Additive Manufacturing – Module 10

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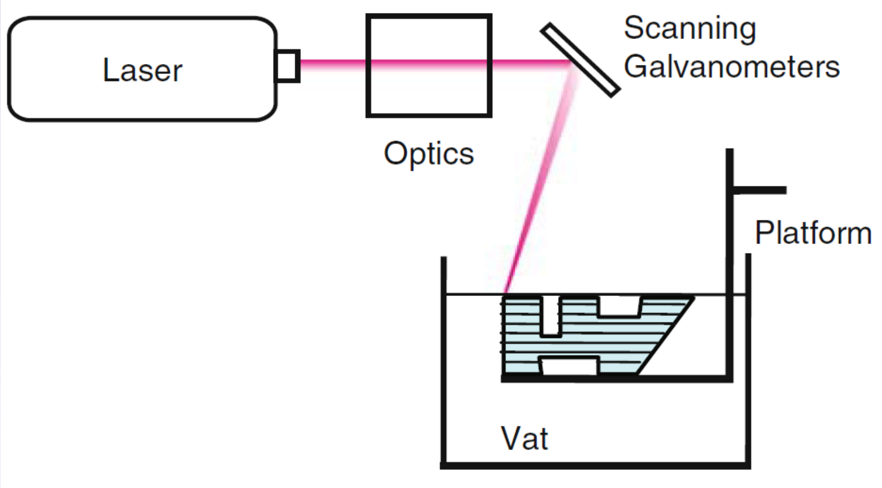
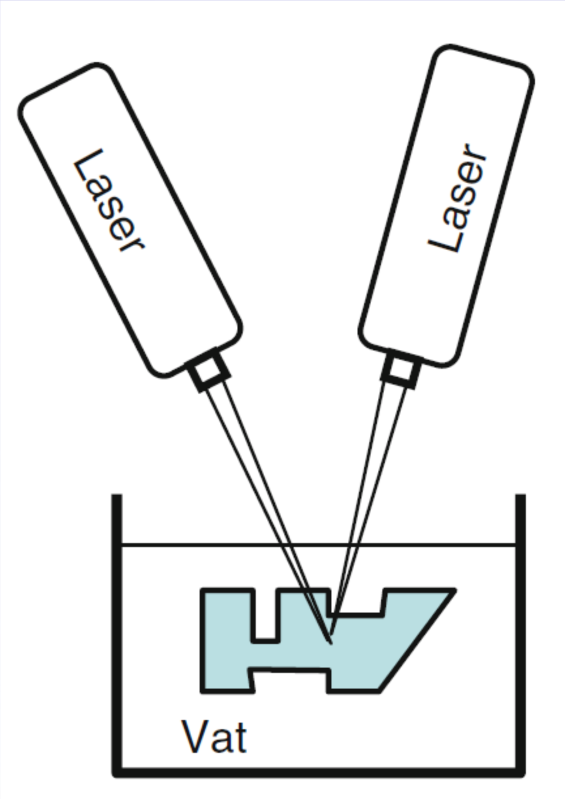
Photopolymerization Processes

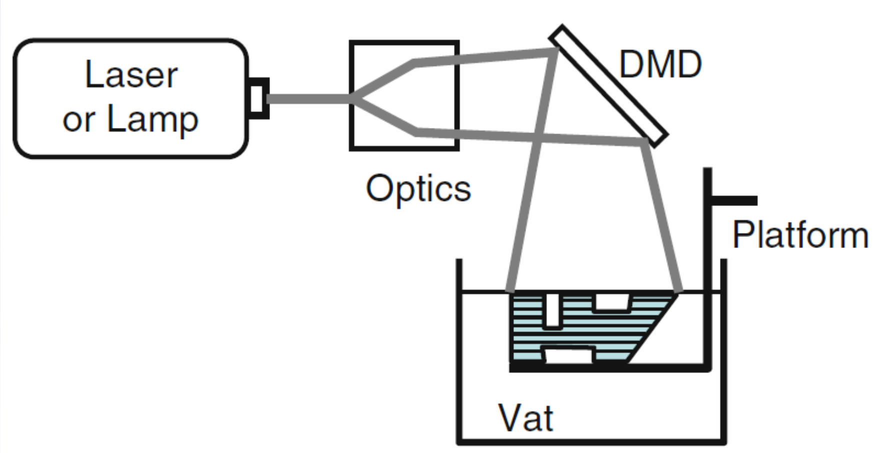
Processes



Vector scan – Stereolithography



Two-photon lithography

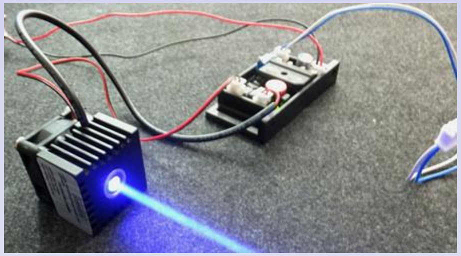


Mask projection – Digital Light Processing

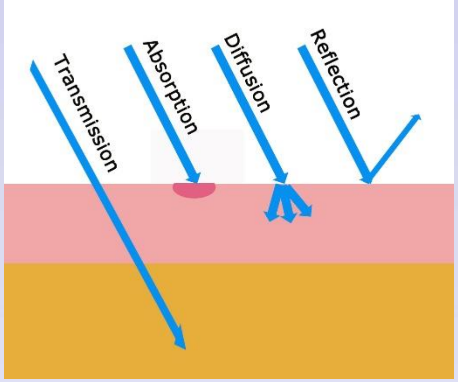
Credit: Gibson, Rosen, Stucker, Textbook

Photopolymerization Processes

Complexities

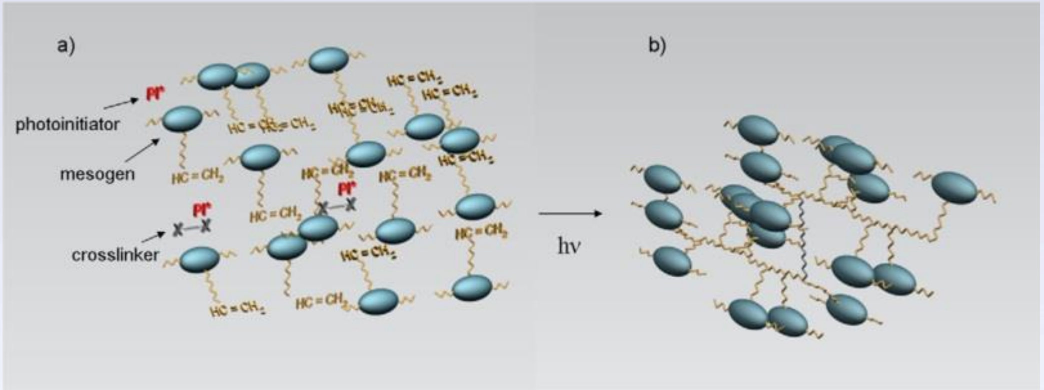


Energy source: UV lamp or LASER

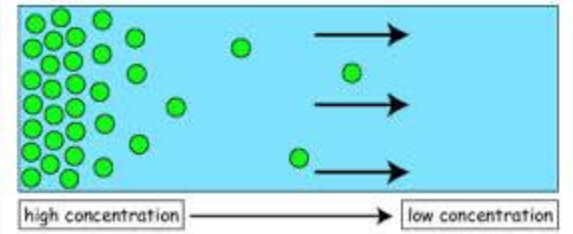


Energy absorption

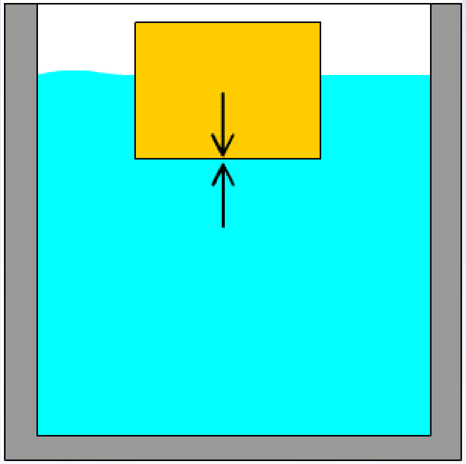
Polymers



Photopolymerization



Diffusion



Fluid mechanics – refill flow, buoyancy

Polymers

- **Polymer: High molecular weight molecule made up of a small repeat unit (monomer).**

A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

- **Monomer: Low molecular weight compound that can be connected together**
- **Oligomer: Short polymer chain**
- **Copolymer: polymer made up of 2 or more monomers**
  - **Random copolymer: A-B-B-A-A-B-A-B-A-B-B-B-A-A-B**
  - **Alternating copolymer: A-B-A-B-A-B-A-B-A-B-A-B-A-B**
  - **Block copolymer: A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B**

Classification

- **Thermoset: cross-linked polymer that cannot be melted (tires, rubber bands)**
- **Thermoplastic: Meltable plastic**
- **Elastomers: Polymers that stretch and then return to their original form: often thermoset polymers**
- **Thermoplastic elastomers: Elastic polymers that can be melted (soles of tennis shoes)**

Polymers

- **Polymer families**
  - **Polyolefins: made from olefin (alkene) monomers**
  - **Polyesters, Amides, Urethanes, etc.: monomers linked by ester, amide, urethane or other functional groups**
  - **Natural Polymers: Polysaccharides, DNA, proteins**

- **Polyolefins (CnH2n)**

Monomer **Polymer**

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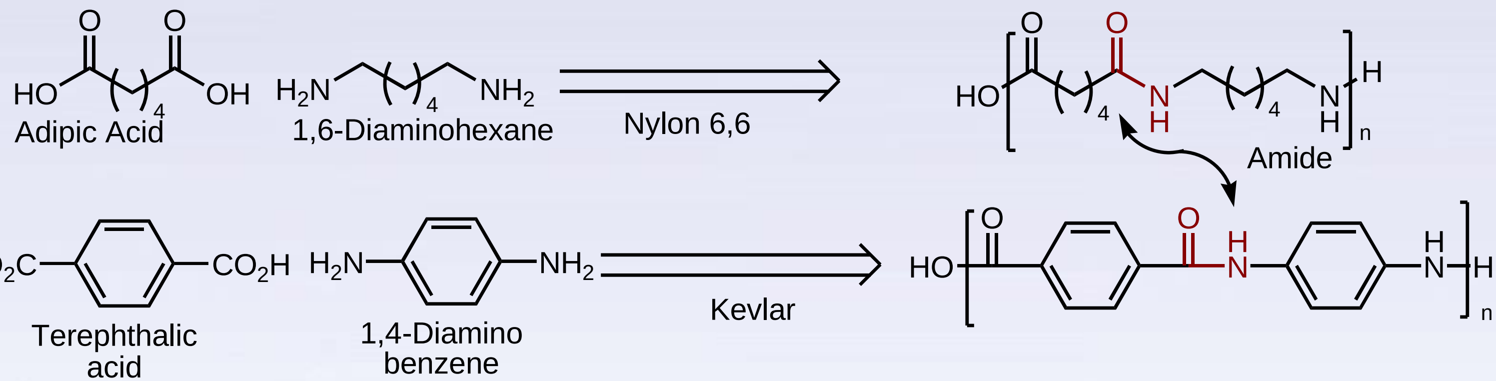
Photopolymerization Processes

AM³ Lab
Advanced Manufacturing | Modeling | Materials

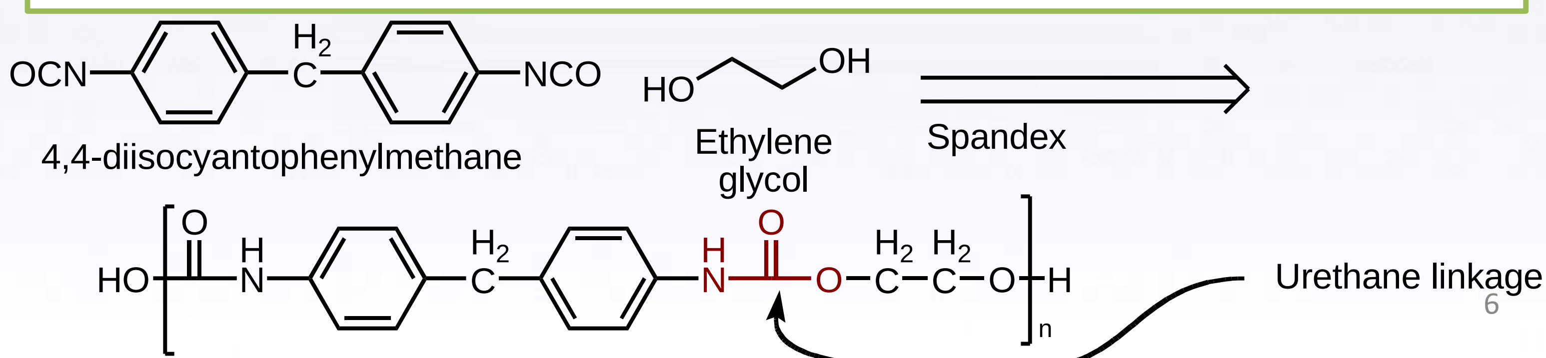
Polymers

Polyester

Polyamides



Polyurethanes



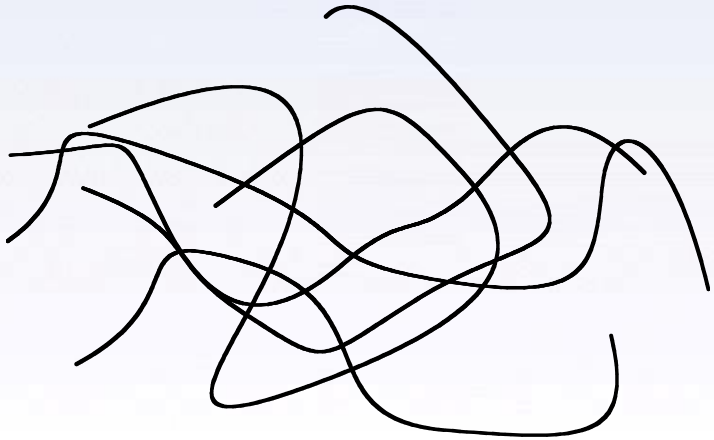
Photopolymerization Processes

Stereolithography
Overview
Polymer
Photo polymerization

Polymers

Characteristics

- **Really big molecules (macromolecules)**
- **Chain entanglement: Long polymer chains get entangled with each other.**
  - **When the polymer is melted, the chains can flow past each other.**
  - **Below the melting point, the chains can move, but only slowly. Thus the plastic is flexible, but cannot be easily stretched.**
  - **Below the glass transition point, the chains become locked and the polymer is rigid**



Stereolithography

Overview

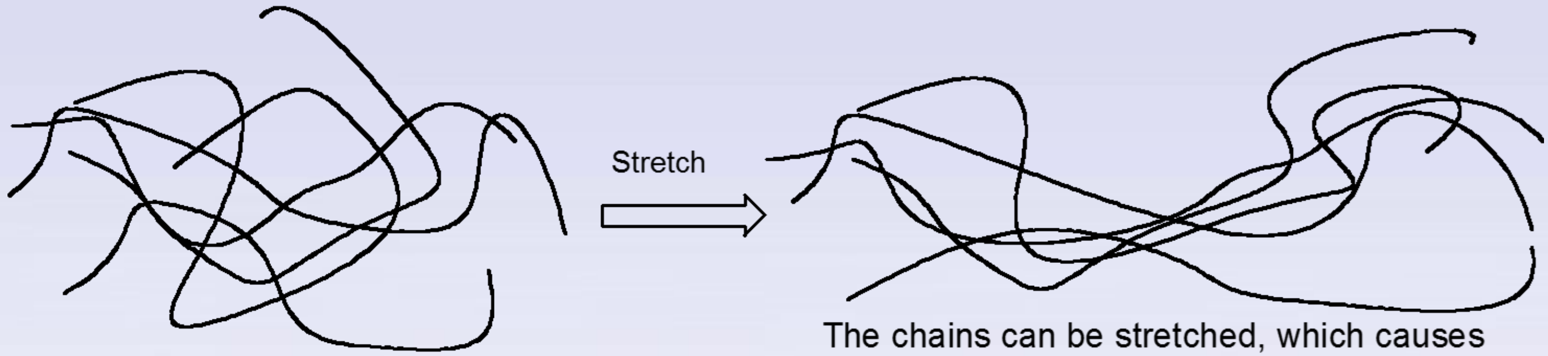
Polymer

Photo polymerization

Polymers

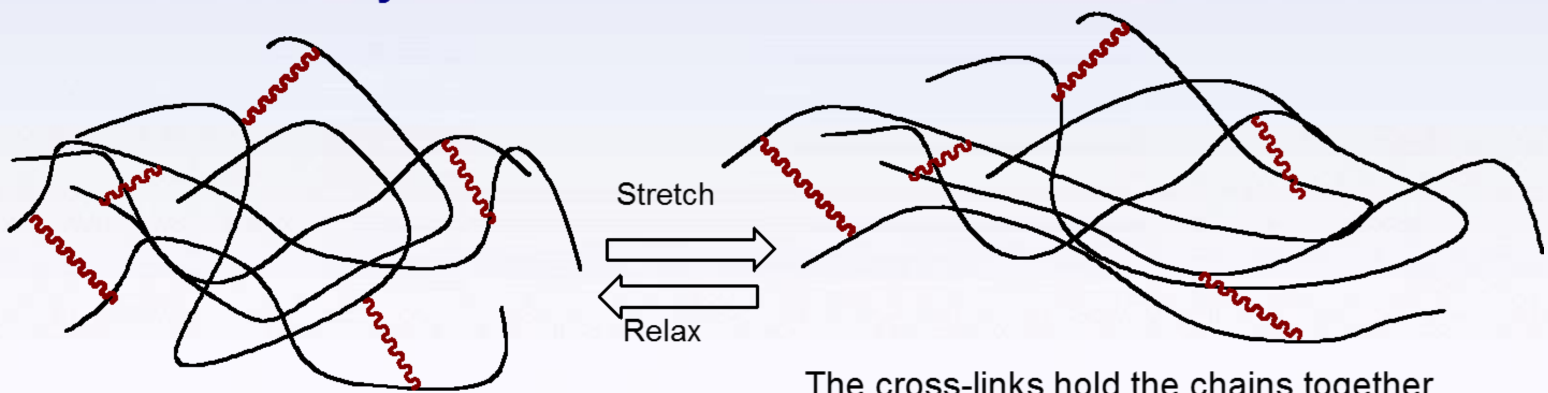
Characteristics

Linear Polymer



The chains can be stretched, which causes them to flow past each other. When released, the polymer will not return to its original form.

Cross-Linked Polymer



The cross-links hold the chains together. When released, the polymer will return to it's original form.

Photopolymerization Processes

Polymers

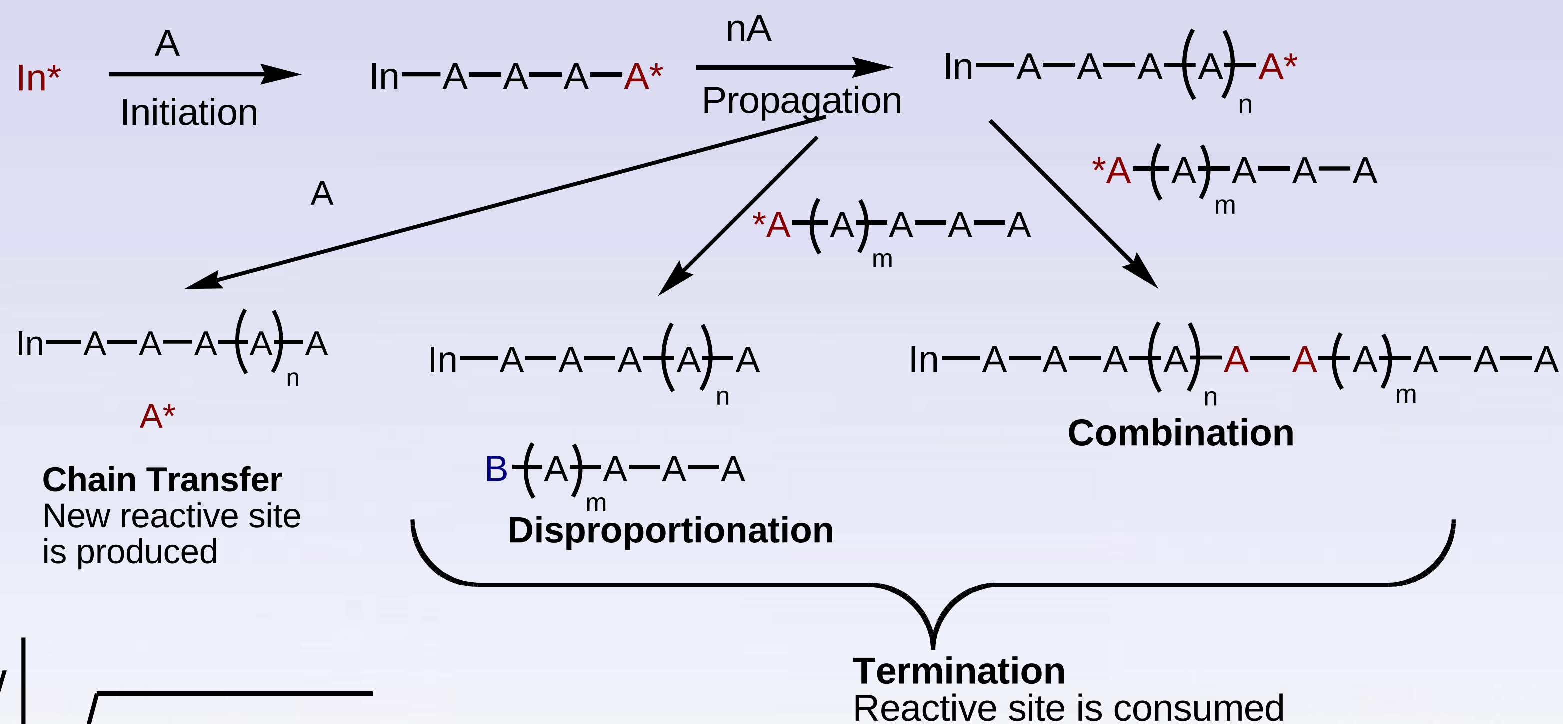
Synthesis

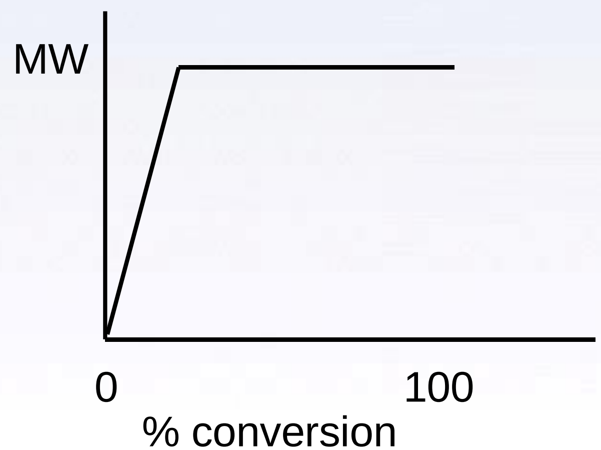
- **Addition polymerization: The polymer grows by sequential addition of monomers to a reactive site**
  - **Chain growth is linear**
  - **Maximum molecular weight is obtained early in the reaction**
- **Step-Growth polymerization: Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.**
  - **Chain growth is exponential**
  - **Maximum molecular weight is obtained late in the reaction**

Photopolymerization Processes

Polymers

Chain-growth polymerization (typically addition polymerization)

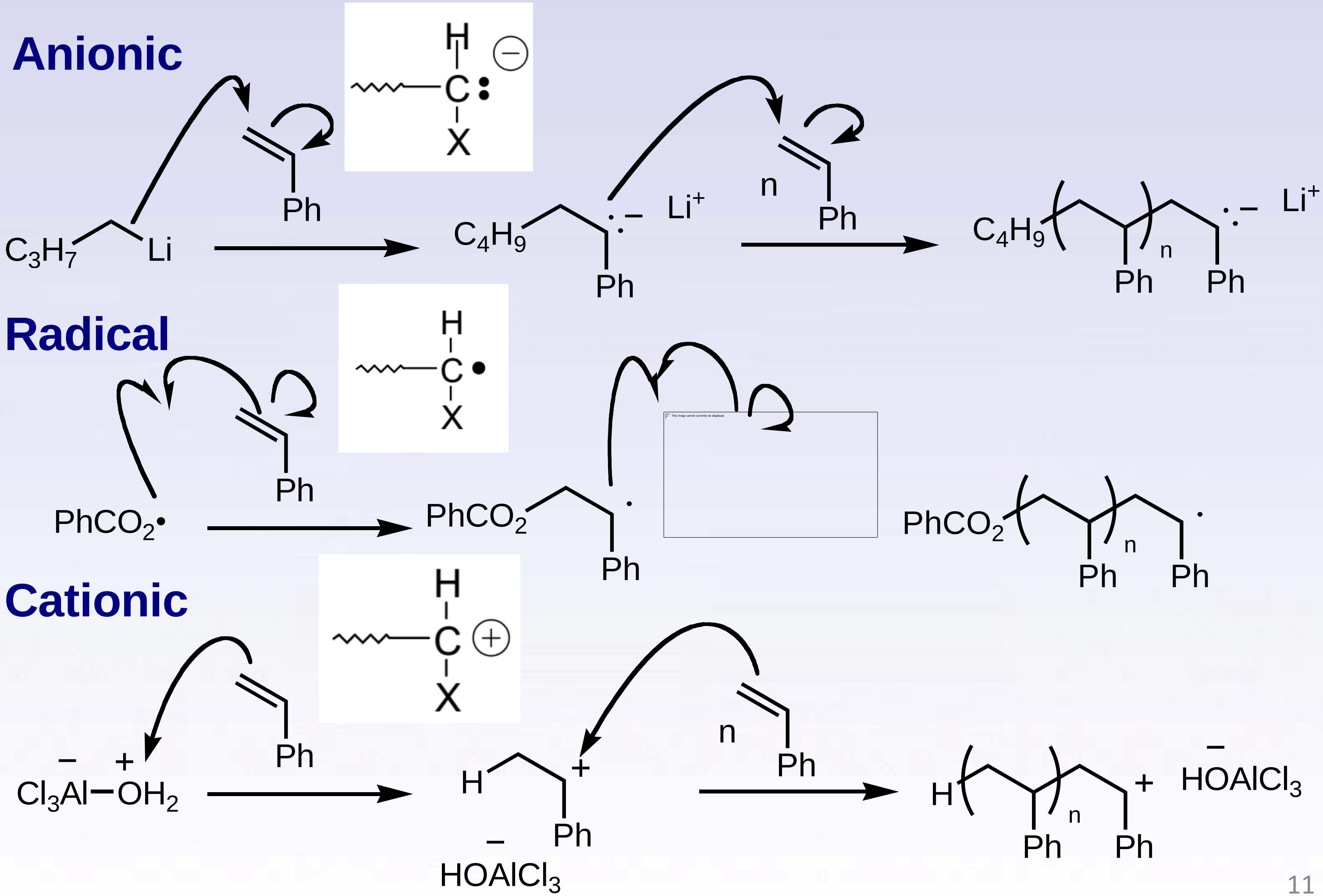




$$MW \propto \frac{k_{propagation}}{k_{termination}}$$

Polymers

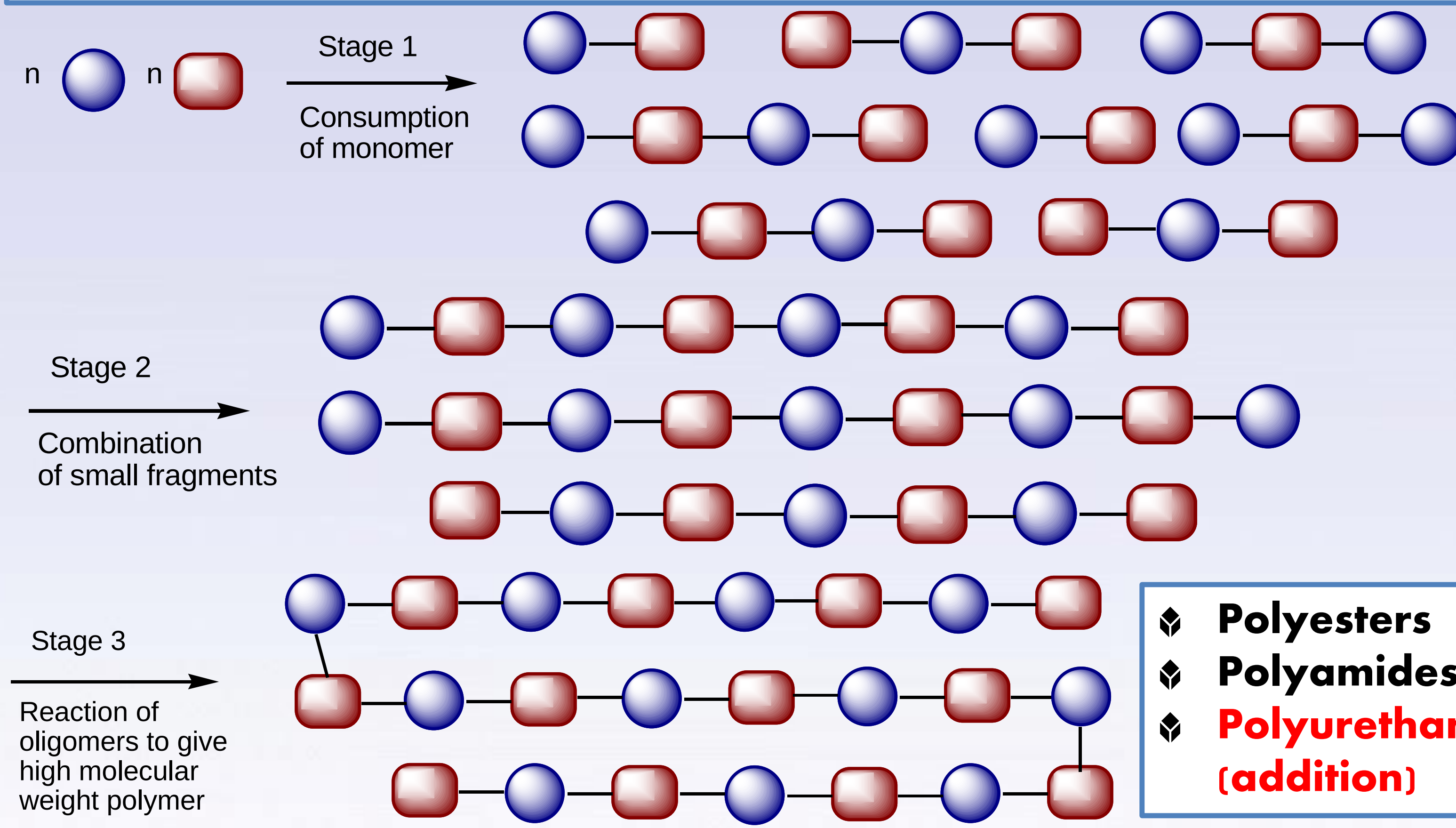
- **Chain-growth polymerization (typically addition polymerization)**



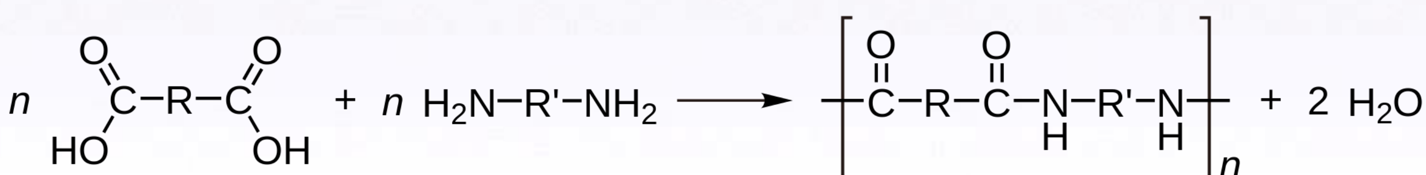
Photopolymerization Processes

Polymers

- **Step growth polymerization (typically condensation polymerization)**



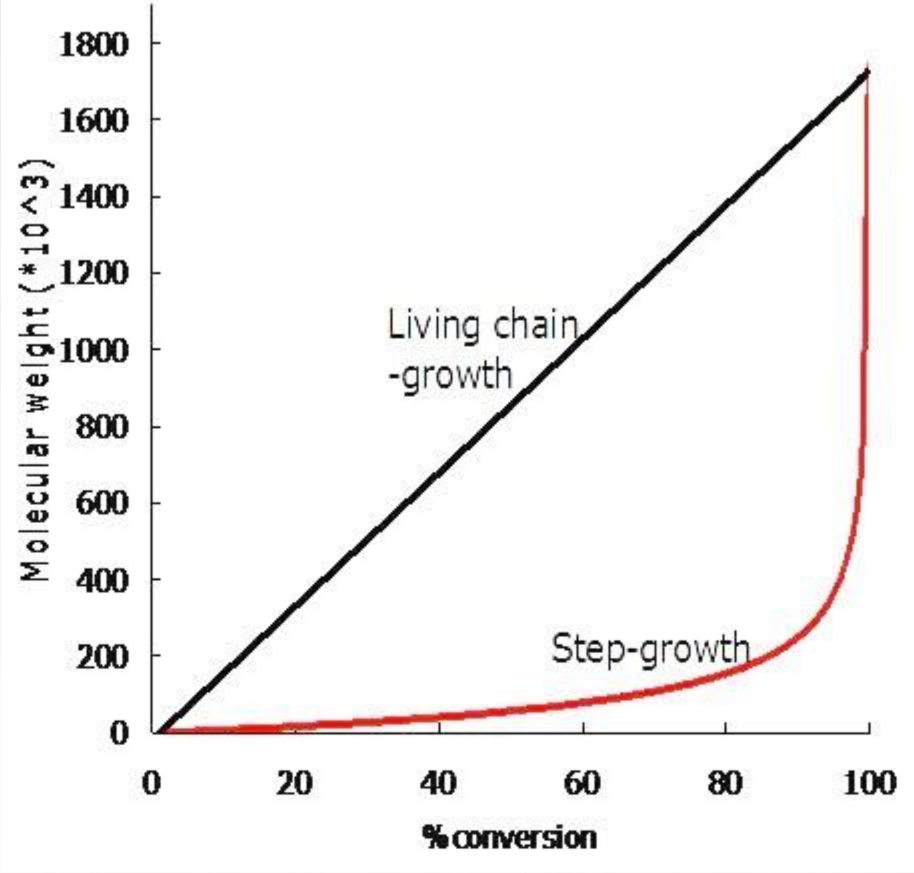
- **Polyesters**
- **Polyamides**
- **Polyurethanes (addition)**



Condensation polymerization

Polymers

Step VS Chain growth



Molecular weight

Photopolymerization Processes

Polymers

Step VS Chain growth

Step-growth polymerization	Chain-growth polymerization
Growth throughout matrix	Growth by addition of monomer only at one end or both ends of chain
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times
Similar steps repeated throughout reaction process	Different steps operate at different stages of mechanism (i.e. Initiation, propagation, termination, and chain transfer)
Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length	Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization
Ends remain active (no termination)	Chains not active after termination
No initiator necessary	Initiator required

Polymerization

- **Producing radicals**

$$A \xrightarrow{+E} A\cdot$$

- **Thermal decomposition:** bond dissociation energy ~ 100 – 165 kJ/mol; temperature range 0 – 100C; slow
- **Photochemical:** use energy from photo to break bonds, typically UV light for high energy photons
- **Redox reagents:** electron transfer reactions involving peroxides, persulfates, and metallic ions
- **Ionizing radiation:** high energy radiation: γ rays, x-rays, α particles, high speed electrons, etc.; Ionizing radiation: E = 10 keV to 100 MeV, VS. 1 – 6 eV for visible to UV light; Least practical

Photopolymerization Processes

Photo polymerization

- **Reactants**
  - **Monomers: M;** **Initiators: I**
  - **Free radicals: R•;** **Polymer chains: P•**
  - **Oxygen: O2;** **Solvent**
- **Reaction Stages**
  - **Initiation;** **Propagation**
  - **Termination;** **Inhibition**

$$\frac{\partial[I]}{\partial t} = -k_d[I] - D_I\left\{\frac{\partial^2[I]}{\partial x^2} + \frac{\partial^2[I]}{\partial y^2} + \frac{\partial^2[I]}{\partial z^2}\right\}$$

$$\frac{\partial[M]}{\partial t} = -k_p[M][R\bullet] - k_p[M][P\bullet] - D_M\left\{\frac{\partial^2[M]}{\partial x^2} + \frac{\partial^2[M]}{\partial y^2} + \frac{\partial^2[M]}{\partial z^2}\right\}$$

$$\frac{\partial[P\bullet]}{\partial t} = k_p[M][R\bullet] - 2k_{tc}[P\bullet]^2 - 2k_{td}[P\bullet]^2 - 2k_t[P\bullet][R\bullet] - k_{toxy}[P\bullet][O_2] - D_{P\bullet}\left\{\frac{\partial^2[P\bullet]}{\partial x^2} + \frac{\partial^2[P\bullet]}{\partial y^2} + \frac{\partial^2[P\bullet]}{\partial z^2}\right\}$$

$$\frac{\partial[P_d]}{\partial t} = k_{tc}[P\bullet]^2 + 2k_{td}[P\bullet]^2 + 2k_t[P\bullet][R\bullet] + k_{toxy}[P\bullet][O_2] - D_{Pd}\left\{\frac{\partial^2[P_d]}{\partial x^2} + \frac{\partial^2[P_d]}{\partial y^2} + \frac{\partial^2[P_d]}{\partial z^2}\right\}$$

$$\frac{\partial[R\bullet]}{\partial t} = 2k_d[I] - k_p[R\bullet][M] - 2k_t[P\bullet][R\bullet] - 2k_t[R\bullet]^2 - k_{tO_2}[O_2][R\bullet] - D_{R\bullet}\left\{\frac{\partial^2[R\bullet]}{\partial x^2} + \frac{\partial^2[R\bullet]}{\partial y^2} + \frac{\partial^2[R\bullet]}{\partial z^2}\right\}$$

$$\frac{\partial[O_2]}{\partial t} = -k_{O_2}[O_2][R\bullet] - k_{O_2}[O_2][P\bullet] - D_{O_2}\left\{\frac{\partial^2[O_2]}{\partial x^2} + \frac{\partial^2[O_2]}{\partial y^2} + \frac{\partial^2[O_2]}{\partial z^2}\right\}$$

$$Conversion = \frac{M_0 - M}{M_0}$$

12% conversion is a typically threshold value to be considered as solid

Initiation

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

$$R\bullet + M \xrightarrow{k_p} P\bullet$$

$$P\bullet + M \xrightarrow{k_p} P\bullet$$

Propagation

$$P\bullet + R\bullet \xrightarrow{k_p} P\bullet\bullet$$

$$P\bullet + P\bullet \xrightarrow{k_p} P\bullet\bullet$$

Termination

$$R\bullet + R\bullet \xrightarrow{k_t} 2R_{dead}$$

$$P\bullet + P\bullet \xrightarrow{k_t} P_{dead}$$

$$P\bullet + R\bullet \xrightarrow{k_t} P_{dead}$$

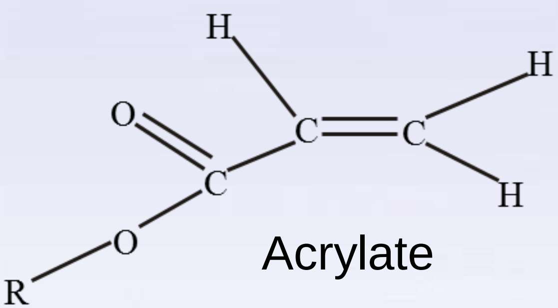
Inhibition

$$R\bullet + O_2 \xrightarrow{k_{tO_2}} R_{dead}$$

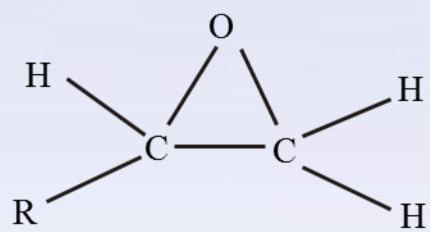
$$P\bullet + O_2 \xrightarrow{k_{tO_2}} R_{dead}$$

Photo polymerization

- **Commercial materials: combinations of acrylates and epoxies**
- **Acrylate: acrylic monomer + free radical photoinitiator**
- **Epoxy: epoxy monomer + cationic photoinitiator**
- **Acrylate and epoxy monomers do not react with one another. Result is interpenetrating polymer network.**
- **Variety of additives to stabilize resin, adjust viscosity, etc.**



Acrylate



Epoxy

- **H = Hydrogen atom**
- **C = Carbon atom**
- **R = Radical group**
  - **Enables cross-linking**

Acrylates

- **First photopolymer for SL**
- **Free radical polymerization**
- **High photospeed**
- **Issues of curled, warped parts (5 to 20% of shrinkage)**

Epoxy

- **Cationic polymerization**
- **Minimal volume change (ring-opening) (1 to 2% of shrinkage)**
- **Slower polymerization**

Credit: Dr. David Rosen @ Georgia Tech

Photopolymerization Processes

Photo polymerization

- **Commercial SL Resins**
  - **Photosensitizer (increase photo-efficiency)**
  - **Cationic reactive modifier (improves mechanical properties)**
  - **Antifoaming agents**
  - **Leveling agents**
  - **Thickening agents**
  - **Antioxidant**
  - **Stabilizers (prevent unwanted reactions)**

- **Acrylate and epoxy hybrids achieve synergy**
  - Interpenetrating Polymer Network (IPN)
  - Acrylate and epoxy monomers undergo independent polymerization.
  - Acrylate enhances the photospeed and reduces the energy requirement of the epoxy reaction.
  - Acrylate polymerizes more extensively in the presence of epoxy; plasticizing effect.
  - Hybrid system requires a shorter exposure to be cured than either of the two monomers taken separately.
  - Acrylate may decrease the inhibitory effect of humidity on the epoxy polymerization.

Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

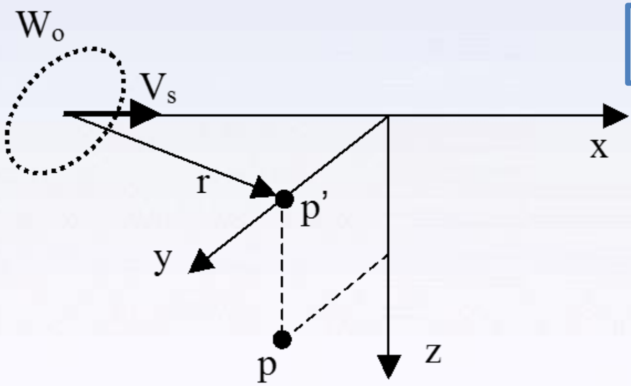
- **Reaction rates**
  - **controlled by concentrations of photoinitiators [I] and monomers [M].**
- **Average molecular weight of polymers is the ratio of the rate of propagation and the rate of initiation**
  - $v_o = R_p/R_i \propto [M]/[I]^{1/2}$
  - **R_i is the rate of initiation**
  - **R_p is the rate of propagation**
  - **Increasing photoinitiator concentration increases polymerization rate, but decreases molecular weight.**

Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

Material characteristics:

- C_d = cure depth = depth of resin cure as a result of laser irradiation [cm] [mils]
- E_c = critical exposure = exposure at which resin solidification starts to occur [mJ/cm2]
- D_p = depth of penetration of laser into a resin until a reduction in irradiance of 1/e is reached = key resin characteristic [cm] [mils]
- H(x,y,z) = irradiance (radiant power per unit area) at an arbitrary point in the resin = time derivative of E(x,y,z).[W/cm2]
- P_L = output power of laser [W]
- V_s = scan speed of laser [m/s]
- W_o = radius of laser beam focused on the resin surface [cm]



- **Irradiance and Exposure**

Beer-Lambert law: irradiance at a depth z

$$H(x,y,z) = H(x,y,0)e^{-z/D_p}$$

For a Gaussian laser

$$H(x,y,0) = H(r,0) = H_0 e^{-2r^2/W_0^2}$$

$$P_L = \int_{r=0}^{r=\infty} H(r,0)dA \Longrightarrow H_0 = \frac{2P_L}{\pi W_0^2}$$

Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

- **Irradiance and Exposure**
  - **Exposure is the energy per unit area and the time integral of irradiance**

$$E(y,0)=\int_{t=-\infty}^{t=\infty} H\left[r(t),0\right]dt$$

$$H(r,0)=\frac{2P_L}{\pi W_o^2}e^{-2r^2/W_o^2}$$

$t = W_0/V_s$

$$E(y,0)=\sqrt{\frac{2}{\pi}}\frac{P_L}{W_0V_s}e^{-2y^2/W_0^2}$$

Exposure at a given coordinate:

$$E(x,y,z)=\sqrt{\frac{2}{\pi}}\frac{P_L}{W_0V_s}e^{-2y^2/W_0^2}e^{-z/D_p}$$

Credit: Dr. David Rosen @ Georgia Tech

Photopolymerization Processes

Stereolithography
Overview
Polymer
Photo polymerization

Photo polymerization

Zone of influence

- **How far away from the scan is beyond the scan's influence?**
- **R = region around spot center that receives 99.99% of its exposure**

$$e^{-2R^2/W_o^2} = 1 - 0.9999$$

- **R = 2.146W_0**
- **The zone of influence is proportional to the beam radius.**

Characteristic exposure time

- $t_e \equiv 2\,R/\,V_s \approx 4.3\,W_o\,/\,V_s$
- **For laser scan velocity of 100 to 10000 mm/sec and W_0 of 100 um.**
- $43\ \mu s \le t_e \le 4.3\ ms$

Credit: Dr. David Rosen @ Georgia Tech

Photopolymerization Processes

Photo polymerization

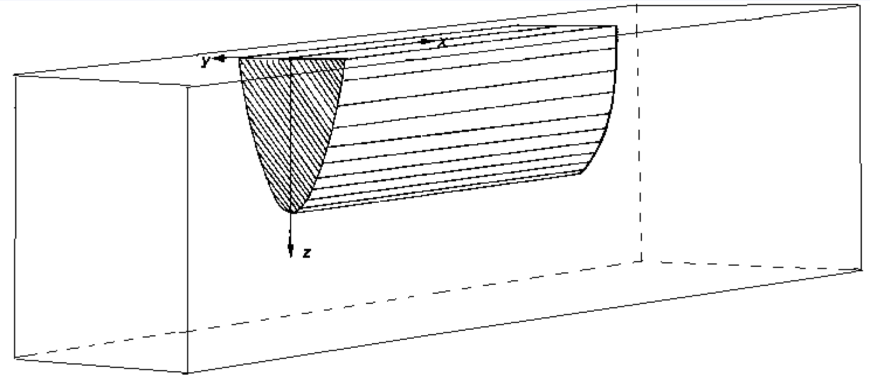
Critical exposure (a material property)

- **$E = E_c$**

$$E(x,y,z) = \sqrt{\frac{2}{\pi}}\frac{P_L}{W_0 V_s} e^{-2y^2/W_0^2} e^{-z/D_p} = E_c$$

- **Take logs of both sides to get cured line shape**

$$2\frac{y^{*2}}{W_o^2} + \frac{z^*}{D_p} = \ln\left[\sqrt{\frac{2}{\pi}}\frac{P_L}{W_o V_s E_c}\right]$$



Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

Cure depth

- **Exposure along the center of a scan vector is given as**

$$E(0,0) \equiv E_{max} = \sqrt{\frac{2}{\pi}} \frac{P_L}{W_o V_s}$$

- **Then, the relationship among E_{max}, C_d, E_c, and D_p can be derived as:** $C_d = D_p \ln(E_{max} / E_c)$

Line width

- **Set $z^* = 0$ (for cured line shape equation) → $L_w = W_o (2 C_d / D_p)^{1/2}$**
- **Line width is proportional to beam spot size.**
- **Line width increases as cure depth increases.**

Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

Photospeed

- Informal term for sensitivity of resin
- Resin characteristic, independent of SL machine, laser, optics system, etc.
- Indicated by E_c and D_p
- The faster the resin can be scanned, the higher the photospeed

$$V_s = \sqrt{\frac{2}{\pi}} \frac{P_L}{W_o E_c} e^{-C_d / D_p}$$

Mechanical properties of cured part

- Elastic modulus, tensile strength, and other properties improve as resin cures.
- Acrylates cure first (provide shape); epoxies cure slower to improve properties.
- Properties also improve with increased exposure, to a point.
- Then, resins age and properties change over time (weeks, months).

Credit: Dr. David Rosen @ Georgia Tech

Photo polymerization

Length scales

- $d_m << \lambda << S << D_p < W_o < R << L$
- d_m = length of polymer molecule 0.001 to 0.007μm,
- λ = laser wavelength = 0.325 to 0.351 μm,
- S = shrinkage length = 1 to 7 μm
- D_p = penetration depth = 0.1 to 0.2 mm = 100 to 200 μm,
- W_o = laser spot size = 250 μm,
- R = zone of influence of laser spot = 2.146 W_o = 540 μm,
- L = typical part dimension = 0.1 m = 10000 μm.

Time scales

- $t_t << t_k << t_e << t_{s,o} < t_{s,c} << t_d$
- t_t = time for a photon to traverse a layer = 10^{-12} seconds,
- t_k = photopolymer kinetic reaction rate = ~1-10 us,
- t_e = exposure time for zone of influence = 50 to 2000 us,
- $t_{s,o}$ = onset of measurable shrinkage = 0.4 – 1 s,
- $t_{s,c}$ = completion of measurable shrinkage = 4 – 10 s
- t_d = scan time for layer = 10 – 300 s.

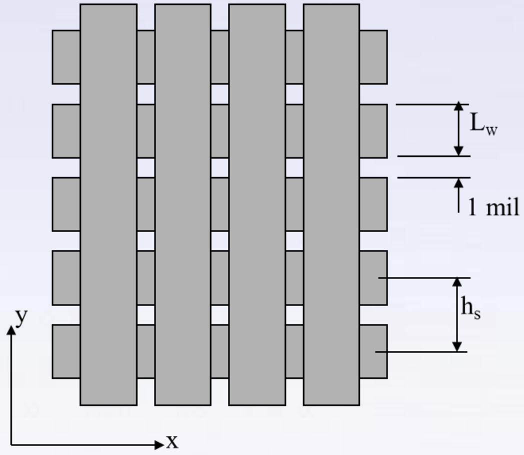
Credit: Dr. David Rosen @ Georgia Tech

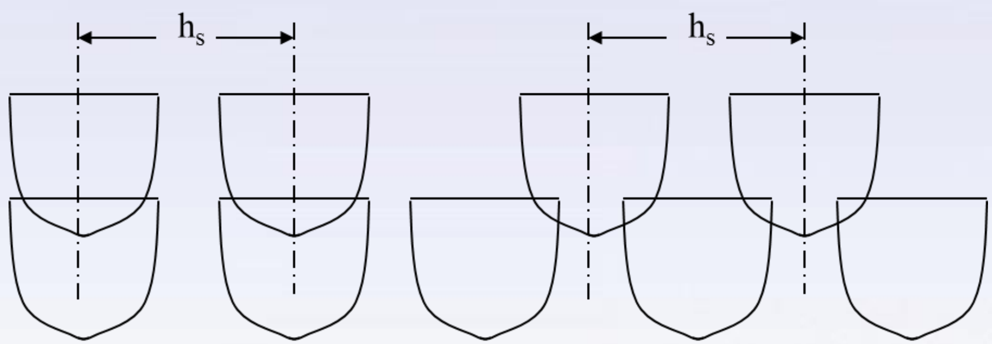
Photopolymerization Processes

Photo polymerization

Scan patterns

- **WEAVE – late 1990**
- **STAR-WEAVE – (Staggered hatch, Alternating sequence, Retracted hatch), late 1991**
- **ACES – Accurate, Clear, Epoxy Solids, 1993. Necessary for emerging epoxy resins.**
- **Prior to WEAVE, scan patterns were ad hoc and did not work well**





a) WEAVE b) STAR-WEAVE

Credit: Dr. David Rosen @ Georgia Tech

Photopolymerization Processes

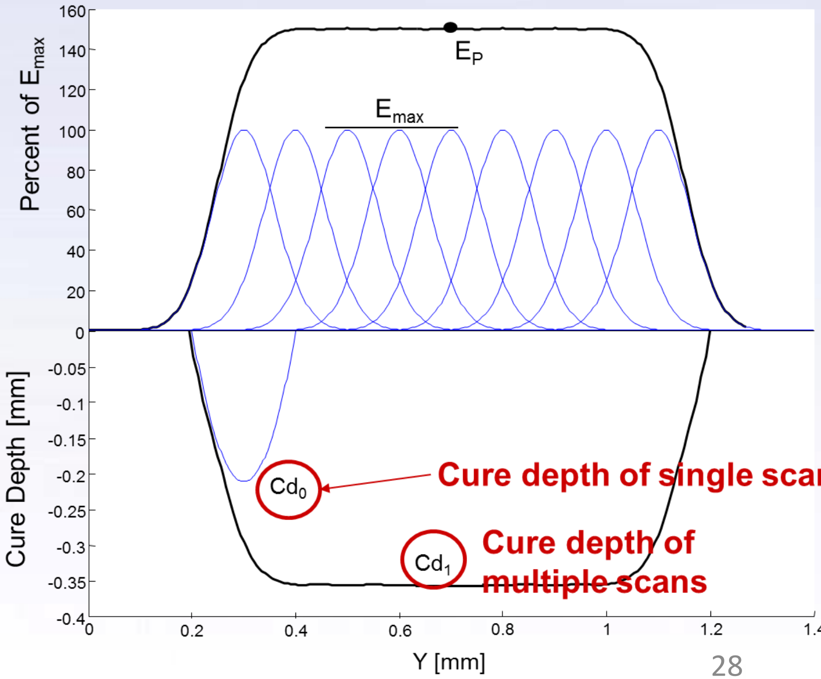
Photo polymerization

WEAVE Scan

- First pass, cure depth $C_d(1)$ is achieved, based on exposure, $E_{max}(1)$.
- Second pass, same amount of exposure is provided -- cure depth increases to $C_d(2)$.
- $C_d(2) = D_p \ln[2\ E_{max}(1) / E_c] = D_p \ln[2] + D_p \ln[E_{max}(1) / E_c]$
- $C_d(2) = C_d(1) + D_p \ln[2] = C_d(1) + D_p(0.693)$
- Second pass provides enough exposure to cure layer to previous layer.

ACES Scan

- Provides SLA machine operator with many scan pattern options.
- Objective: cure more resin in a layer before proceeding to next layer (98%).
- Accomplished by overlapping hatch vectors.
- X and Y scans, similar to STAR-WEAVE.



Credit: Dr. David Rosen @ Georgia Tech

Stereolithography

Overview

Polymer

Photo polymerization