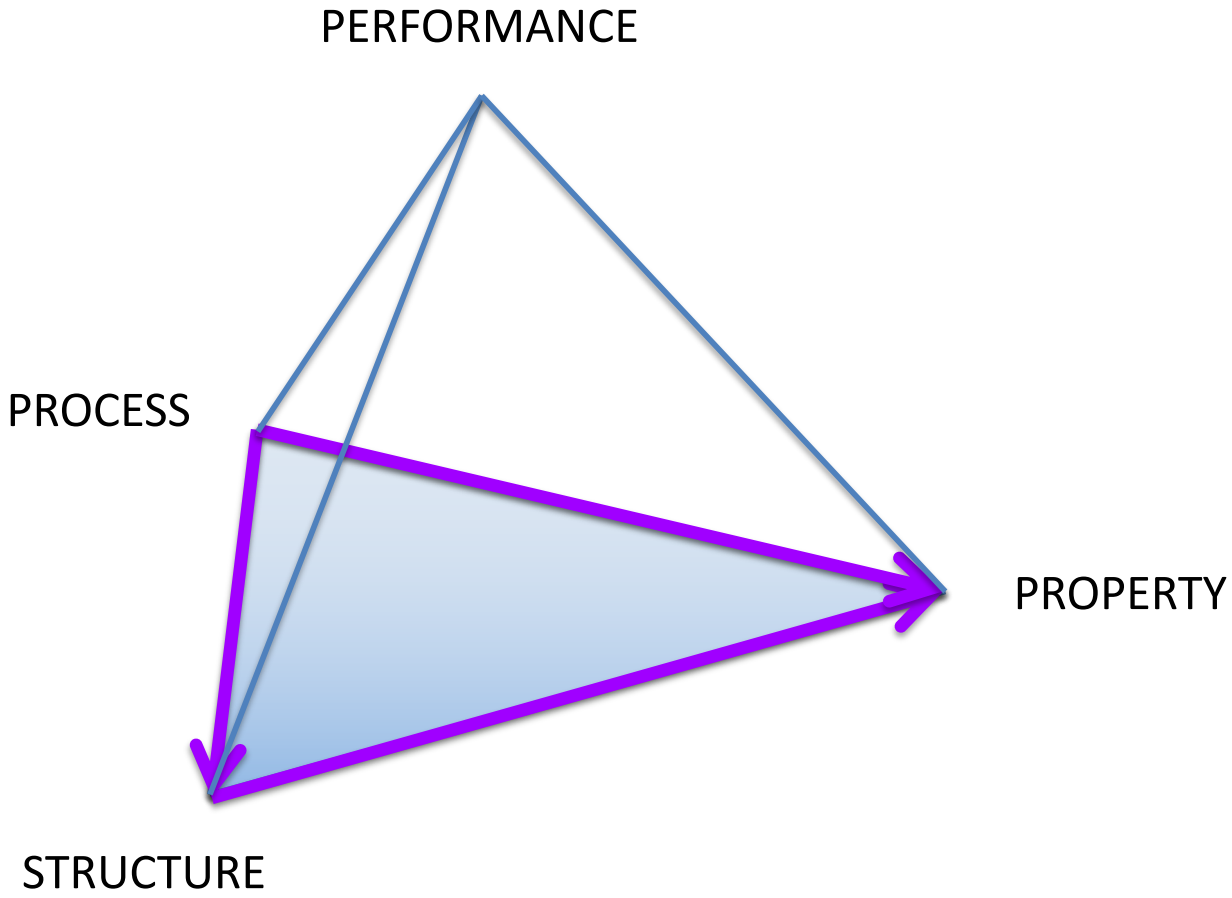
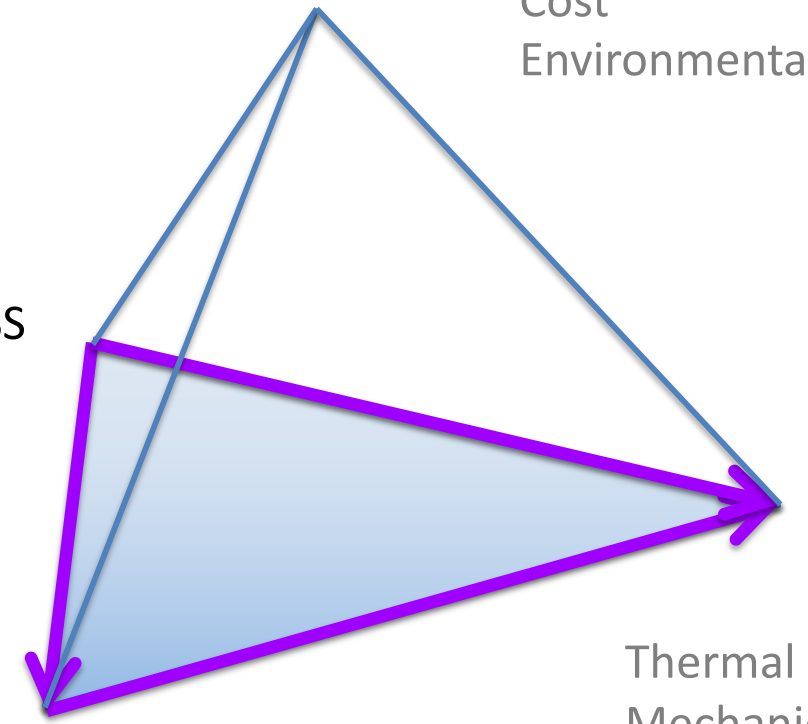
PROCESS–STRUCTURE–PROPERTY RELATIONS


PERFORMANCE
PROCESS
PROPERTY
STRUCTURE

PERFORMANCE

Durability
Cost
Environmental impact



Light energy
Light dose
[PI]
Temperature
O2, H2O

PROCESS

PROPERTY

Thermal properties (Tg, CTE)
Mechanical properties (hardness, adhesion)
Optical properties (transparency)
Dimension (thickness, pattern)

STRUCTURE

Conversion state
Gelation
Vitrification

ULTRAVIOLET

Name	Abbreviation	Wavelength range [nm]	Energy per photon [eV]	Notes/alternative names
Ultraviolet	UV	400 – 100	3.10 – 12.4	
Ultraviolet A	UVA	400 – 315	3.10 – 3.94	long wave, black light
Ultraviolet B	UVB	315 – 280	3.94 – 4.43	medium wave
Ultraviolet C	UVC	280 – 100	4.43 – 12.4	short wave, germicidal
Near Ultraviolet	NUV	400 – 300	3.10 – 4.13	visible to birds, insects and fish
Middle Ultraviolet	MUV	300 – 200	4.13 – 6.20	
Far Ultraviolet	FUV	200 – 122	6.20 – 10.16	
Hydrogen Lyman-alpha	H Lyman-α	122 – 121	10.16– 10.25	
Extreme Ultraviolet	EUV	121 – 10	10.25 – 124	
Vacuum Ultraviolet	VUV	200 – 10	6.20 – 124	

[Source: ISO 21348 Process for Determining Solar Irradiances]

$$E = \frac{hc}{\lambda}$$

E Photon energy
λ wavelength
c speed of light in vacuum (299,792,458 m/s)
h Plank constant (6.6261×10^{-34} J s = 4.1356×10^{-15} eV s)

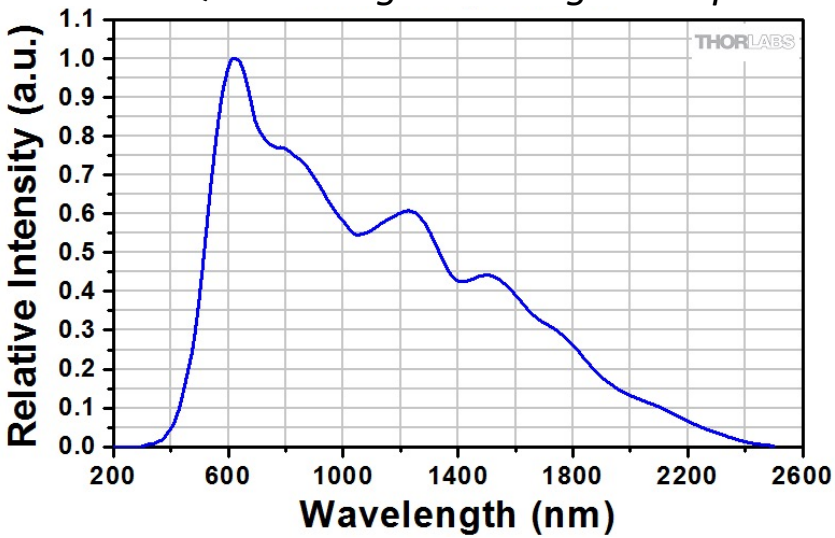
Edison lightbulb
October 22, 1879
lasted 13.5 hours

HALOGEN LAMPS

Incandescent light bulb consisting of a tungsten filament surrounded by halogen gases.

Work at wavelengths between 400 and 500 nm (*in fact the lamps emit white light, so to produce the blue light required for curing, unwanted portions of the spectrum are filtered out. Because the light spectrum of the lamp is limited only by filter, all possible portions of the spectrum are available if required*).

Quartz tungsten halogen lamp



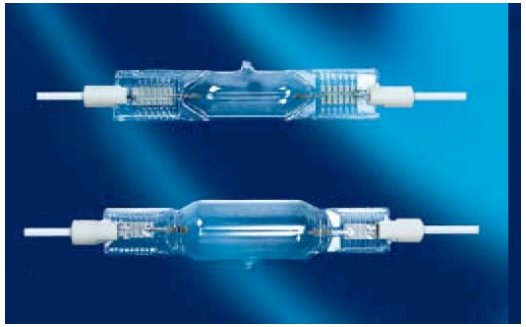
Drawbacks:

- low energy performance
- wastes a great deal of radiation since use of the filter
- generation of high temperatures
- loss of lamp power
- needs for a filter and a ventilating fan
- requires considerable maintenance

ARC LIGHT

Clear fused quartz tubing in which a halogen gas is enclosed. When a direct current is applied through two electrodes to generate an arc, the gas is discharged and light is emitted. The output of the lamp depends on the pressure and type of gas used. The most common gases are Hg and Xe.

- 370 and 450 nm (low spectrum)
- 430 and 500 nm (high spectrum)
- ‘Low pressure’ (< 1 bar): fluorescent lamps
- ‘Medium pressure’ (~ 1 bar)
- ‘High pressure’ (1 bar – 10 kbar): Hg lamps

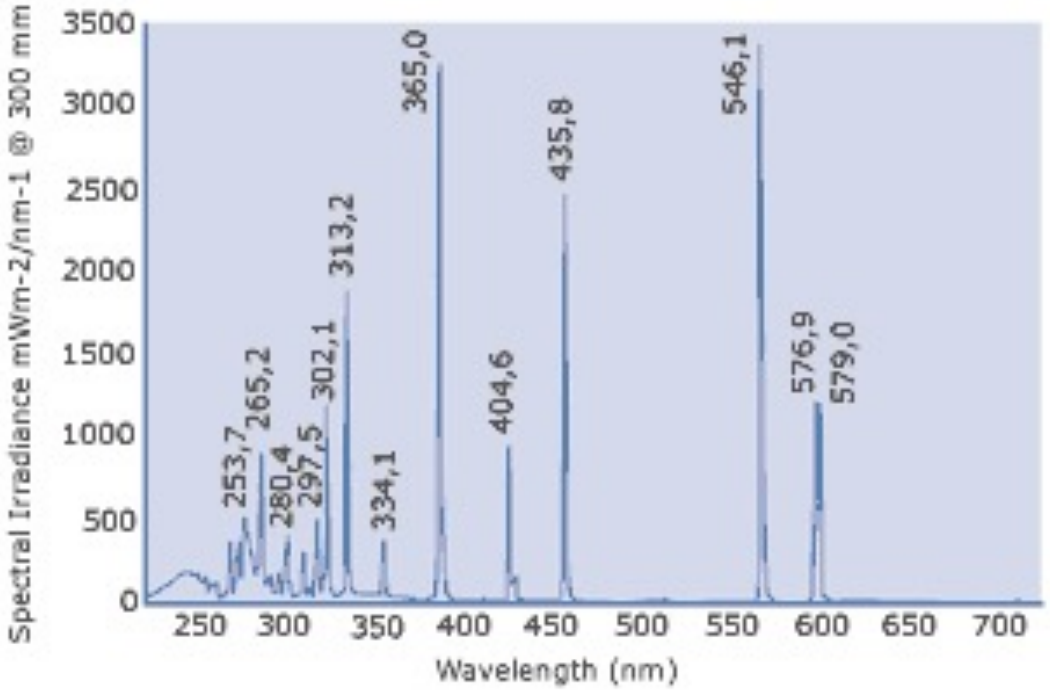


The disatvantages of plasma arc-light are:

- low energy performance
- operate at high temperature
- need filters and ventilating fan
- high cost

ARC LIGHT

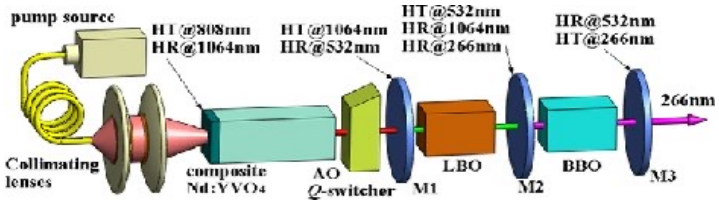
HPK 125W Mercury Lamps from Heraeus Noblelight

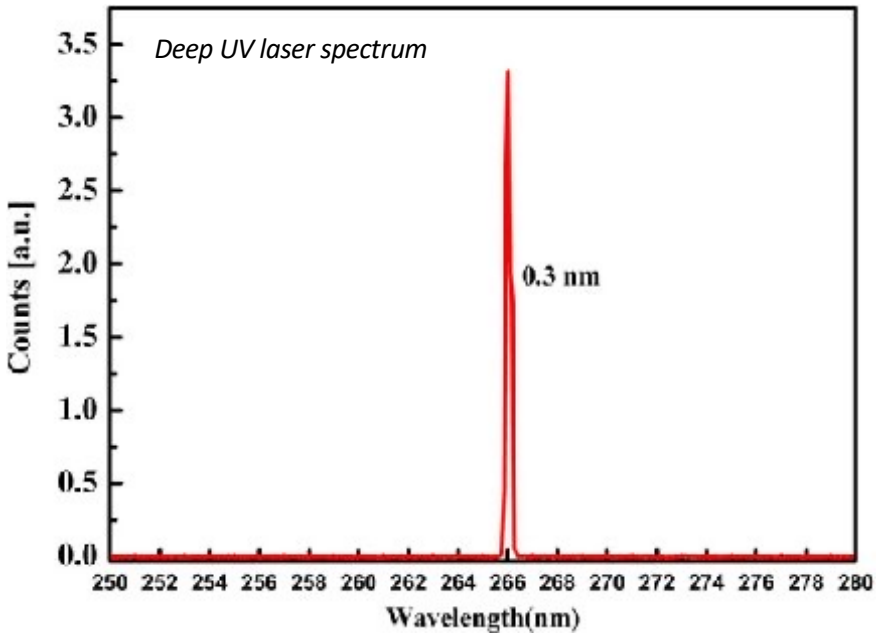


LASER

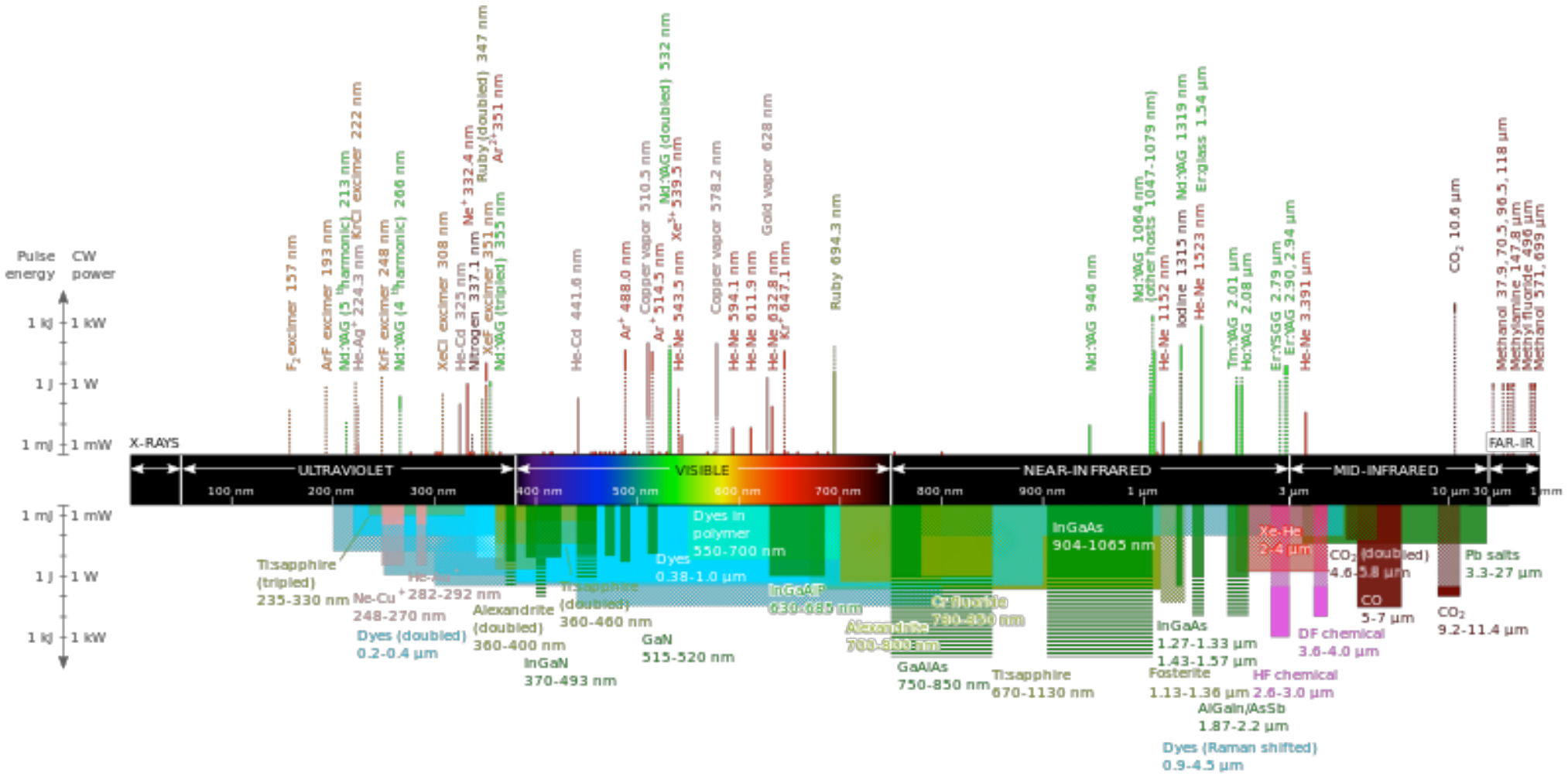
Lasers offer the prospect of an excitation source of exceeding high intensity compared to classical light sources. Their output is available in both UV and visible wavelengths.

This light is produced by stimulation of excited atoms, which, to stabilize, tend to release energy in the form of electromagnetic radiation. They do so at a wavelength that will depend on the material used (e.g. argon produces blue light). These high-intensity lamps work over a very limited range of wavelengths and do not require filters; however, they are very expensive.





LASER



Weber, Marvin J. Handbook of laser wavelengths, CRC Press, 1999

LIGHT EMITTING DIODES

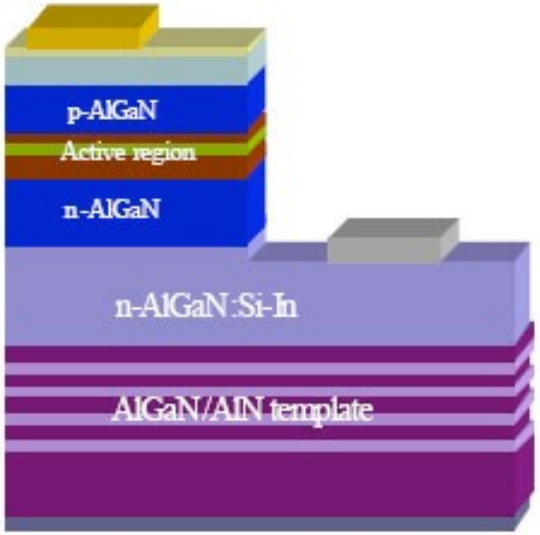
LED lamps comprise 2 semiconductor crystals, one type “n” and the other type “p,” each having a different electron density. When an electrical current passes through these crystals, energy produced at the “np” junction is released in the form of light at a wavelength determined by the crystals used. Light is thus emitted at a specific wavelength, and no filters are required; however, the formation mechanism is limited.

- offer high-energy performance, since all emitted light is useful
- do not generate high temperatures
- do not require filters or ventilating fans
- ensure constant effectiveness, with no drop-off in intensity and a long life

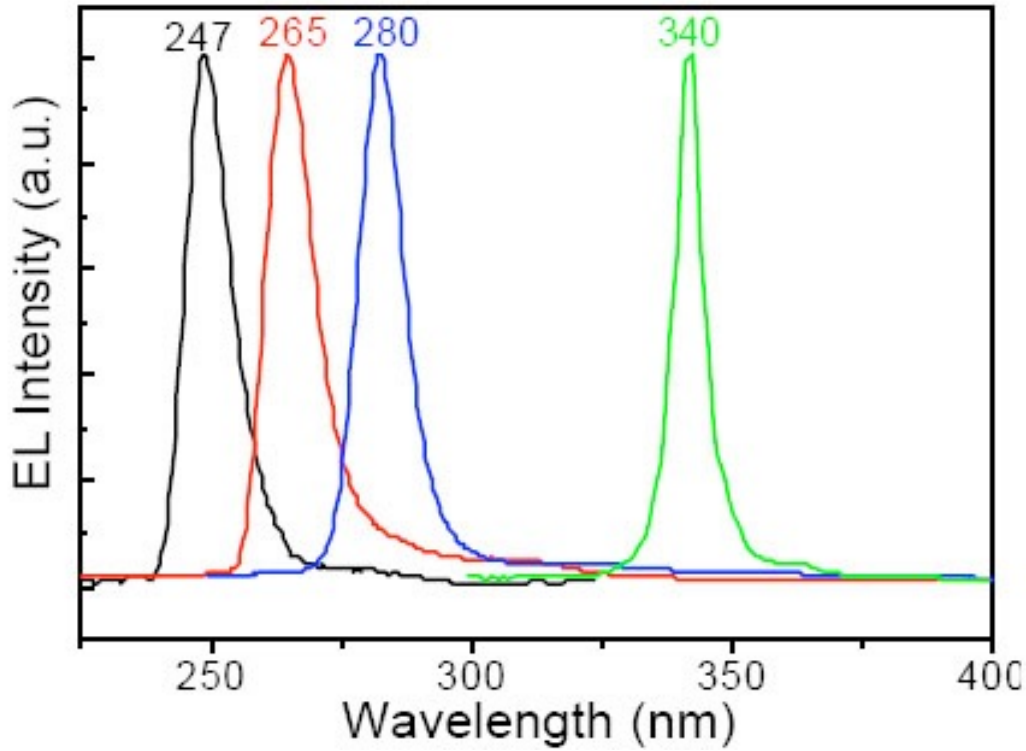
LIGHT EMITTING DIODES

Semiconductor materials:

Diamond (235 nm)
Boron nitride (215 nm)
Aluminium nitride (AlN) (210 nm)
…



Courtesy Center for Quantum Devices, Northwestern U



ACCESSORIES

(liquid) light guide

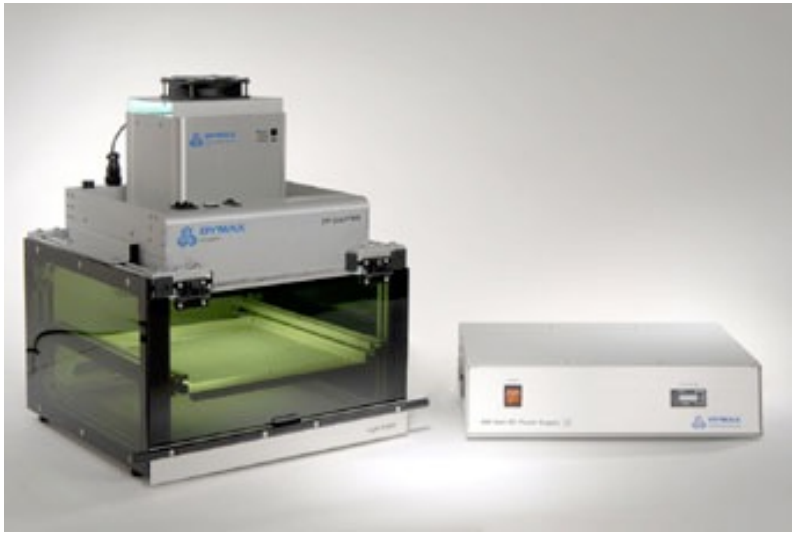
filters

lightmeter

collimator

ARRANGEMENT

Static arrangement. The cured material is placed in an exposure frame and then exposed to UV irradiation of the appropriate wavelength and intensity in a fixed geometrical position. The exposure time is varied to ensure the substance receives sufficient energy to cause a successful cure.



Dynamic arrangement. It is usually carried out with conveyor-type systems using tubular UV lamps. In a typical industrial photocuring device a web or chain type conveyor travels in the direction of the UV lamps. A system of mirrors is provided from all sides of a web or under the conveyor chain so that a product or small object subjected to photocuring is cured without rotating a part.

ILLUMINATION FACTORS

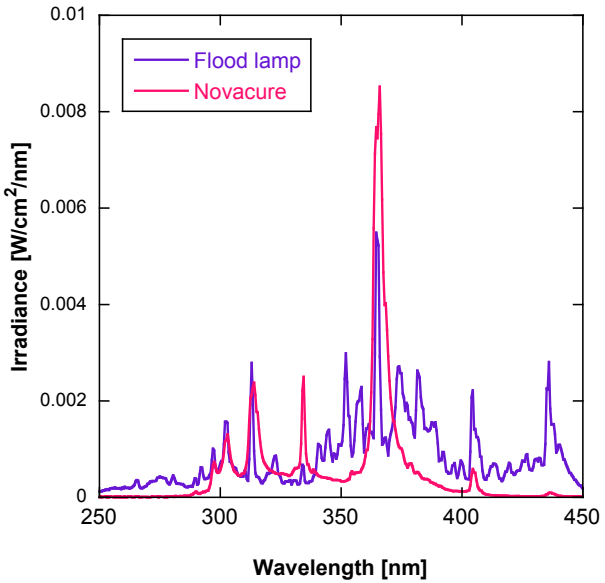
The amount of radiation reaching a given point in the material will depend on several factors:

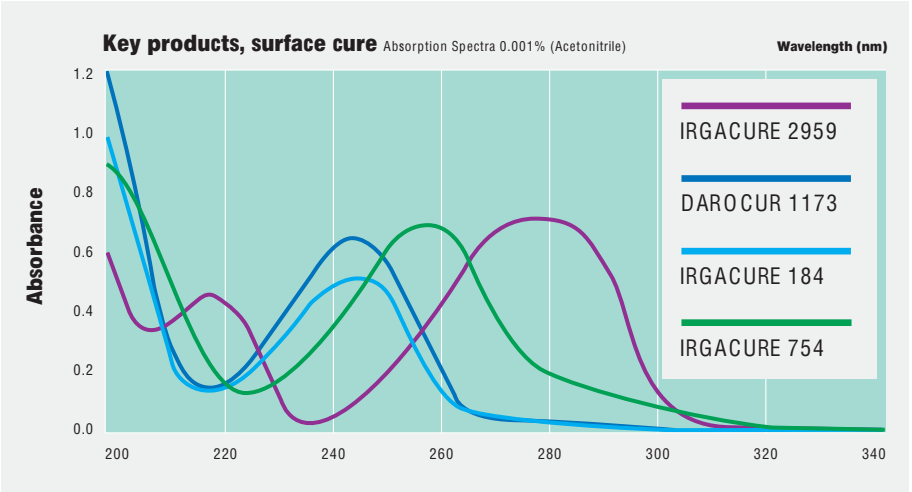
- Lamp output intensity governed by lamp power rating and lightguide diameter
- Distance from light source to material, due to absorption in the air and collimation ($1/r^2$).
- Presence of elements between light source and target material. The amount of light absorbed by intervening elements will vary according to the thickness and optical behavior of the elements concerned.
- Exposure time. Since lamp energy output is the product of intensity multiplied by exposure time, the same energy can be consumed at high or low intensity, as the exposure time is adjusted to maximize energy efficiency.
- Curing depth. Light is gradually absorbed within the working material, so that for any given target depth, the amount of energy required will be equal to the product of the intensity reaching that point and the duration of exposure.

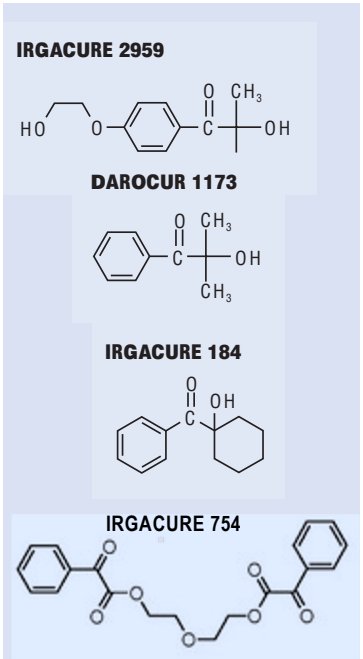
WHAT AND HOW PHOTOPOLYMERIZATION

In photopolymerizable formulations only the first reaction step, which is the production of an initiating species, is a photochemical reaction. The polymerization itself is exclusively a thermal chain reaction. This chain process amplifies the first photochemical event by a factor of several hundreds and explains in part why photopolymerization is very efficient and therefore an industrially acceptable process.

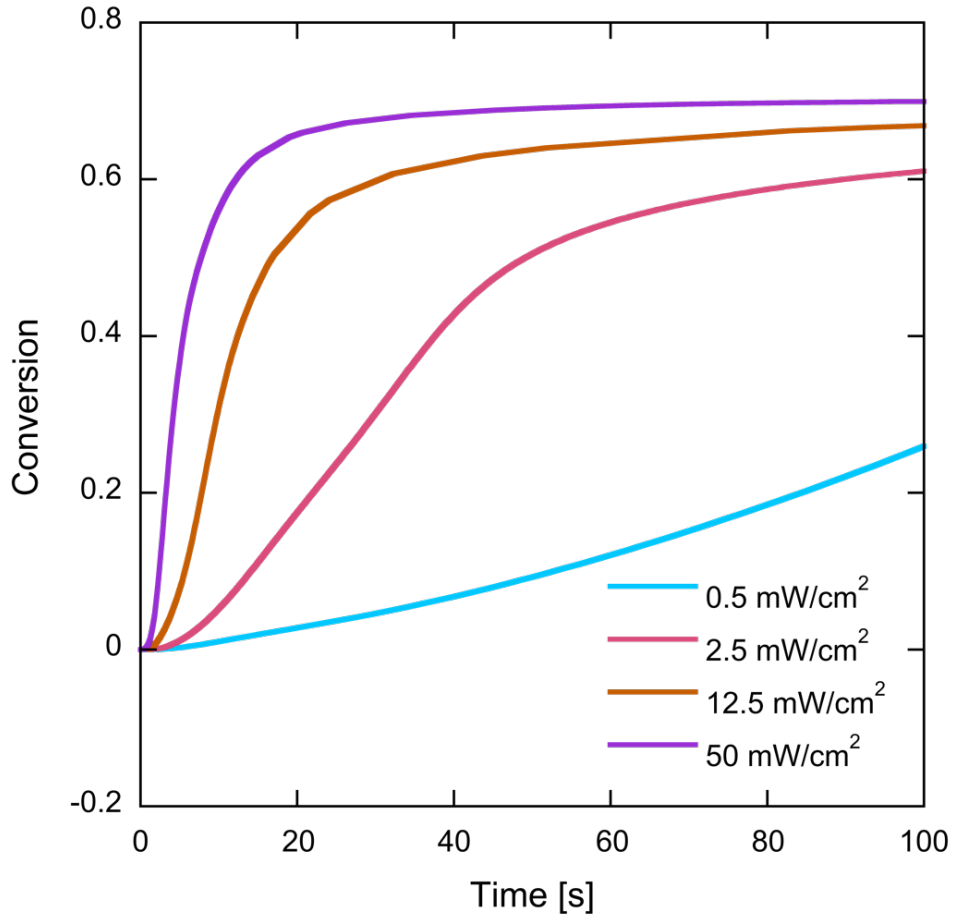
UV-radiation <–> photoinitiator



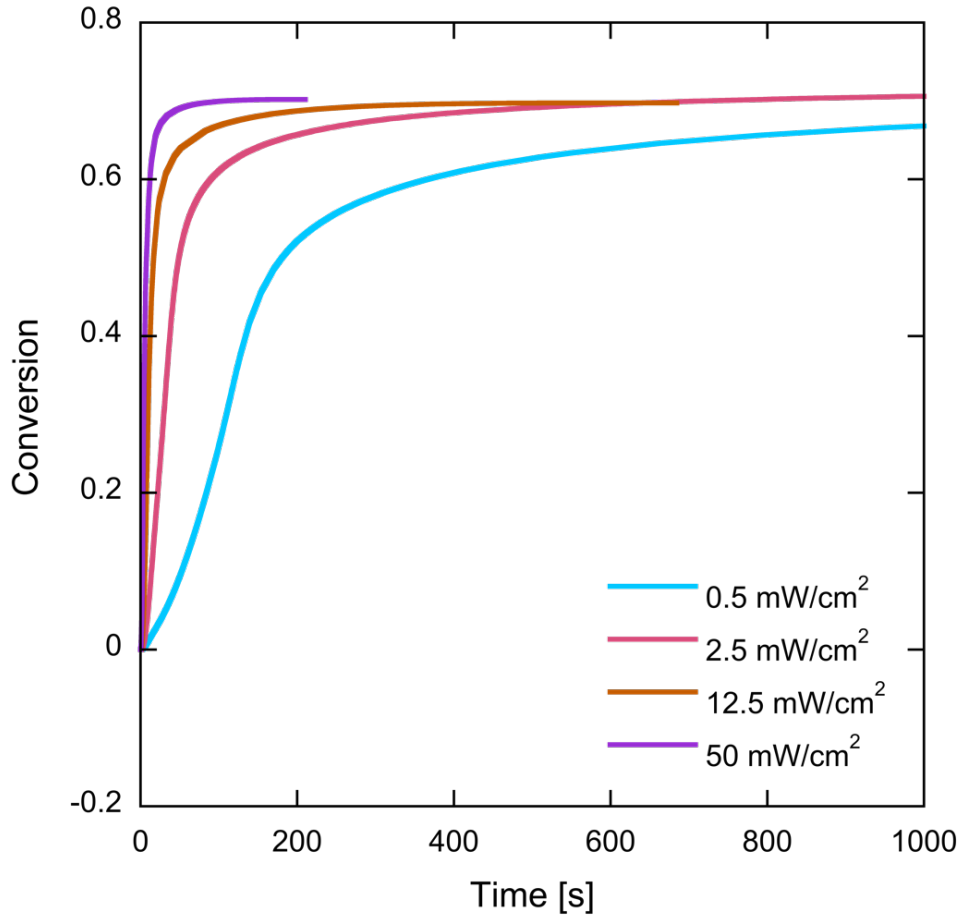




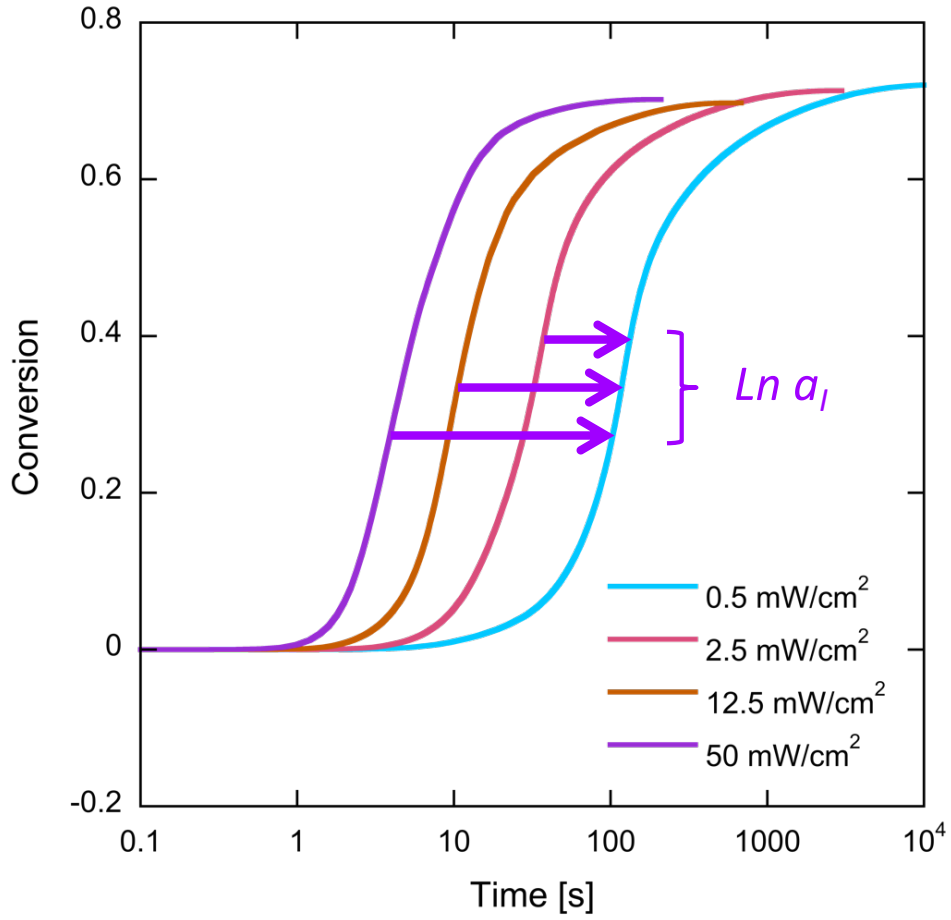
INFLUENCE OF LIGHT ENERGY



INFLUENCE OF LIGHT ENERGY

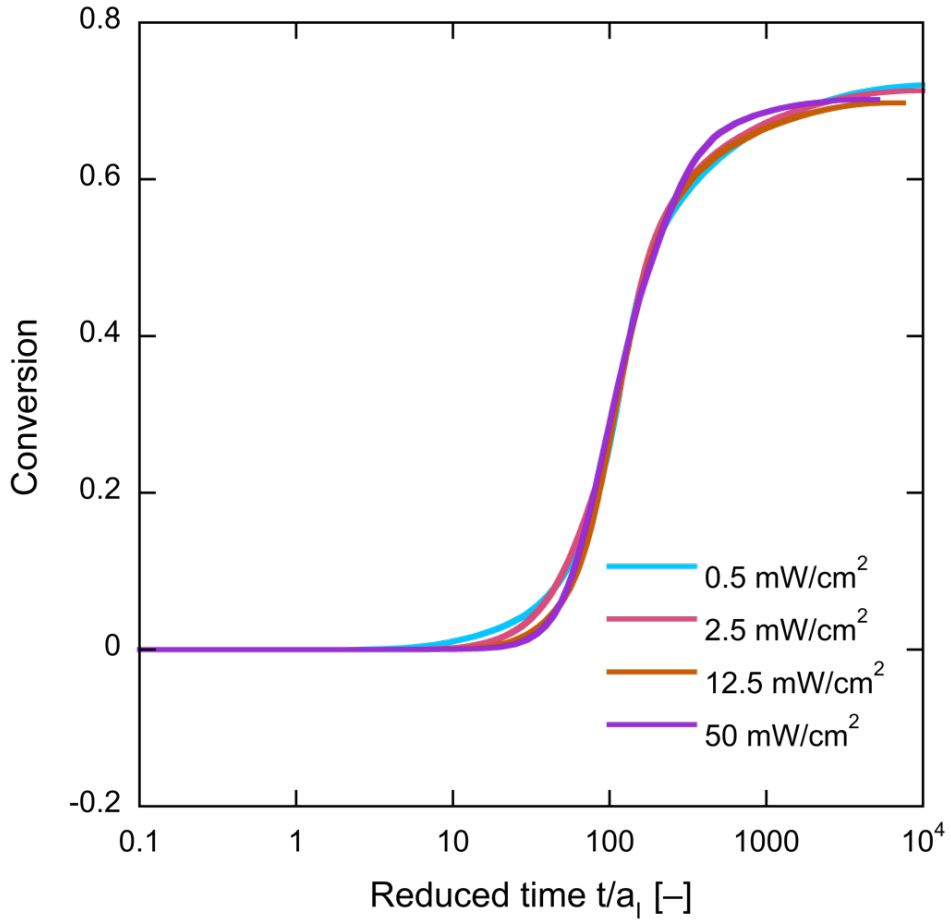


INFLUENCE OF LIGHT ENERGY



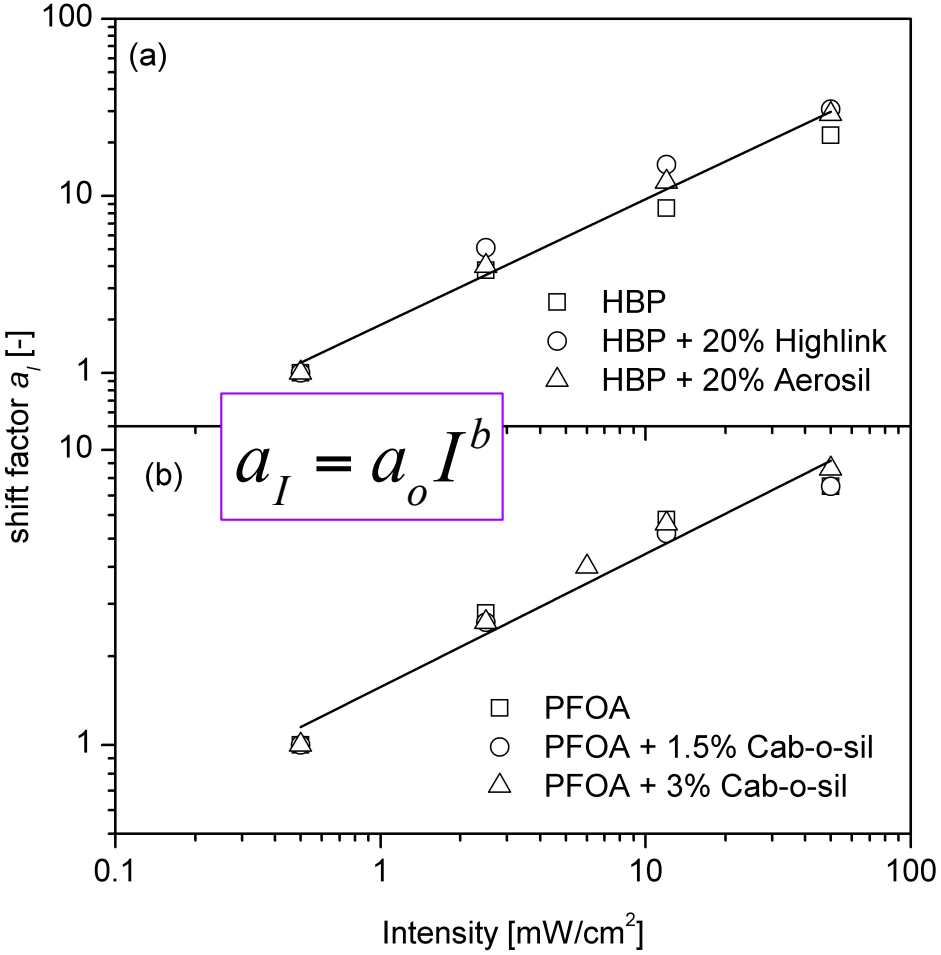
$$\alpha\left(t_1, I_1\right) = \alpha\left(t_0, I_0\right) \Leftrightarrow t_1 = \frac{t_0}{a_I}$$

INFLUENCE OF LIGHT ENERGY



$$\alpha\left(t_1, I_1\right) = \alpha\left(t_0, I_0\right) \Leftrightarrow t_1 = \frac{t_0}{a_I}$$

INFLUENCE OF LIGHT ENERGY



Radiation dose equivalence:
Property = $f(t \cdot I)$?

$$\frac{d\alpha}{dt} = k\left(I;T\right) f\left(\alpha\right) \Rightarrow \frac{d\alpha}{f\left(\alpha\right)} = k\left(I;T\right) dt$$

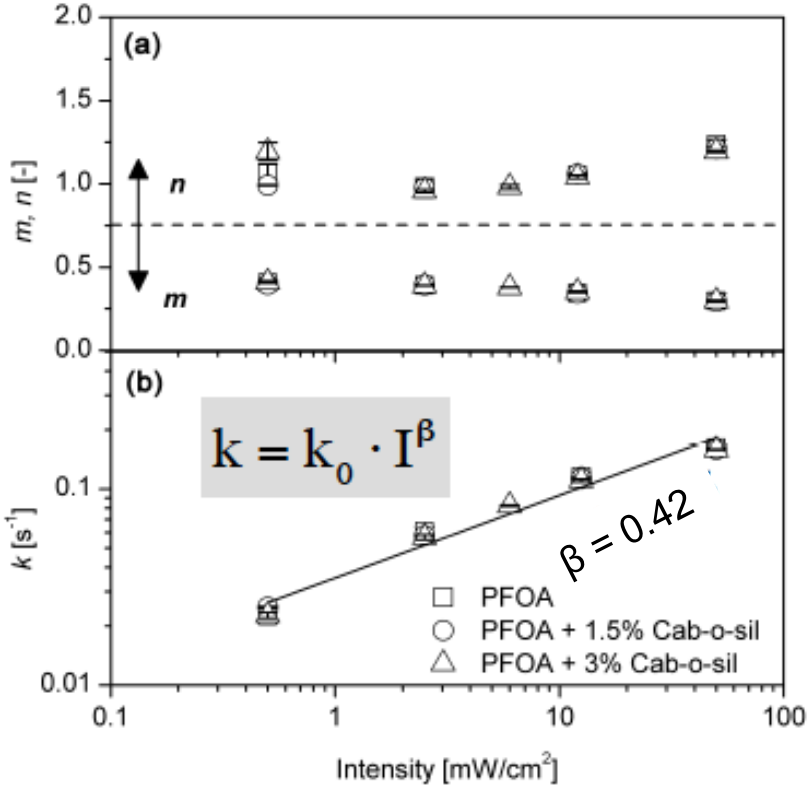
$$k = k_0 \cdot I^{\beta}$$

b = β ➔ Property = $f(t \cdot I^b)$

Dalle Vacche, Leterrier et al, Polymer (2010)

INFLUENCE OF LIGHT ENERGY

$$\frac{d\alpha}{dt} = k(I)\left(1 - \frac{\alpha}{\alpha_v(I)}\right)^n \left(\frac{\alpha}{\alpha_v(I)}\right)^m$$



Andrzejewska, Prog Polym Sci 2001
Dalle Vacche et al., Polymer (2010)

In free-radical systems:

power law intensity dependence for rate constant *k*

weak intensity dependence of the conversion at vitrification α_v
(polymerization shrinkage lags behind conversion)

Reaction order exponent *n* and autocatalytic exponent *m* are independent of intensity

$\beta < 0.5$ primary radical termination, i.e. reaction of an initiator radical with a polymer radical

$\beta = 0.5$ indicates second order termination, i.e. reaction of two polymer radicals

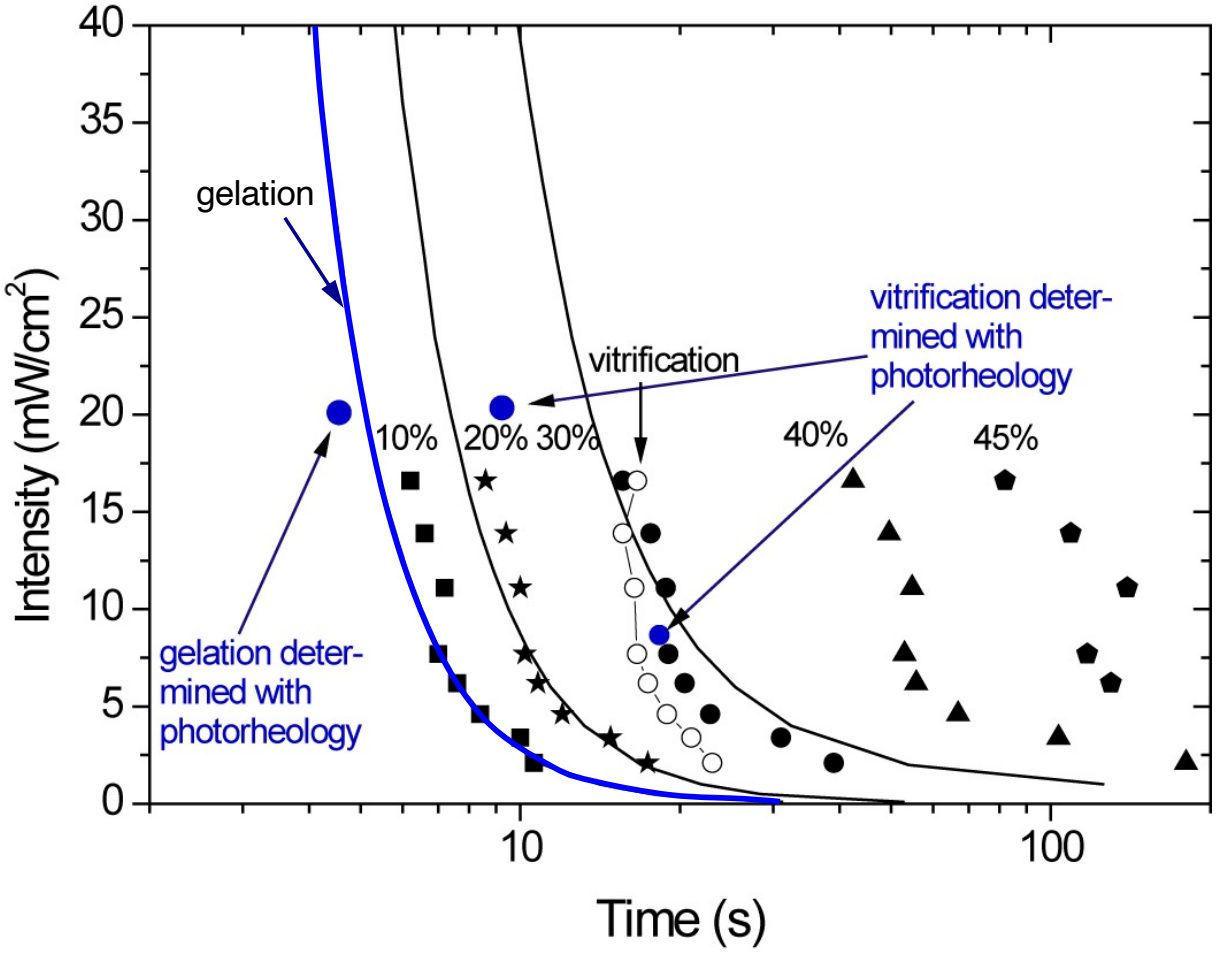
$\beta = 1$ indicates first order termination, i.e. trapping of the radical end in the forming network or recombination with oxygen.

For $0.5 < \beta < 1$ first order and second order termination happen in parallel.

TIME-INTENSITY-TRANSFORMATION DIAGRAMS

Processing maps with combined information from photo DSC and photorheology

Infra-red spectroscopy in-situ in the rheometer would be useful!

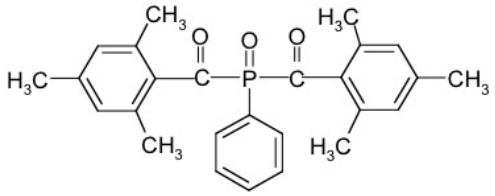


Lee et al., Polymer J (2003)
Corcione et al., Polymer (2005)
Schmidt et al. JAPS (2007)

INFLUENCE OF PHOTOINITIATOR

PI1: Irgacure 819

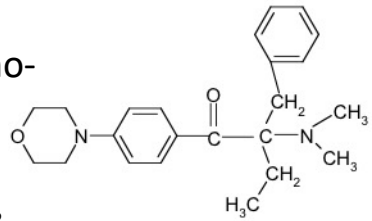
phenyl bis (2,4,6-trimethyl benzoyl)



phosphine oxide derivative recommended for clear coat applications and which enables thick sections to be cured

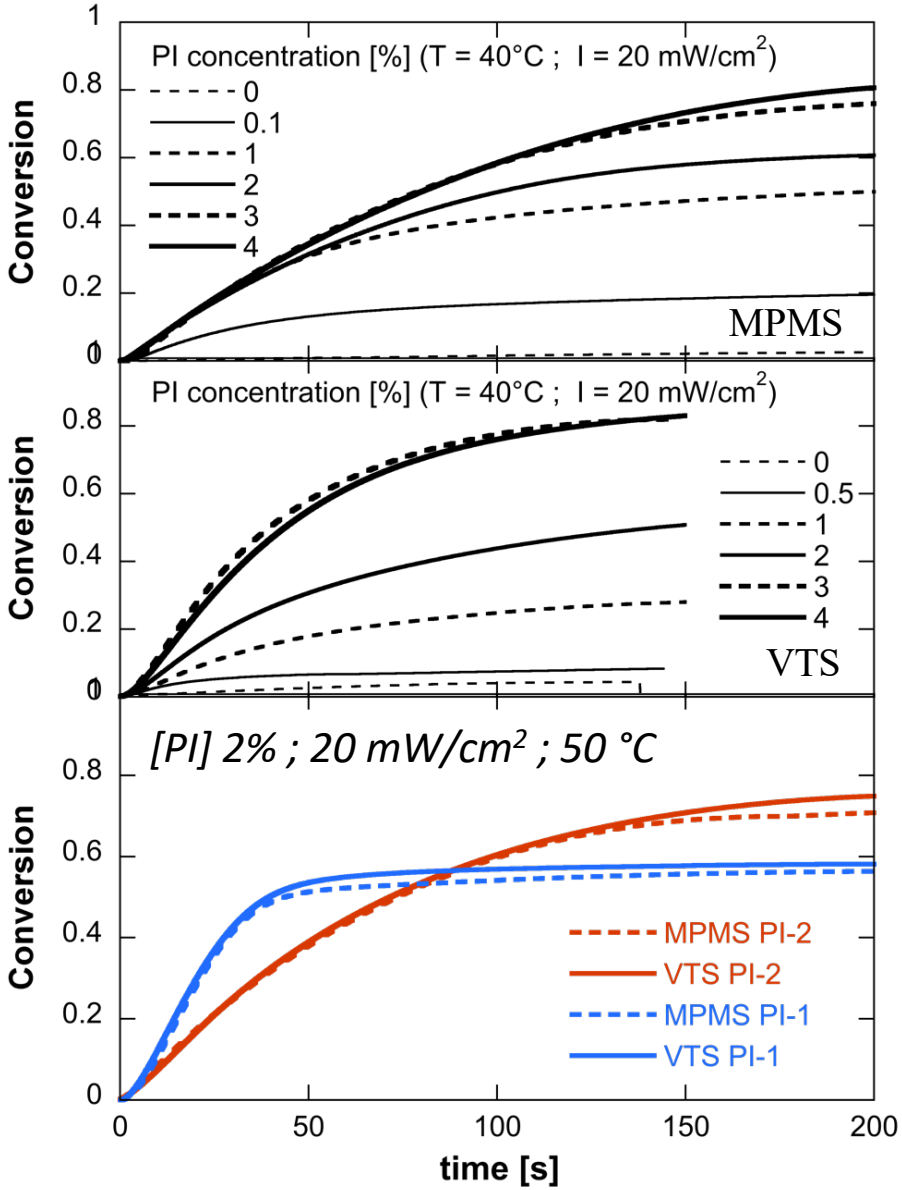
PI2: Irgacure 369

2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1



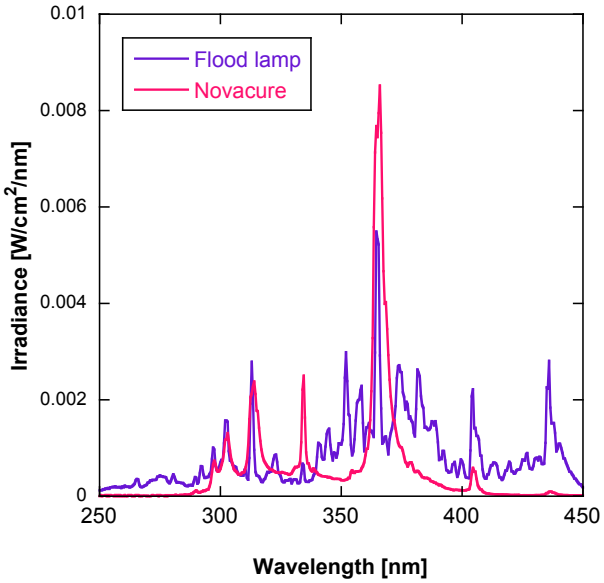
contains a tertiary amine, which should catalyze the silane-oxide surface interactions

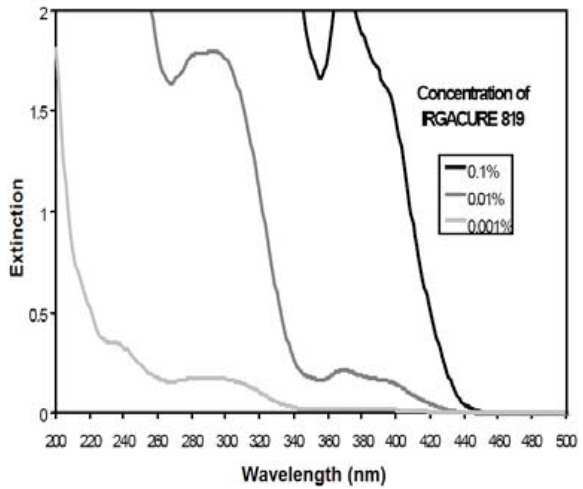
MPMS: γ-methacryloxypropyl triethoxysilane
VTS: vinyl trimethoxysilane



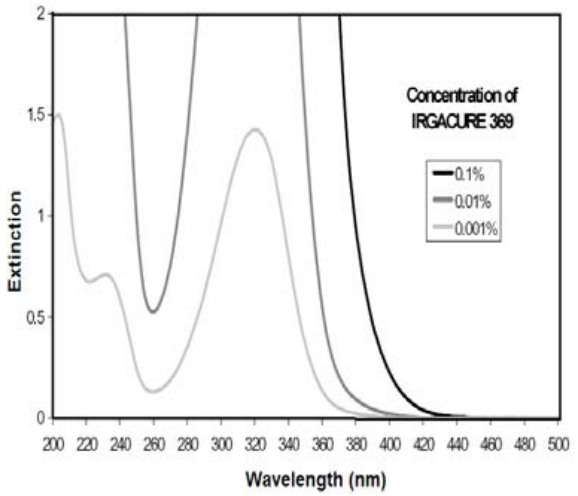
Singh, Leterrier et al, Surf Coat Technol (2009)

INFLUENCE OF PHOTOINITIATOR





PI-1



PI-2

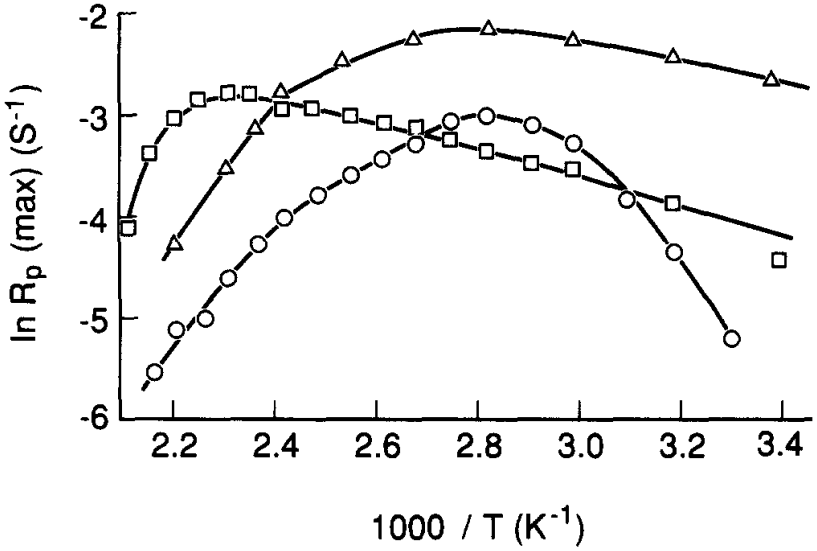
INFLUENCE OF TEMPERATURE

$$k(T) = k_0 \cdot \exp\left\{-\frac{E_a}{RT}\right\} \qquad E_a = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t$$

- E_i for thermal initiators ~ 120-150 kJ/mol
- E_i for photoinitiation process ~ 0 kJ/mol
- E_p for monomers ~ 20-40 kJ/mol
- E_t ~ 4-10 kJ/mol

E_a for thermal polymerization ~ 80 kJ/mol (reaction rate x 2-3/10 K)

E_a for photopolymerization ~ 20 kJ/mol (reaction rate x 1.2-1.3/10 K)

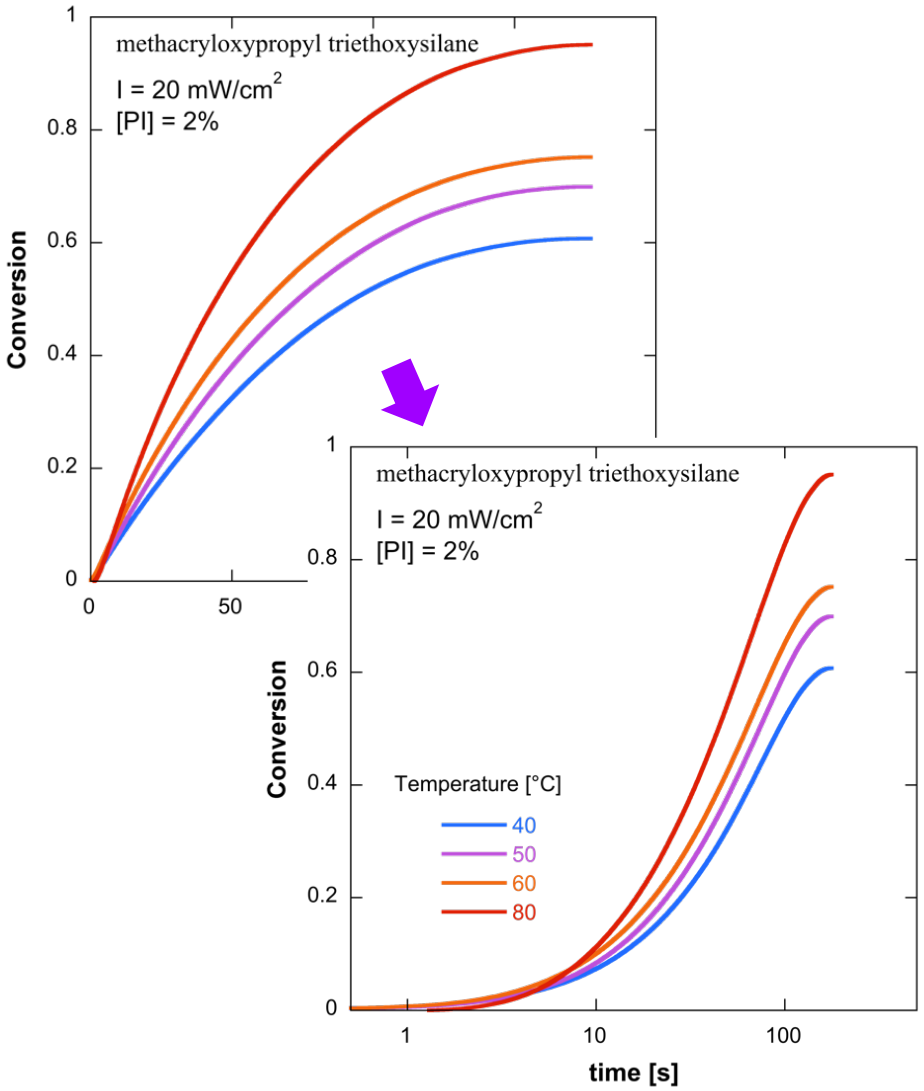


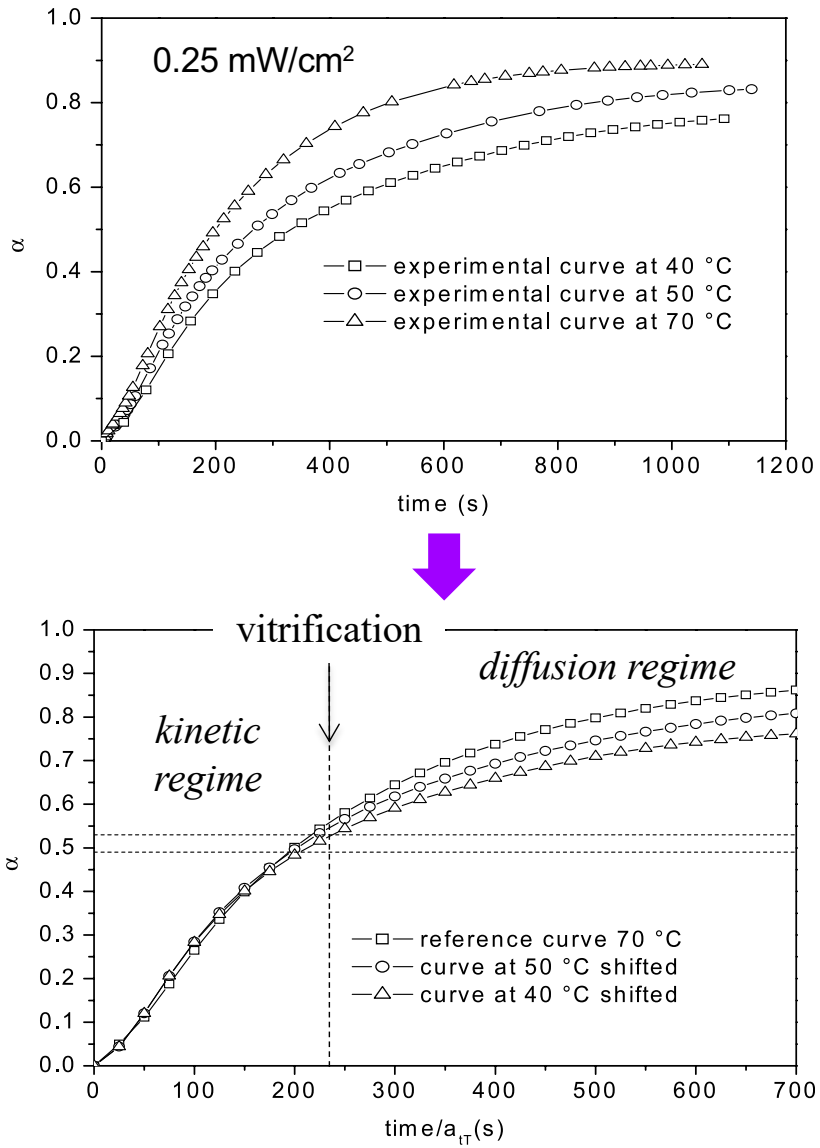
Monomer	LT region R_p^{max}	LT region 30%	LT region 40%	MT region R_p^{max}	MT region 30%	MT region 40%	HT region R_p^{max}	HT region 30%	HT region 40%
1	10	14	30[a]	−16	−22	−22	−57	−64	−59
2	40 − 116[a]	–[a]	–[a]	−21	0	22	−52	−62	−54
3	10	29	33	10	29	33	−100[a]	−130[a]	−160[a]

[a] In this temperature region no linear Arrhenius plot was obtained; indicated data are estimations and depend largely on the temperature limits

Broer et al, Polymer (1991)
Barner-Kowollik et al., Chapter 4 in Handbook of Radical Polymerization, Matyjaszewski and Davis, Eds. (2002)

INFLUENCE OF TEMPERATURE





Corcione et al, Polymer (2005)
Singh, Leterrier et al, Surf Coat Technol (2009)

AUTOCATALYTIC MODEL

$$\frac{d\alpha\left(I;T\right)}{dt} = k_0 I^{\beta} \exp\left\{-\frac{E_a}{RT}\right\}\left(1-\alpha\right)^n \left(\alpha\right)^m$$

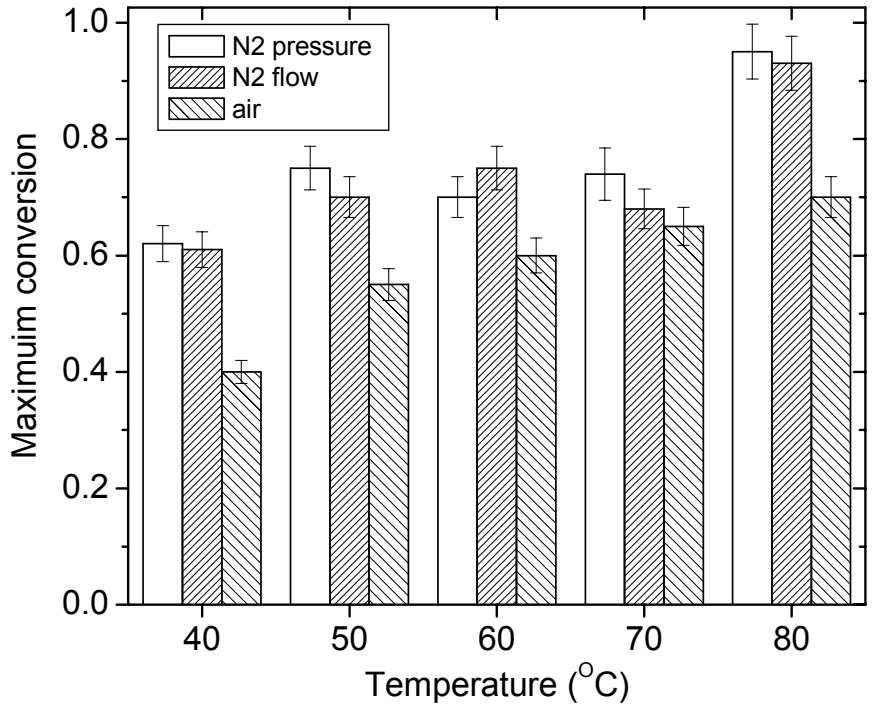
OXYGEN INHIBITION

Oxygen inhibition occurs in the case of free-radical cure when dissolved oxygen reacts with the growing polymer radical resulting in the formation of a relatively inactive peroxy radical, and a significant slow down of the rate of propagation.

Solutions

- Cure under N_2
- Use protective layer (wax, cover foil, inorganic fillers and additives which can bloom to the surface)
- Increase concentration of photoinitiator
- Increasing functionality
- Increasing cure temperature (to reduce the solubility of oxygen)
- Use thiolene chemistry

Methacrylsilane

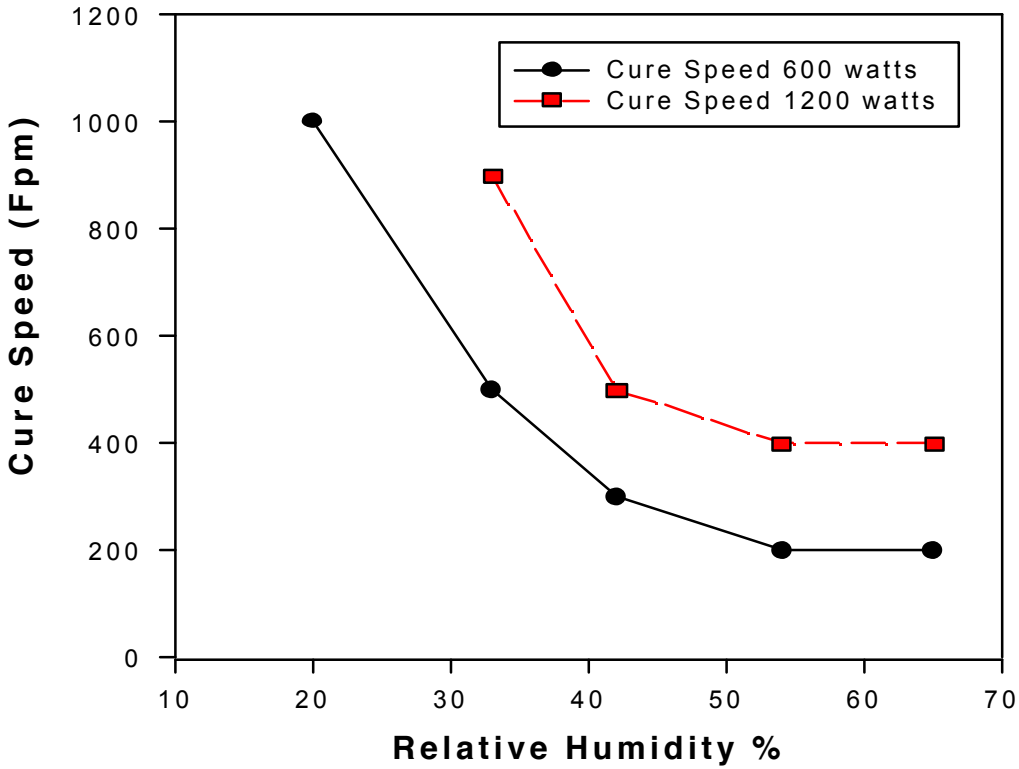


Singh, PhD thesis, EPFL (2007)

MOISTURE

Cationic polymerization is retarded by water (either dissolved in the monomer, or through permeation of ambient water vapor) due to hydrolysis reactions.

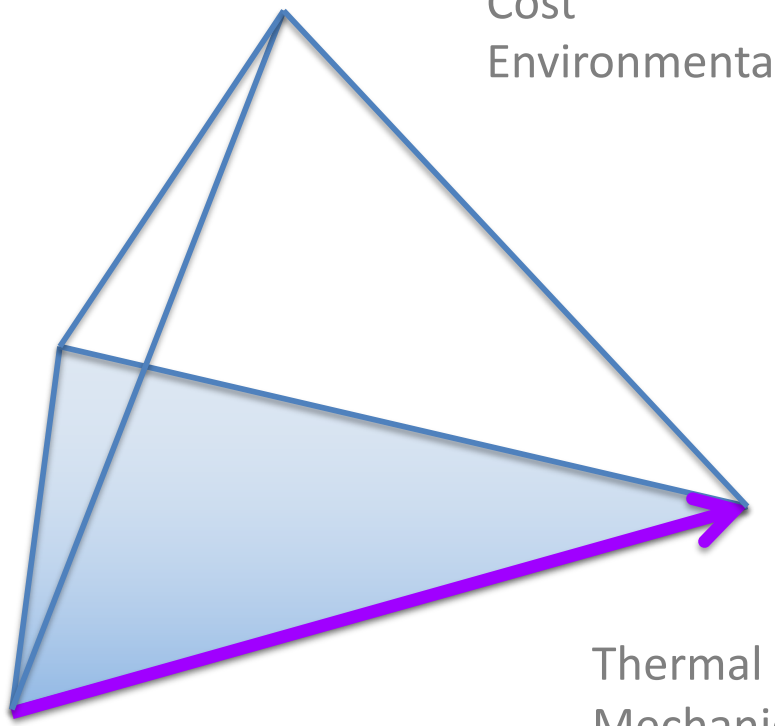
(*the addition of low levels of water to a formulation may actually accelerate the rate of cationic polymerization by chain transfer*)



Hupfield et al., Radtech 1998

PERFORMANCE

Durability
Cost
Environmental impact



Light energy
Light dose
[PI]
Temperature
O2, H2O

PROCESS

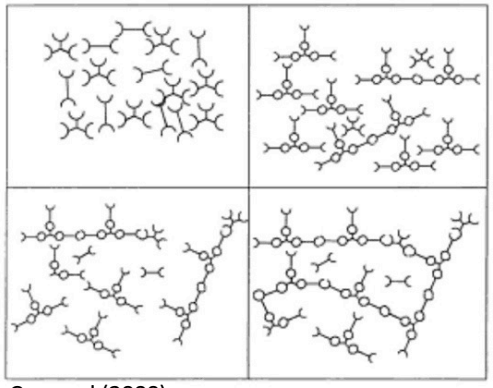
PROPERTY

Thermal properties (Tg, CTE)
Mechanical properties (hardness, adhesion)
Optical properties (transparency)
Dimension (thickness, pattern)

STRUCTURE

Conversion state
Gelation
Vitrification

STRUCTURE – PROPERTY: GLASS TRANSITION



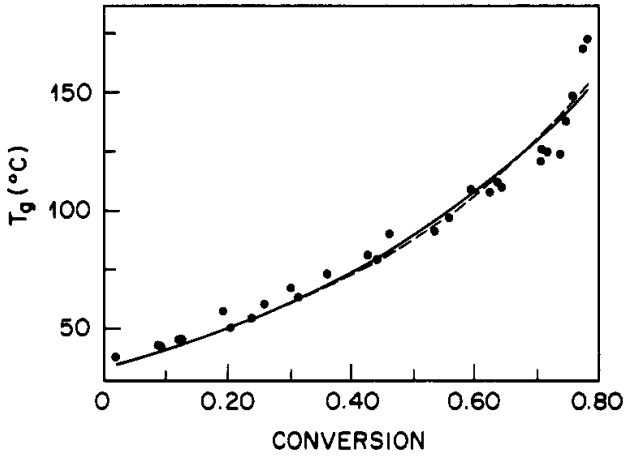
Cognard (2000)

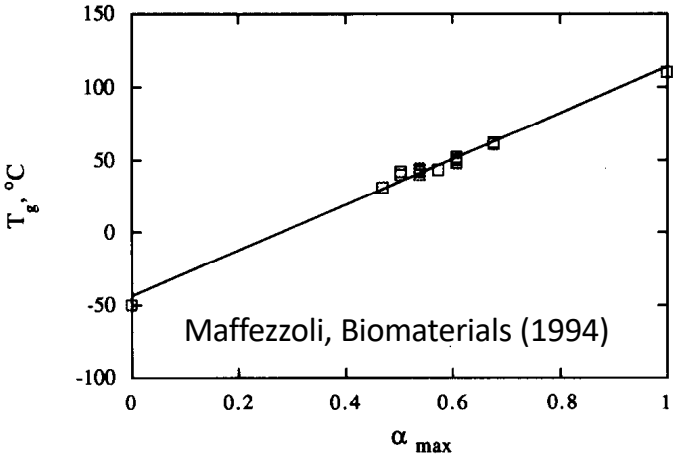
DiBenedetto (1969)

$$\frac{T_g - T_g^0}{T_g^0} = \frac{\left(\varepsilon_\infty/\varepsilon_0 - c_\infty/c_0\right)\alpha}{1-\left(1-c_\infty/c_0\right)\alpha}$$

ε : lattice energy

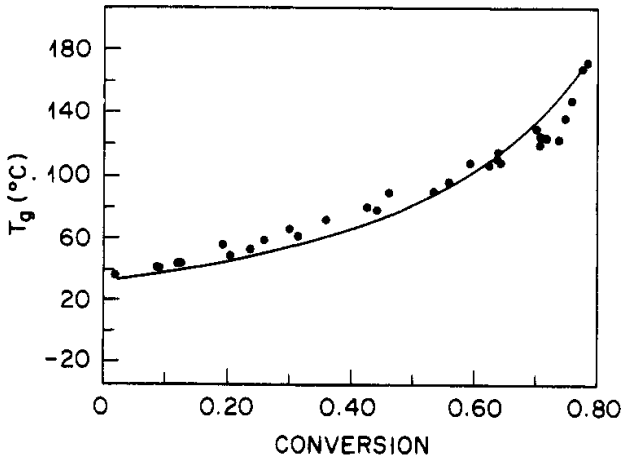
c : segmental mobility





Pascault & Williams (1990)

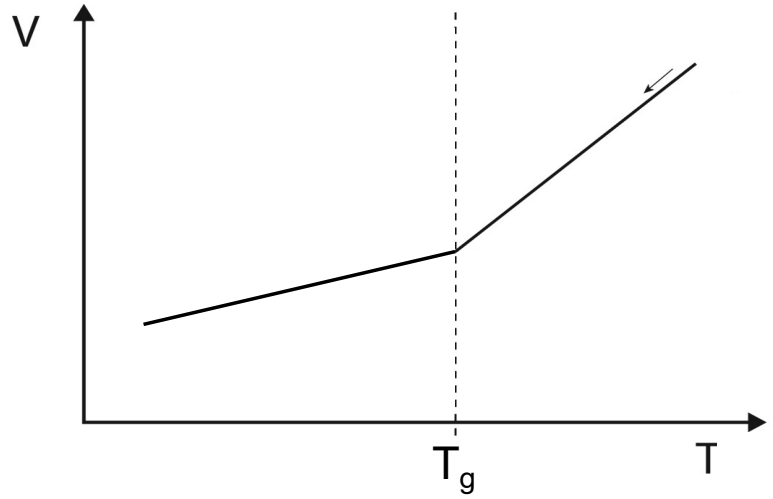
$$\frac{T_g - T_g^0}{T_g^\infty - T_g^0} = \frac{\lambda\alpha}{1-\left(1-\lambda\right)\alpha};\ \lambda = \frac{\Delta C_p^\infty}{\Delta C_p^0}$$

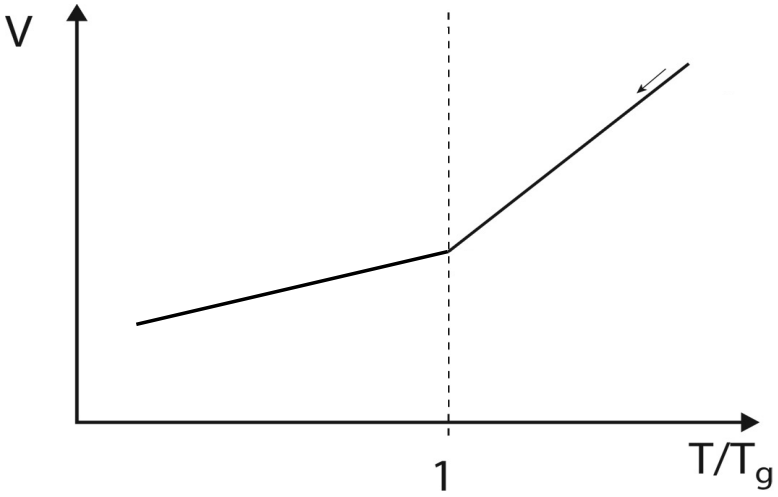


Nielsen, Macromol. Sci., Rev. Macromol. Chem. (1969)

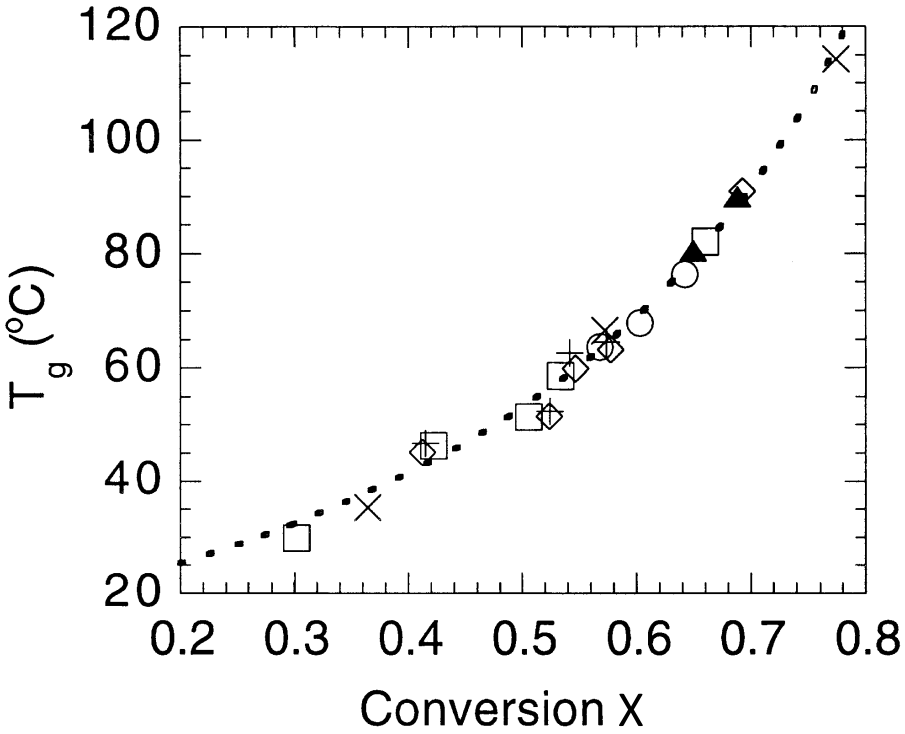
Hale, Macosko, Bair, Macromolecules (1991)

STRUCTURE – PROPERTY: GLASS TRANSITION





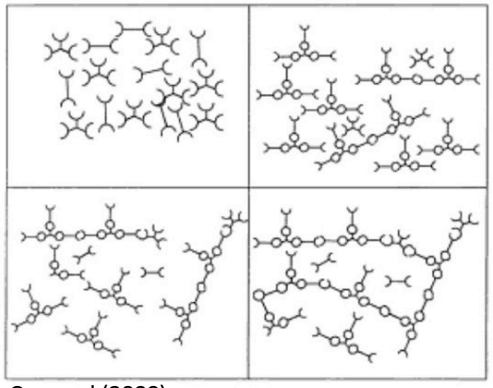
$$T_g = \frac{\alpha_m T_{gm} + (\alpha_p T_{gp} \nu_p - \alpha_m T_{gm})X}{\alpha_m \nu_m + (\alpha_p \nu_p - \alpha_m \nu_m)X}$$



where ν_m is the specific volume of the monomer (0.888 cm^3/g); ν_p is the specific volume of the polymer (0.835 cm^3/g); α_m (0.0005°C^{-1}) and α_p (0.000075°C^{-1}) are the difference in the thermal expansion coefficients between the liquid and the glassy state for the monomer and polymer, respectively.

Lovell et al., Dental Materials 17 (2001) 504-511

CROSSLINK DENSITY ξ

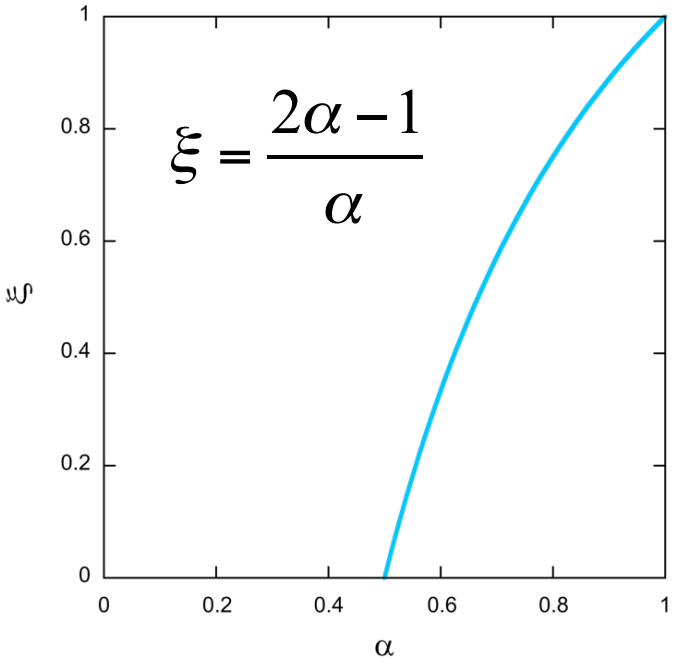


Cognard (2000)

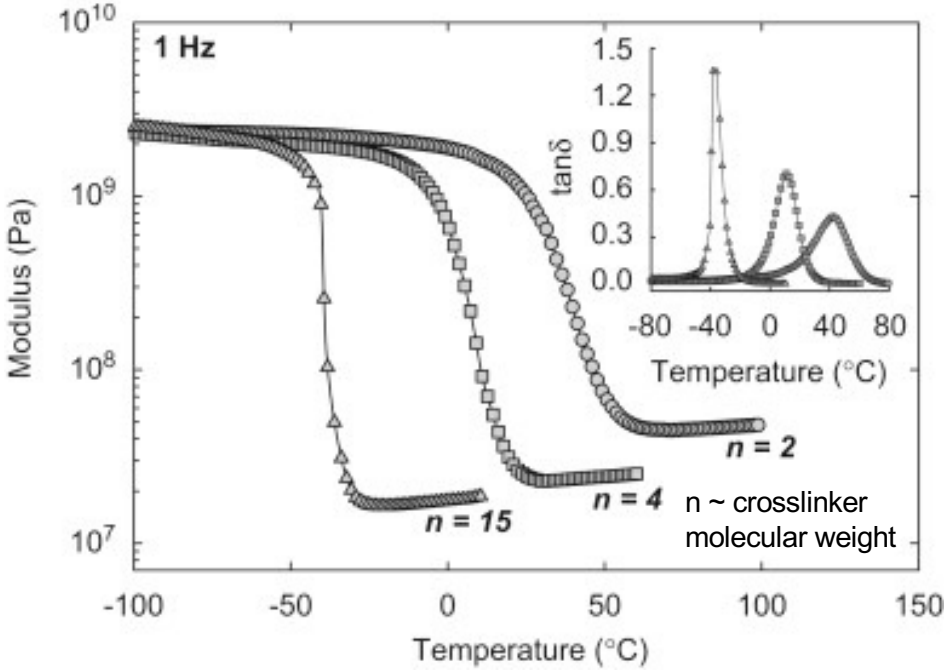
$$E = 3NkT = \frac{3\rho A\xi}{M_n}kT$$

E : elastic modulus @ $T > T_g$
ρ : density
M_n : molecular weight monomer
A : Avogadro's number

Conversion of diacrylates



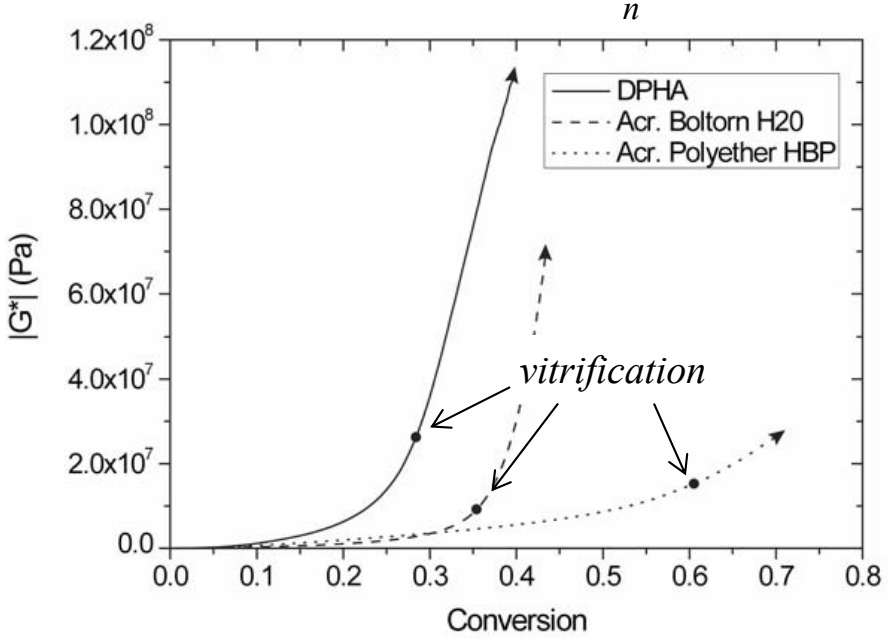
Barszczewska-Rybarek, Gibas, Kurcok, Polymer (2000)



Richards et al, Chemical Engineering Science (2009)

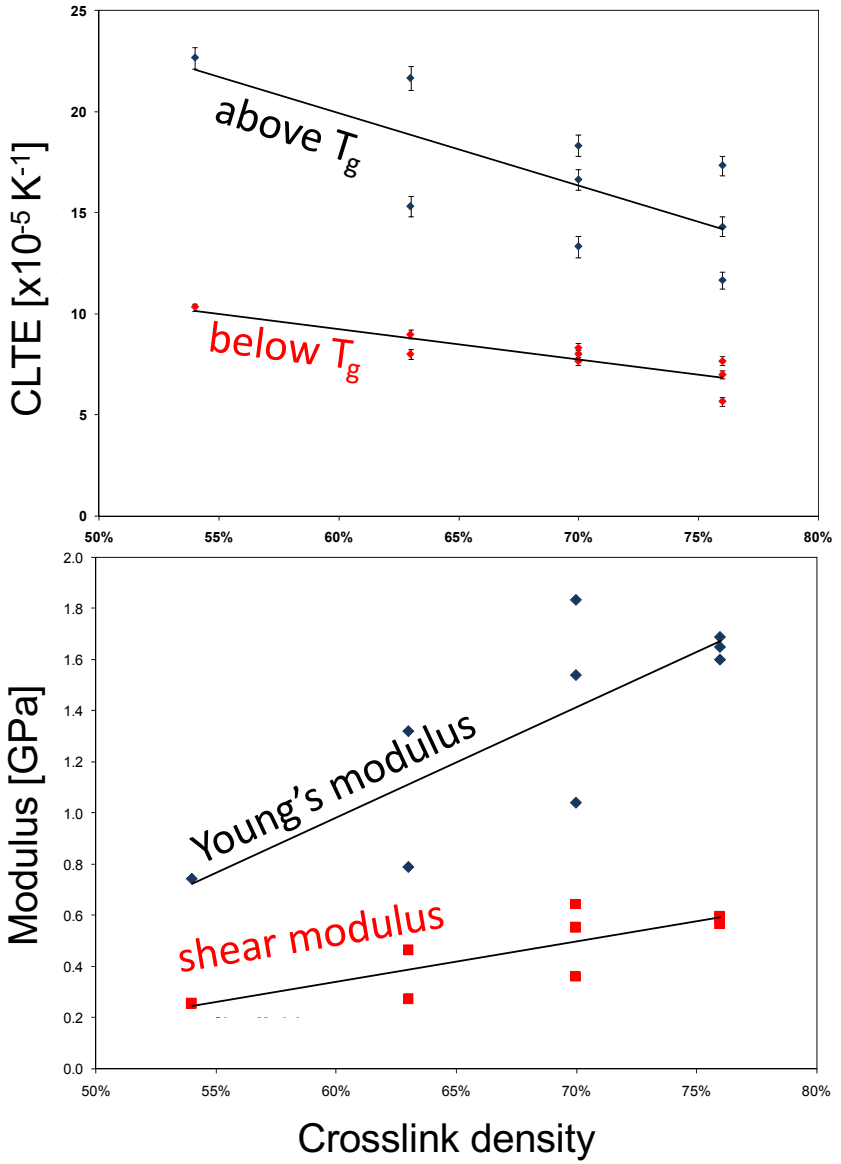
THERMO-MECHANICAL PROPERTIES

$$G = NkT = \frac{\rho A \xi}{M_n} kT$$



Schmidt, PhD thesis (EPFL 2006)

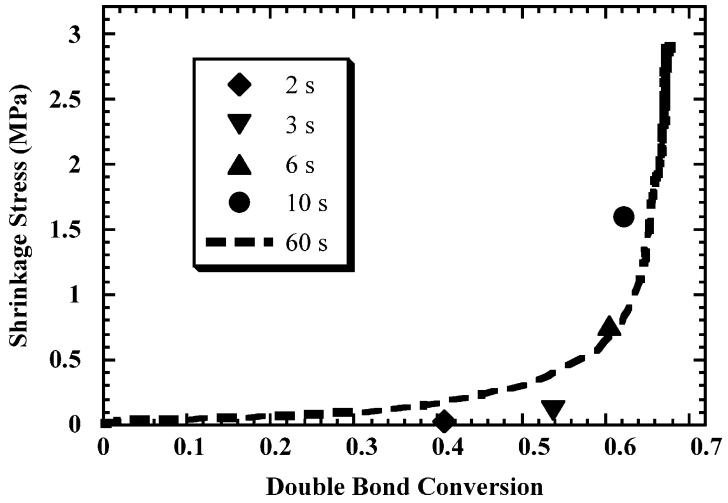
$$\frac{1}{1-n}$$



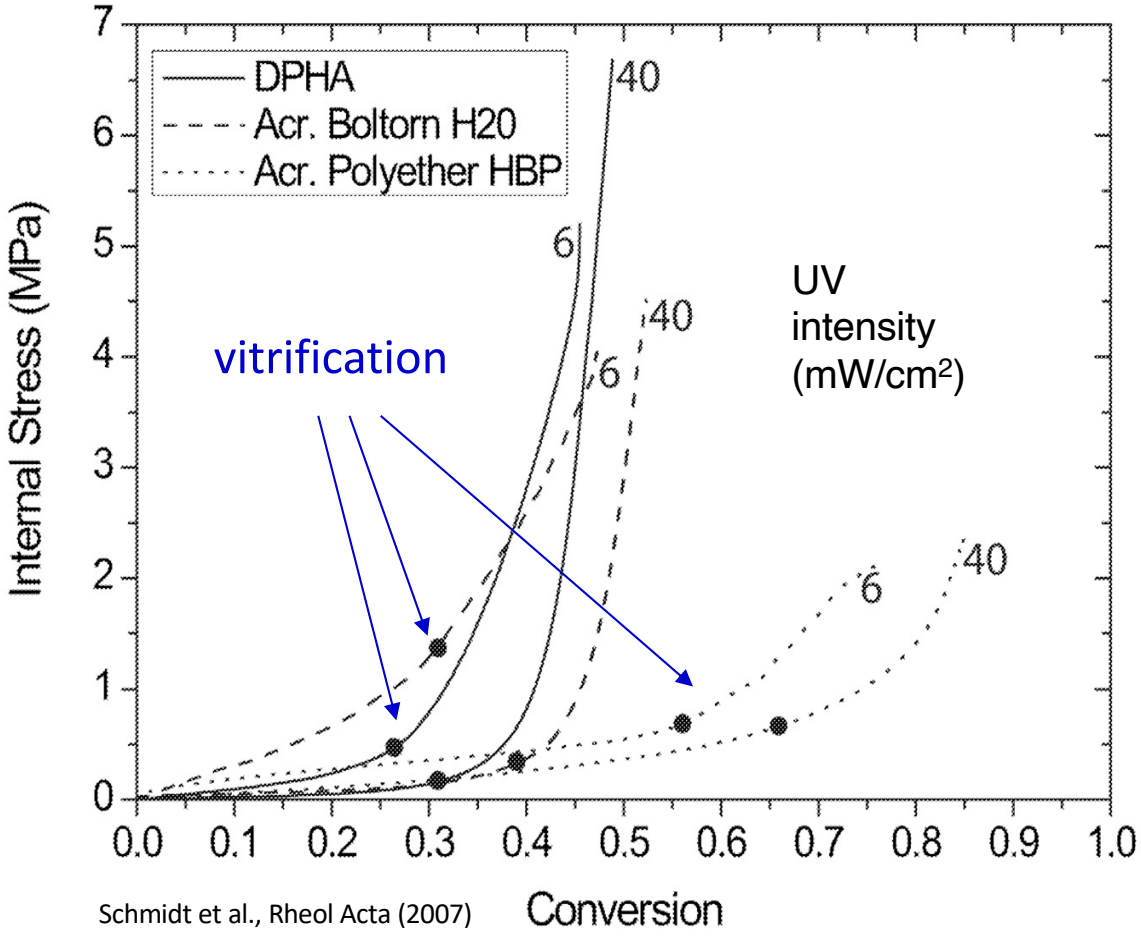
Bandyopadhyay, Odegard, Model Simul Mater Sci Eng (2012)

IMPACT OF UV INTENSITY ON INTERNAL STRESS

Combination of bending and calorimetry data OBTAINED UNDER THE SAME CONDITIONS (intensity, atmosphere)

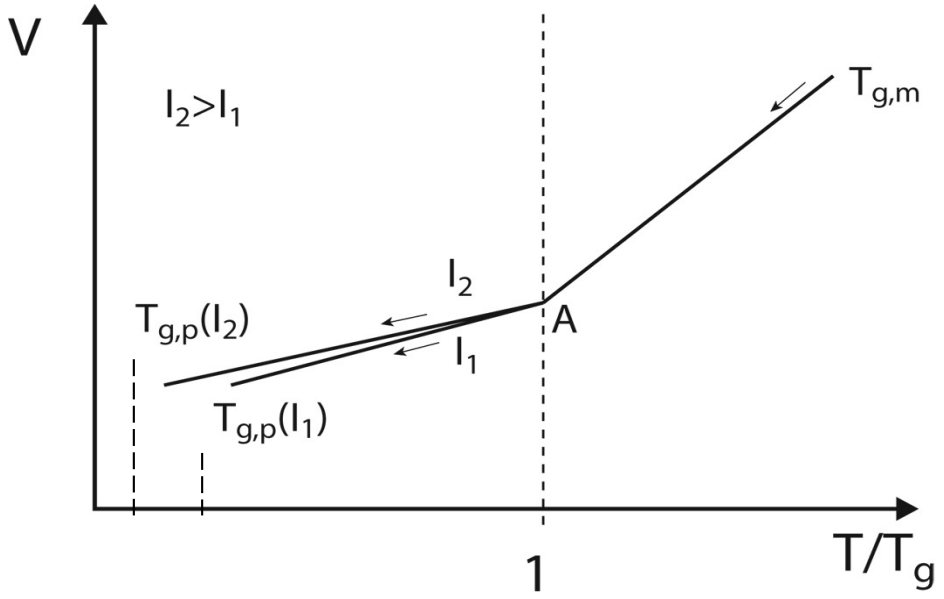


Bowman and coworkers, Dental Mater (2004)



Schmidt et al., Rheol Acta (2007)

VOLUME EVOLUTION DURING CURING



- When the polymer starts to cure, the volume relaxation is able to follow the conversion up to the point A, where the material vitrifies.
- The material cured at a higher intensity I_2 will reach higher conversion and T_g due to enhanced mobility

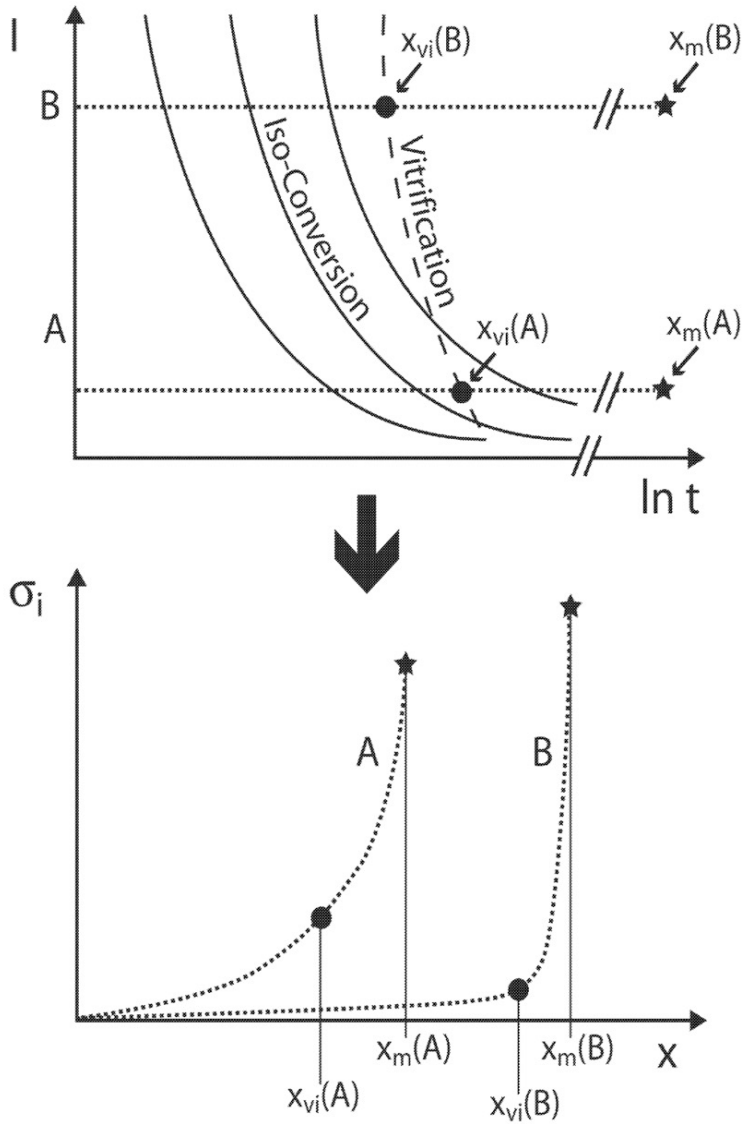
IMPACT OF UV INTENSITY ON INTERNAL STRESS

Curing at a low intensity:

- earlier vitrification, hence earlier stress build-up
- limited final conversion and limited internal stress
- additional viscoelastic stress relaxation

Curing at a high intensity:

- later vitrification, hence later stress build-up
- higher final conversion, hence higher internal stresses



Bowman and coworkers, Dental Mater (2004)
Schmidt et al., Rheol Acta (2007)

SUMMARY

- Process–structure relations
  - Time-intensity superposition with power law scaling (invalidates the radiation dose equivalence principle)
  - Time-temperature superposition with Arrhenius scaling up to vitrification
  - Activation energy for photopolymerization ~ 20 kJ/mol (vs. ~ 80 kJ/mol for thermal polymerization)
  - Oxygen inhibition in free radical systems and moisture uptake in cationic systems!
  - Conversion behavior predictable for any intensity and temperature with autocatalytic model
  - Time-intensity-transformation as process map

- Structure–property relations
  - Crosslink density controls thermal and mechanical properties
  - Stress develops in the vitreous state