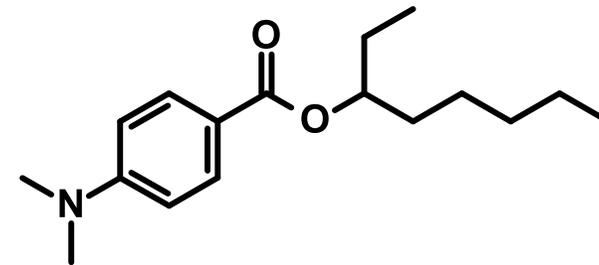
thioethers



Thioxanthone (TX)



Various alkylated TX derivatives

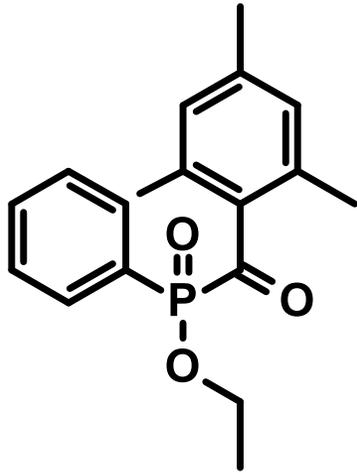


EHB

Considerations when choosing a PI

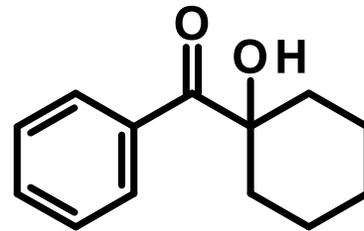
Solubility

- Solid PIs
 - BP, ITX, TPO, BAPO, CPK, BKL
- Liquid PIs
 - HDMAP, TPO-L

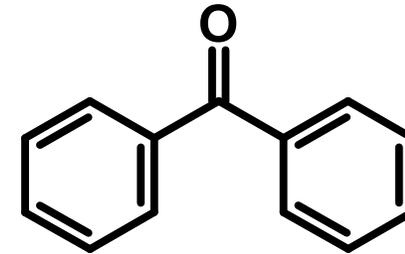


TPO-L

- Eutectic mixtures
 - Mixtures of certain solids at specific ratios can have melting points below room temp
 - BCPK is a popular eutectic
 - Combination of benzophenone and CPK



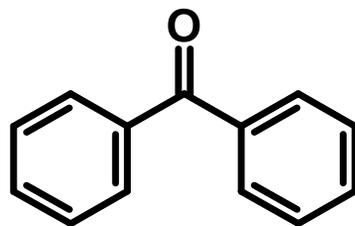
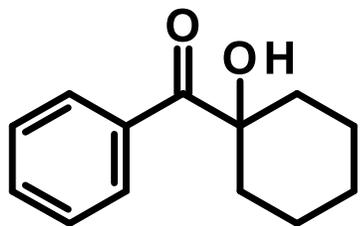
CPK



BP

Type I vs Type II

- Norrish type I
 - Single component system
 - Less robust to oxygen
 - Sometimes more expensive
 - Generally lower yellowing



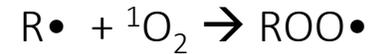
- Norrish type II
 - Require synergist tertiary amines or thioethers
 - May have smell
 - Synergists can reduce surface cure problems
 - Two component system to keep track of and adjust
 - Amines often incompatible with litho ink systems
 - Regulation of benzophenones
 - Yellowing from sideproducts
 - BP derivs usually cheap

Oxygen inhibition

O₂



Singlet oxygen inhibits radical polymerization by reacting to form peroxides



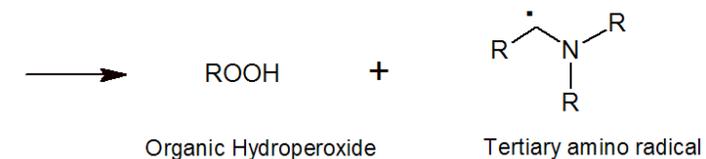
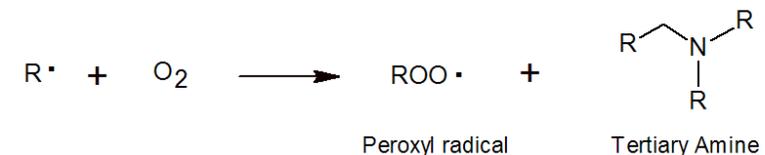
Peroxy radicals are much worse propagating species than carbon radicals

Oxygen inhibition is strongest at the surface of a material due to the kinetics of gas diffusion, so surface cure is the primary inhibition defect

Type I initiators, especially phosphines, are more subject to surface cure issues

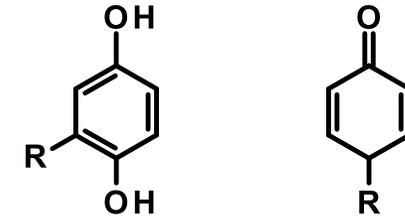
Blending in some type II systems, or just adding synergists to type I systems can help address surface cure

Initiator system is critical to addressing oxygen inhibition!

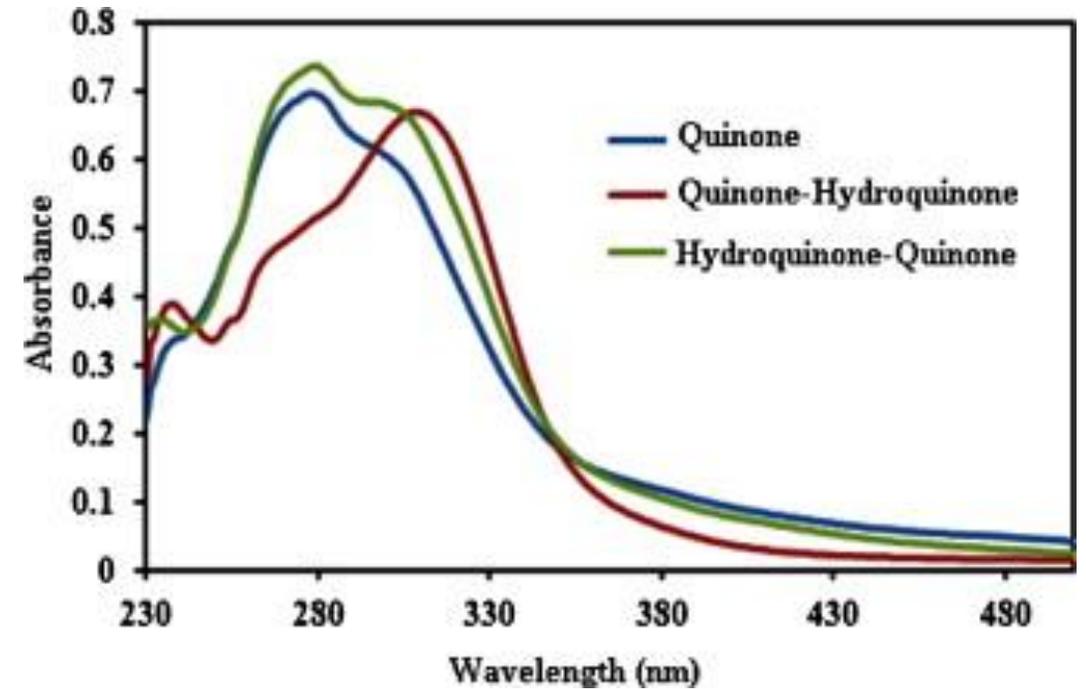
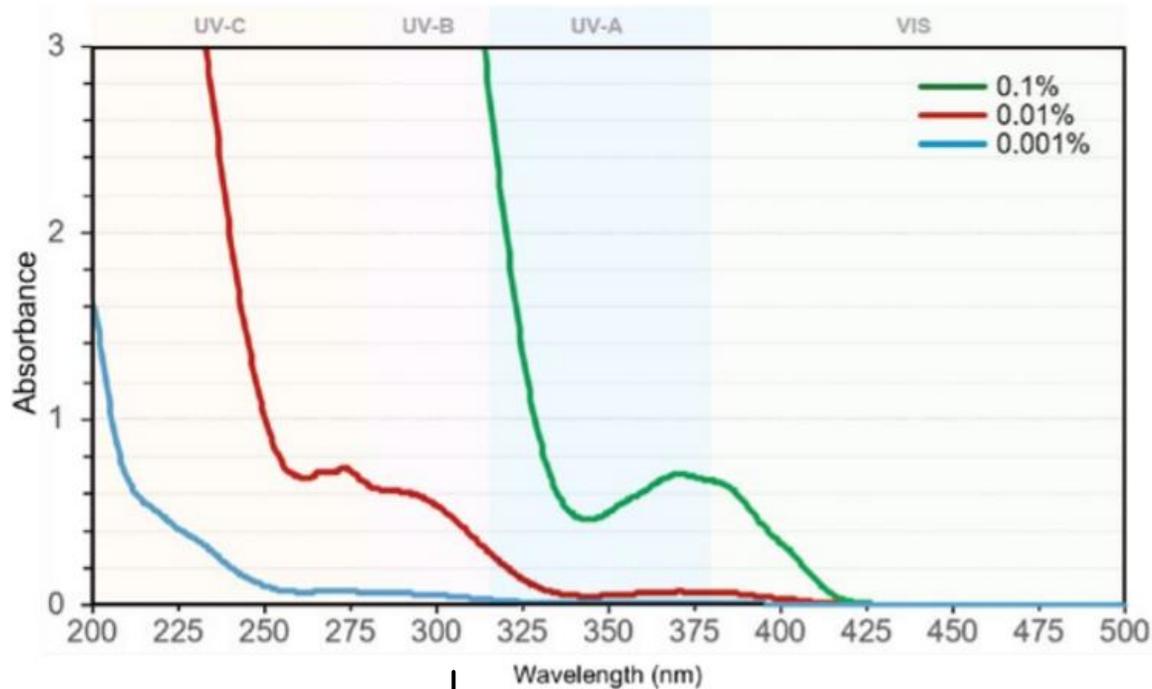


Yellowing and photobleaching

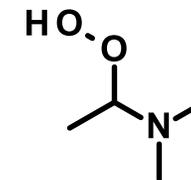
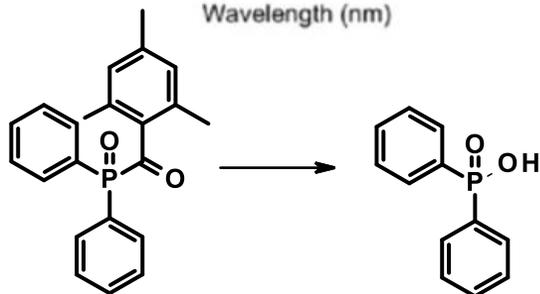
- Yellowing and photobleaching are two sides of the same coin
- During irradiation some visible products are degraded, others are created



TPO



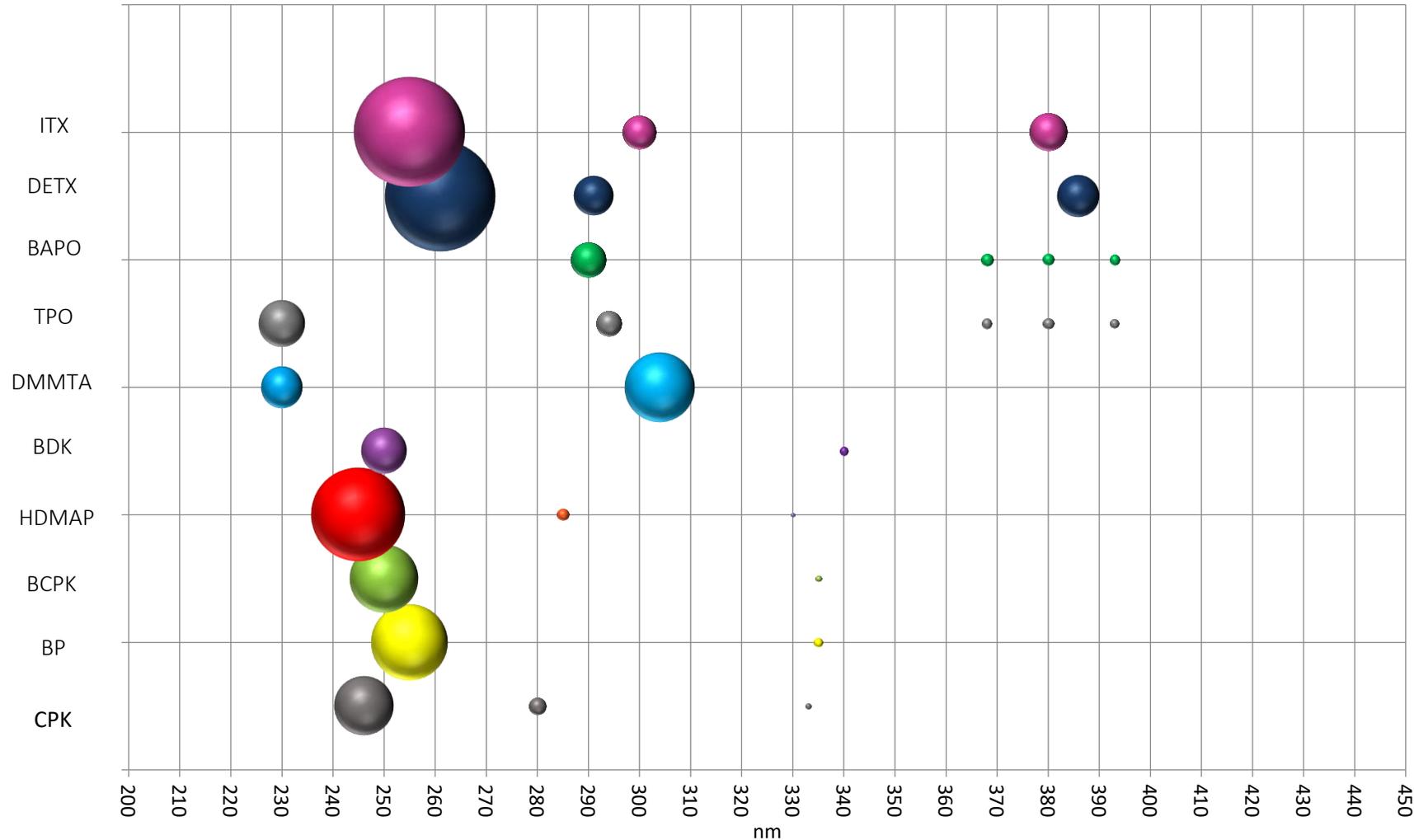
Photocleavage to noncolored



Amine peroxide oxidizing agent

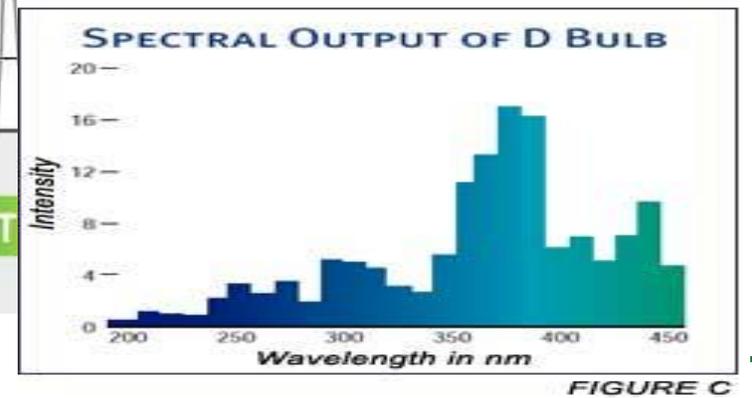
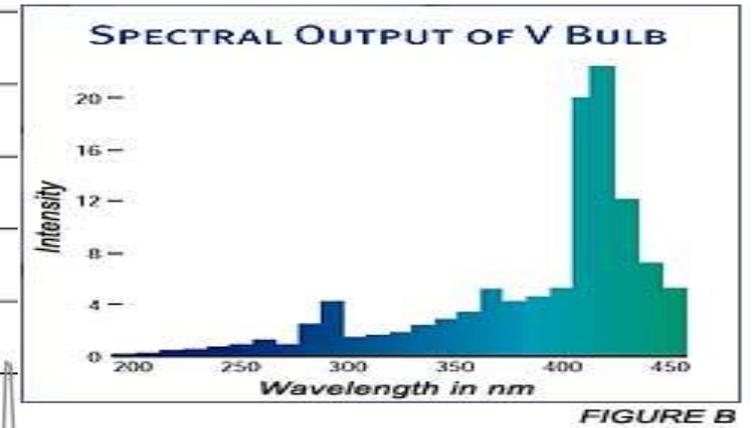
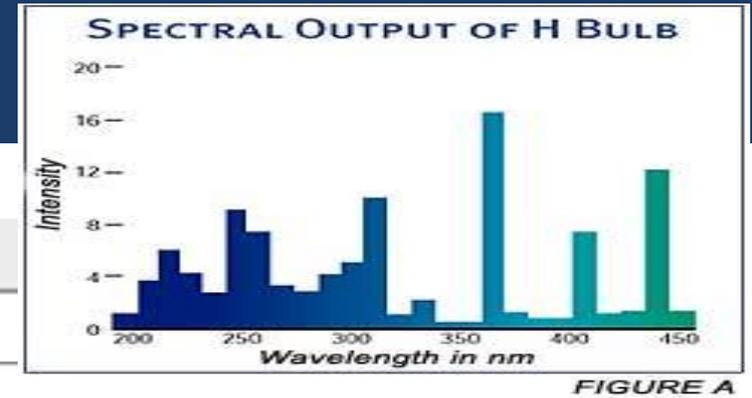
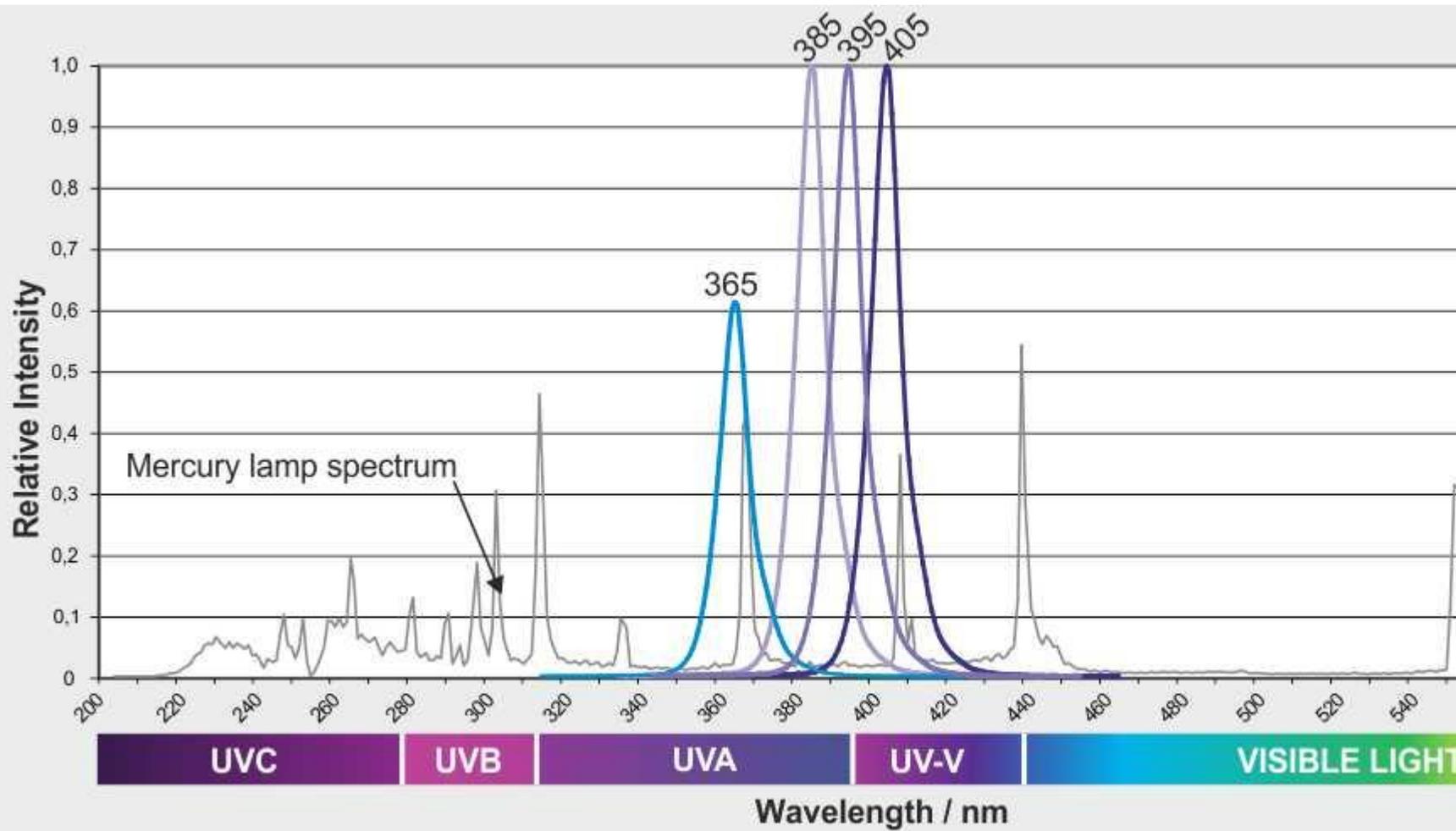
PI Absorbance Chart

Relative Extinction Coefficients @ λ_{max}

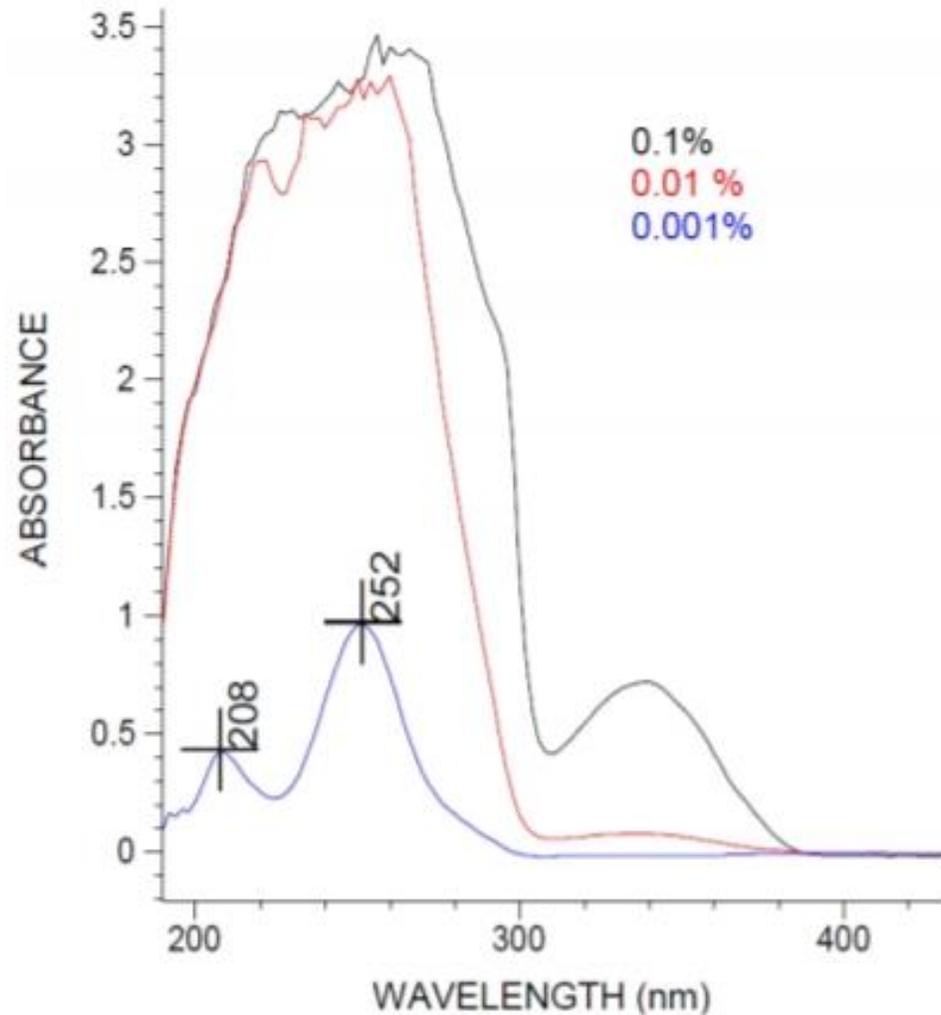


Blends can address issues like pigmentation penetration, yellowing, and spectral output matching

UV light sources



ABSORPTION SPECTRUM



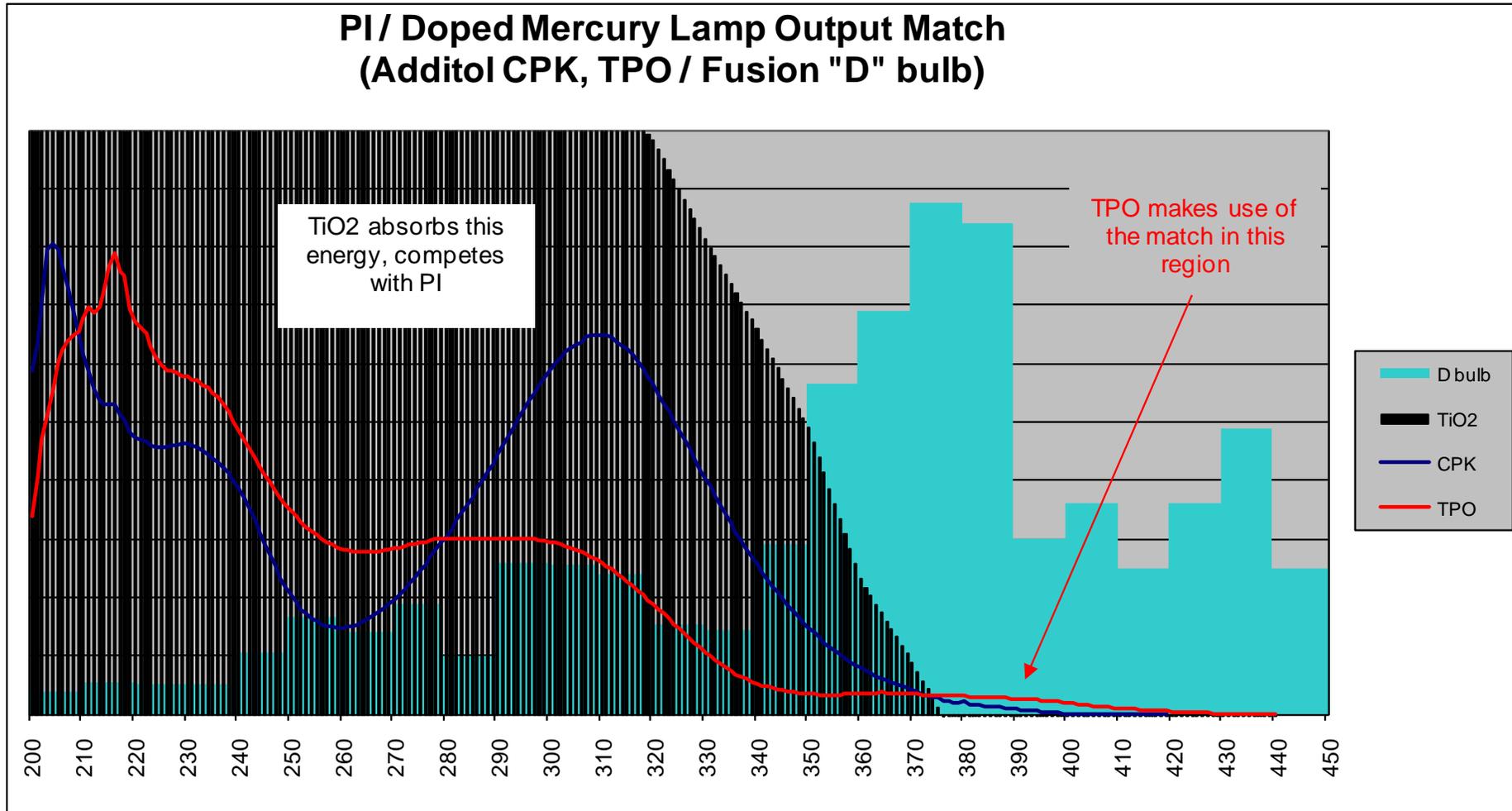
Lamp choice

Best: mercury H lamp

Possibly usable: LED 365 nm
or mercury D lamps

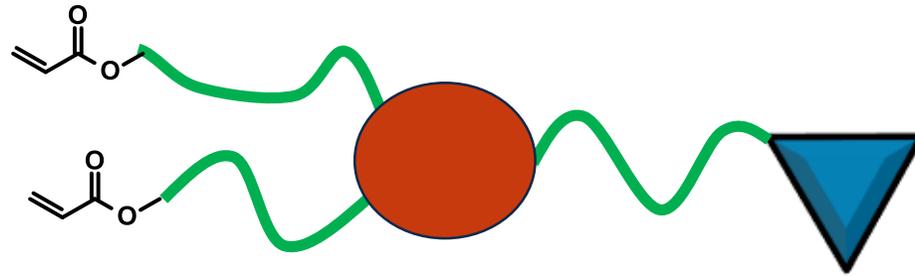
Not a direct correlation
between extinction coefficient
at a given wavelength and
photo-efficiency, but you need
something!

TPO in TiO₂ containing formulation



allnex self-curing resins

- Self curing resins are technologies to address the low migration draw from the market
- A self curing resin is a material which incorporates both a photoinitiator and polymerizable groups and is of moderate molecular weight



- The oligomeric nature of the resin prevents it from leeching out of a crosslinked polymer matrix in food, health, or eco-sensitive applications

Product	Viscosity (cP)	MW	Features
LEO 10101	4000	~1000	Hg cure, included amine synergist, GMP
LEO 10103	6000	~1000	Hg cure, synergist required, but gives freedom-to-formulate (esp in inks), GMP

10-20%
inclusion

THANK YOU FOR YOUR ATTENTION!

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Application Chemist



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