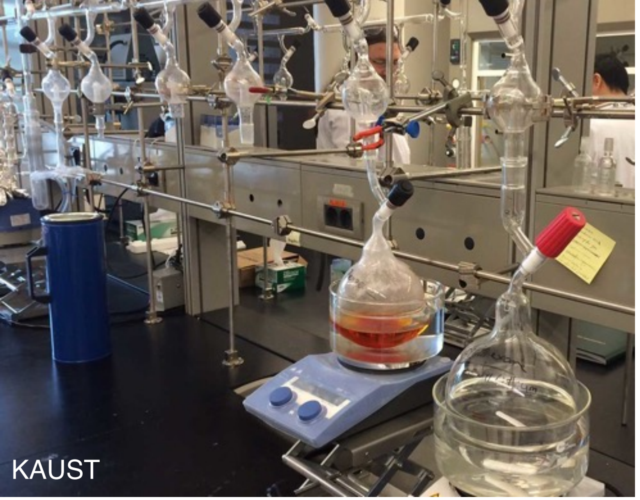
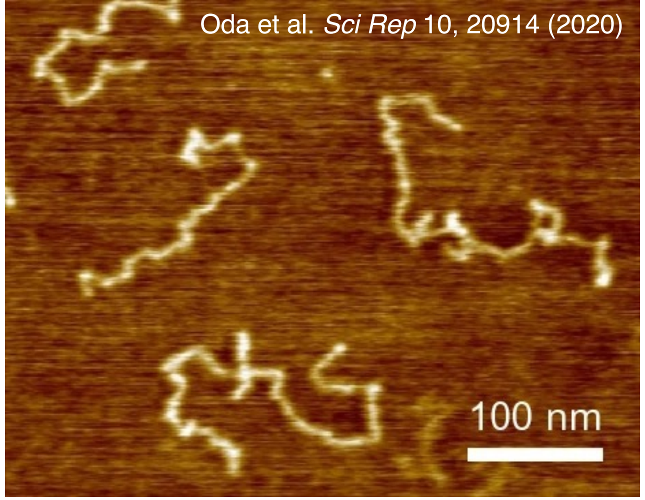

KAUST


Oda et al. *Sci Rep* 10, 20914 (2020)

Materials Engineering I (MSE 214)

Lecture 5: Properties and Processing

Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

Exercise 3 Recap

Q4. For a radical polymerization with bimolecular termination, the polymer produced contains an average of 1.30 initiator fragments per polymer molecule. Calculate the relative extents of termination by disproportionation and coupling, assuming that no chain-transfer occurs.

Key thing to remember:

$$\mathrm{I\text{-}(M)_n\text{-}M^\bullet + {}^\bullet M\text{-}(M)_y\text{-}I \xrightarrow{k_{tc}} I\text{-}(M)_{n+y+2}\text{-}I}$$

Coupling = each chain has 2 initiator fragments

$$\mathrm{I\text{-}(M)_n\text{-}M^\bullet + {}^\bullet M\text{-}(M)_y\text{-}I \xrightarrow{k_{td}} I\text{-}(M)_n\text{-}M + M{=}M\text{-}(M)_{y-1}\text{-}I}$$

Disproportionation = each chain has 1 initiator fragment

$$b = \frac{2}{2-a}$$

b is the average number of initiator fragments per polymer

a is the fraction of chains that terminate by coupling

Exercise 3 Recap

Q5. Using what you know about chain transfer, draw a schematic that describes the formation of long branches.

Intra-chain transfer

Inter-chain transfer

Key thing to remember: Chain transfer can happen with many things!
(Monomer, solvent, polymer, atmosphere, etc.)

Exercise 3 Recap

Q7. This question is basically about finding the right formulas to use.

Question: Why do k_t and k_p have different units?

Ans: The units for *k* depend on the order of the reaction

First order reaction:

Rate = *k* [A]

The unit for rate is always mol/L.s

The unit for [A] is always mol/L

↓

The unit for *k* has to be 1/s

Second order reaction:

Rate = *k* $[A]^2$

The unit for rate is always mol/L.s

The unit for [A] is always mol/L

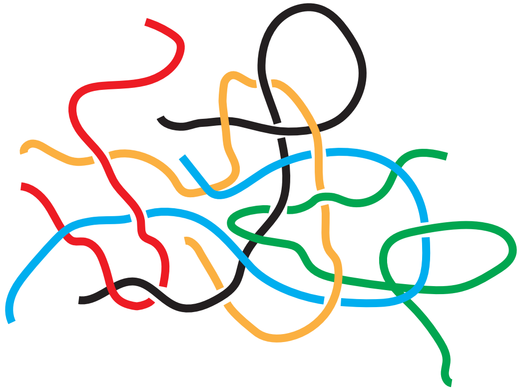
The unit for $[A]^2$ is mol^2/L^2

↓

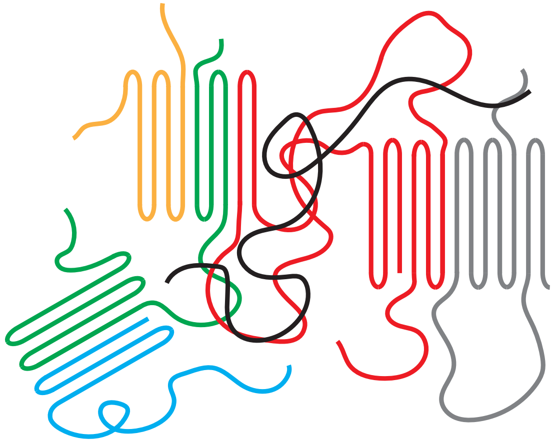
The unit for *k* has to be L/mol.s

Week 4 Recap

Amorphous



Semi-crystalline



Polymers states:

Can be completely amorphous

Can be semi-crystalline

Can never be 100% crystalline

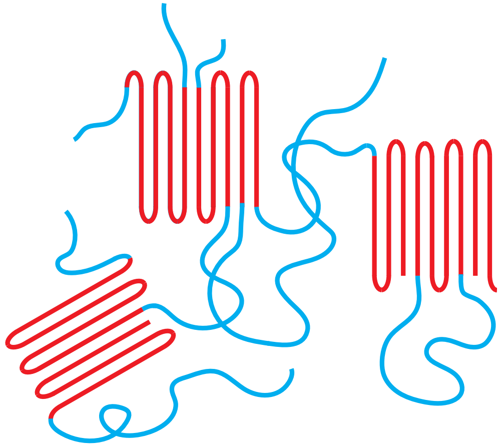
Crystallization is **thermodynamically** favorable

→Lowers energy state

Crystallization also depends on **kinetics** →

Is there enough time to crystallize?

Thermal Transitions



Glass transition temperature (T_g)

→ Temperature range where <u>amorphous regions</u> starts to move

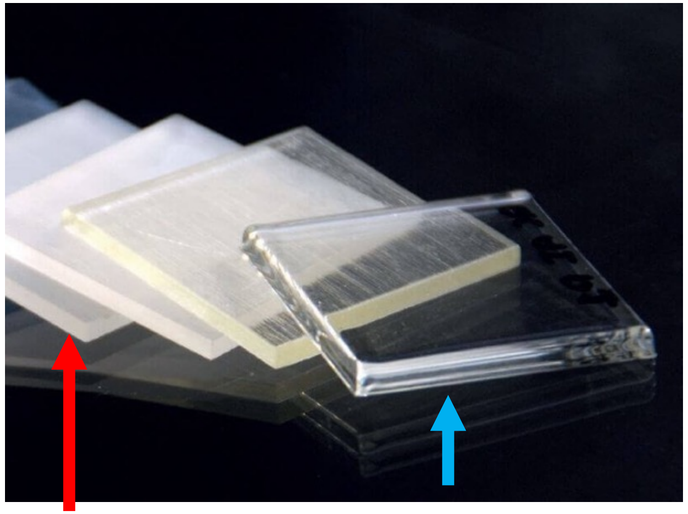
Melting temperature (T_m)

→ Temperature range where <u>crystalline regions</u> starts to move

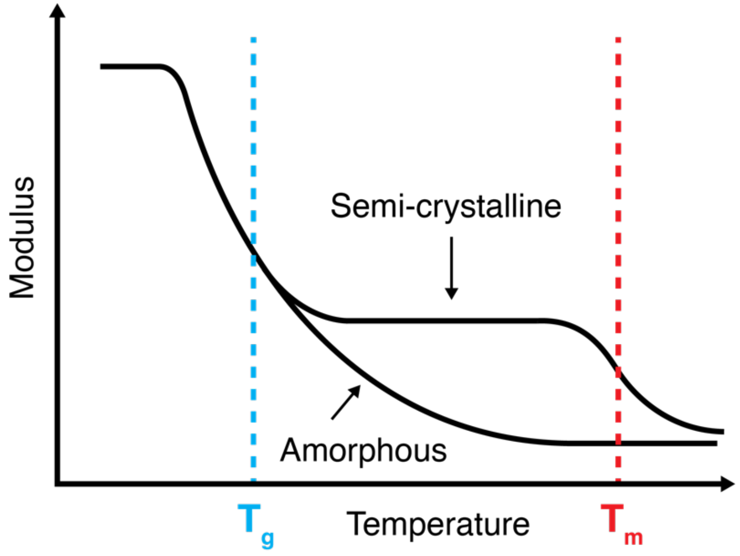
Week 4 Recap

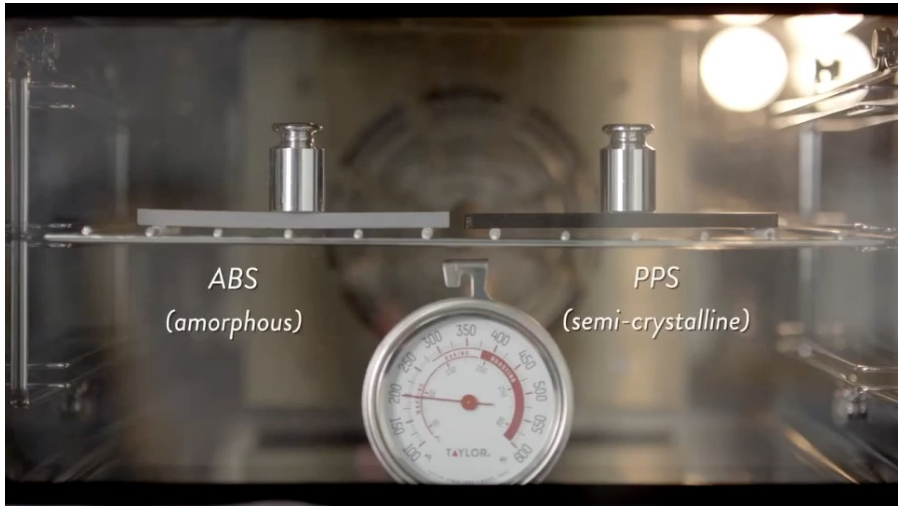
The T_g and T_m impacts polymer properties

Optical



Mechanical





Degree of crystallinity is inversely proportionate to light transmission

The T_g and T_m impact the mechanical properties of the polymer at the operating temperature

Week 4 Recap

The degree of crystallinity impacts polymer properties

Density

Crystalline polymers are more dense than amorphous ones

Determine degree of crystallinity using density

$$X_c = \frac{\rho_c(\rho - \rho_a)}{\rho\,(\rho_c - \rho_a)}$$

X_c = crystalline mass fraction
ρ = density of semicrystalline sample
ρ_c = density of 100% crystalline polymer
ρ_a = density of 100% amorphous polymer

Solvent/chemical resistance

Crystallinity imparts chemical and solvent resistance

Key takeaway 1:

If you understand the impact of $\mathbf{T_g}$ and $\mathbf{T_m}$ on properties, you can select polymers for your own use cases

Key takeaway 2:

If you understand the impact of **crystallinity** on properties, you can select polymers for your own use cases

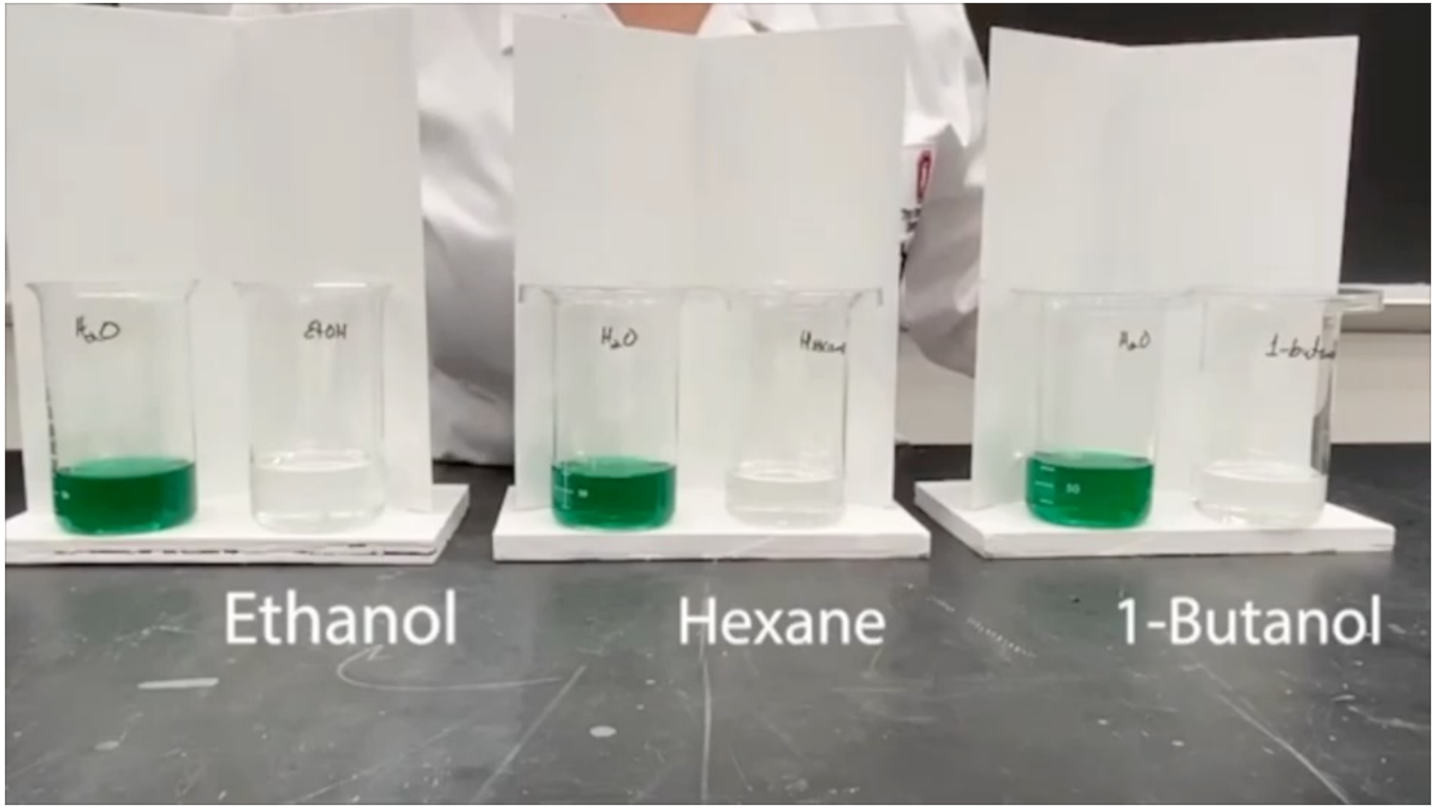
Week 5 Learning Objectives

- **Understand why polymer blends are used**
- **Understand that polymers are viscoelastic materials**
- **Understand the difference between a good and poor solvent**
- **Understand the general properties of polymers**
- **Be aware of the common polymer manufacturing methods used today**
- **Understand the basic working principles of material extrusion and vat photopolymerization additive manufacturing**
- **Understand the basic working principles of photolithography**

Polymer Blends: Beyond a Single Polymer

Similar in concept to composites: mix two polymers* to get in-between properties

But polymers don't always like to mix with each other! → Degree of miscibility



Miscible blends → Homogenous

Immiscible blends → Phase separation

Partially miscible blends → Homogenous only under certain conditions

*not to be confused with copolymerization!

T_g of Polymer Blends

Miscible blends

One T_g value that is inbetween the T_gs of both polymers

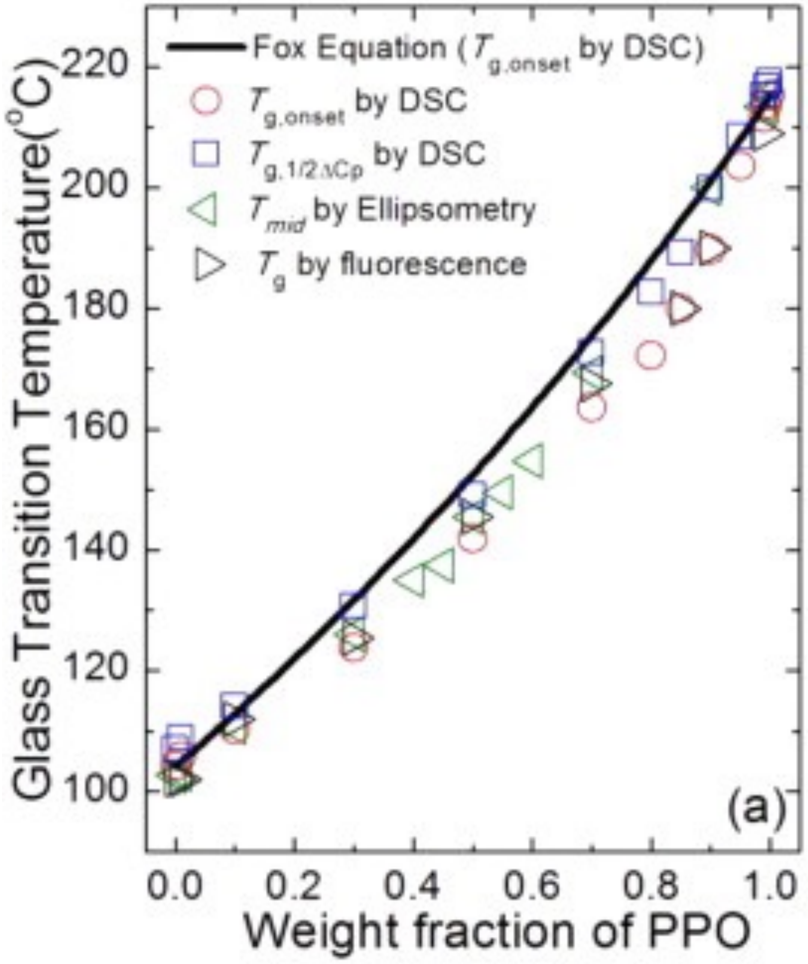
$$\frac{1}{T_g} = \frac{M_1}{T_{g,1}} + \frac{M_2}{T_{g,2}} \quad \left(\text{Fox equation}\right)$$

T_g = Glass transition for polymer blend
$T_{g,1}$ = Glass transition for polymer 1
$T_{g,1}$ = Glass transition for polymer 2

M_1 = Mass fraction of polymer 1
M_2 = Mass fraction of polymer 2

Miscible blends allow you to tune properties without having to resynthesize the polymer

Poly(phenylene oxide) (PPO) blended with polystyrene



Aside from tuning T_g, other properties can also be tuned, e.g. mechanical properties

Jin, Kailong, and John M. Torkelson. *Polymer* 65 (2015): 233-242.

T_g of Polymer Blends

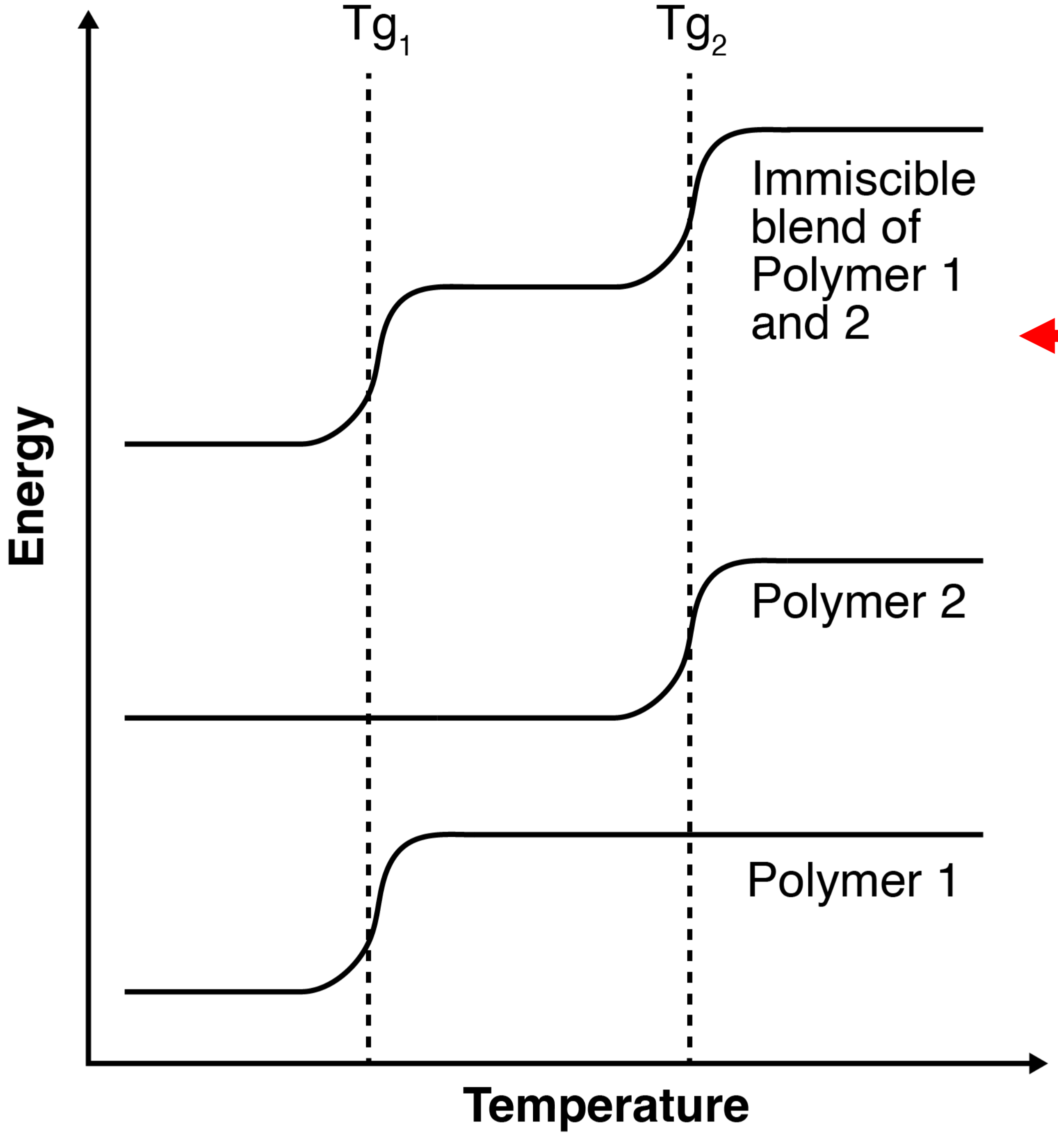
Immiscible blends

Two T_g values

Each T_g value is associated with one polymer in the immiscible blend

T_g(s) can be used to determine if a blend is miscible or not

(If these were semi-crystalline polymers, you would expect 2 T_ms as well!)



We won't cover this but Differential Scanning Calorimetry is one technique used to determine T_g

Why use immiscible blends?

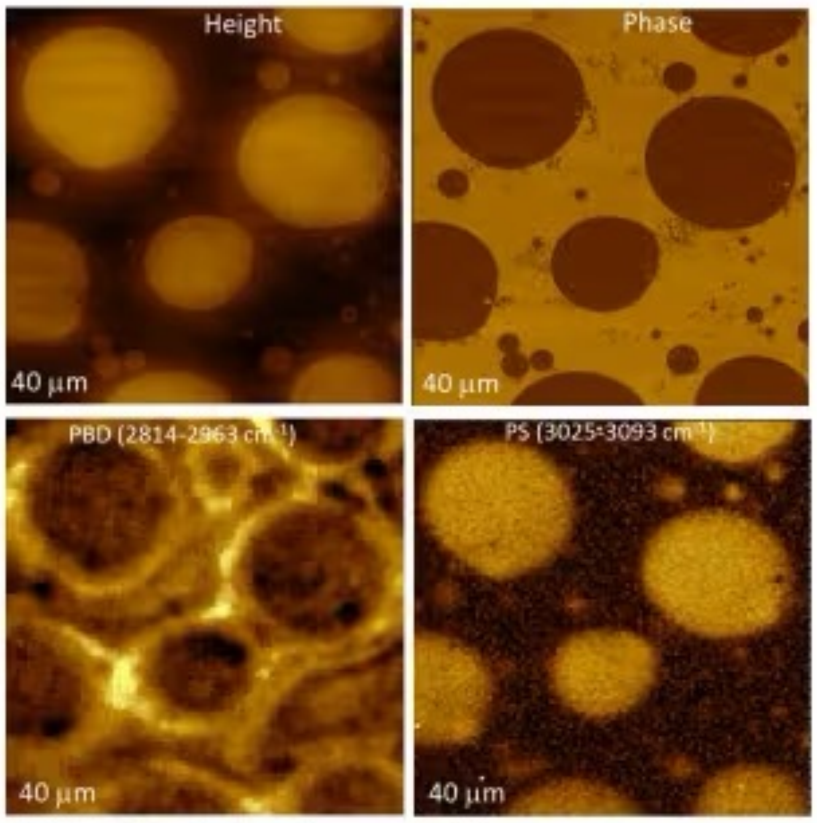
Access to unique microstructures that are inaccessible to homogenous polymers
→ New properties → New applications

High Impact Polystyrene (HIPS)

HIPS = Immiscible blend of polystyrene and polybutadiene

Atomic Force Microscopy (AFM) of HIPS →

Polybutadiene spheres in polystyrene matrix



Polystyrene = strong and brittle

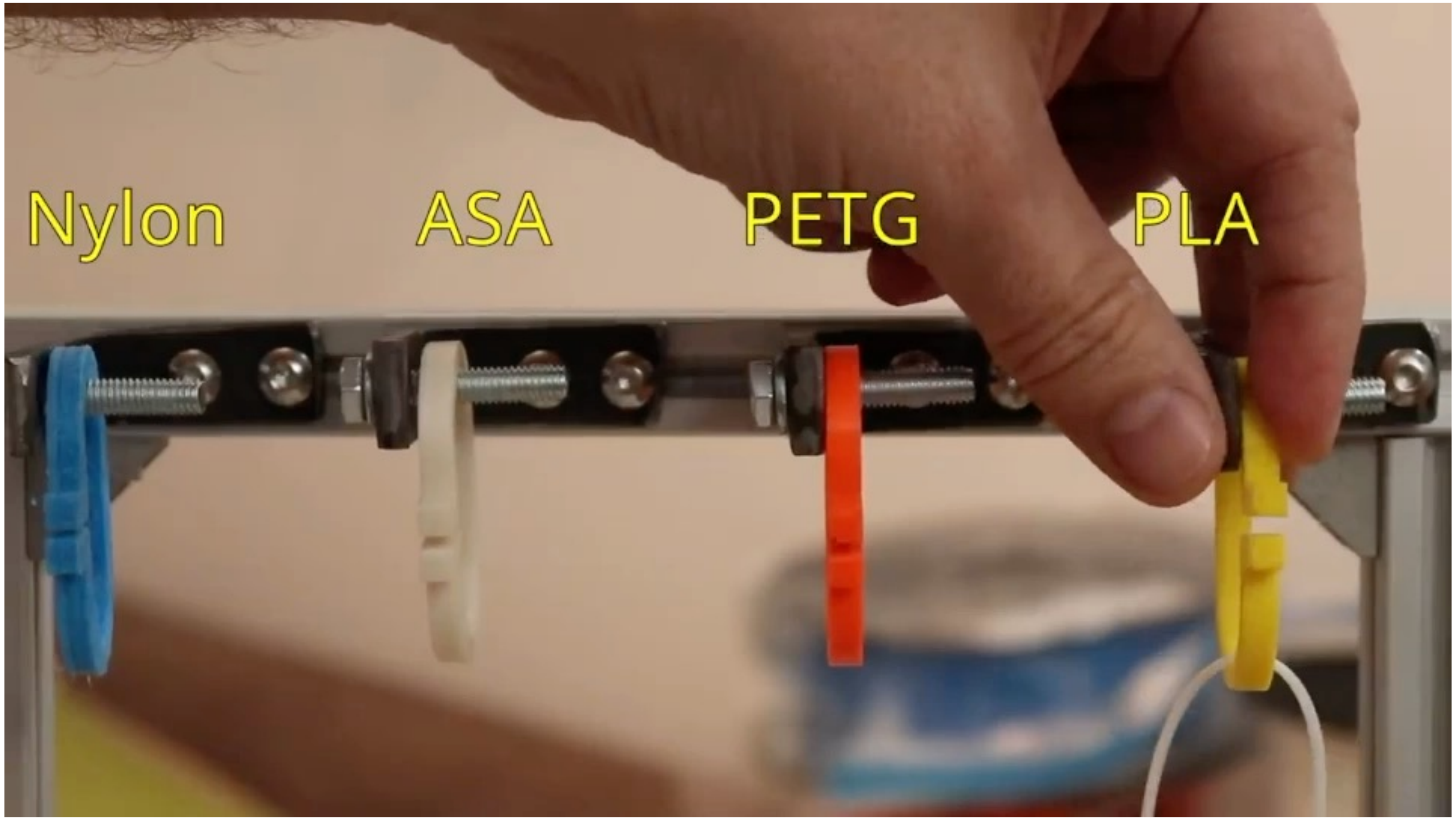
Polybutadiene = soft and tough

Rubbery polybutadiene phases helps to dissipate energy that would have caused the polystyrene to break

HIPS = Strong and tough

Mechanical Properties of Polymers

Polymers are viscoelastic* materials → Time-dependent mechanical properties



Creep:
Slow deformation over time
with a constant load

*viscoelasticity can be an entire course in itself!

Mechanical Properties of Polymers

Polymers are viscoelastic* materials → Time-dependent mechanical properties

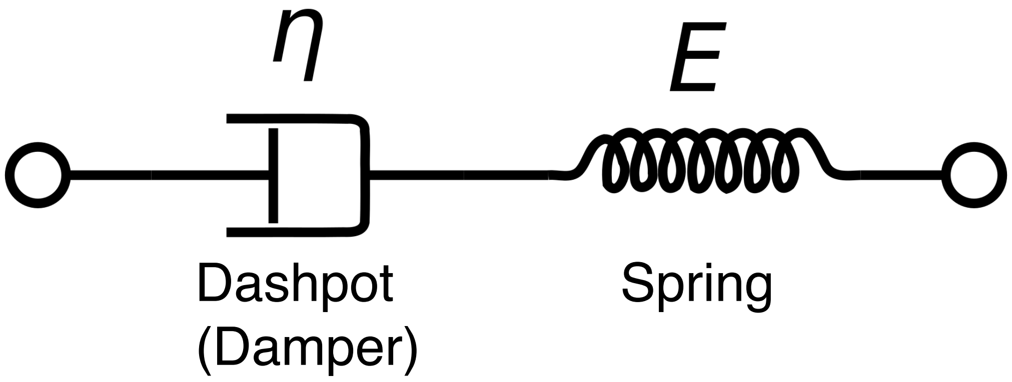
Polymers can deform in two ways:

1. Distortion between atoms → This is small and quick
2. Movement and deformation of the polymer chains itself → Depends on chain mobility

Below T_g, we only see the first behavior
Way above T_g, we see both behaviors, but chains can move quickly to respond to deformation

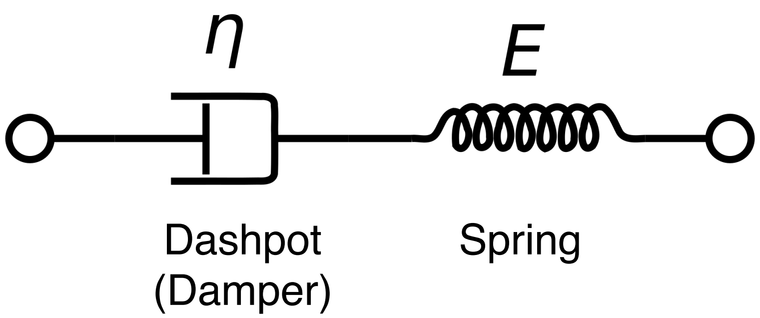
Close to T_g, we see both behaviors but chains move slowly to respond to deformation
→ Time and temperature dependent response to deformation

A very simplified model to describe this: Maxwell model



*viscoelasticity can be an entire course in itself!

Maxwell model



Spring has an elastic constant *E*

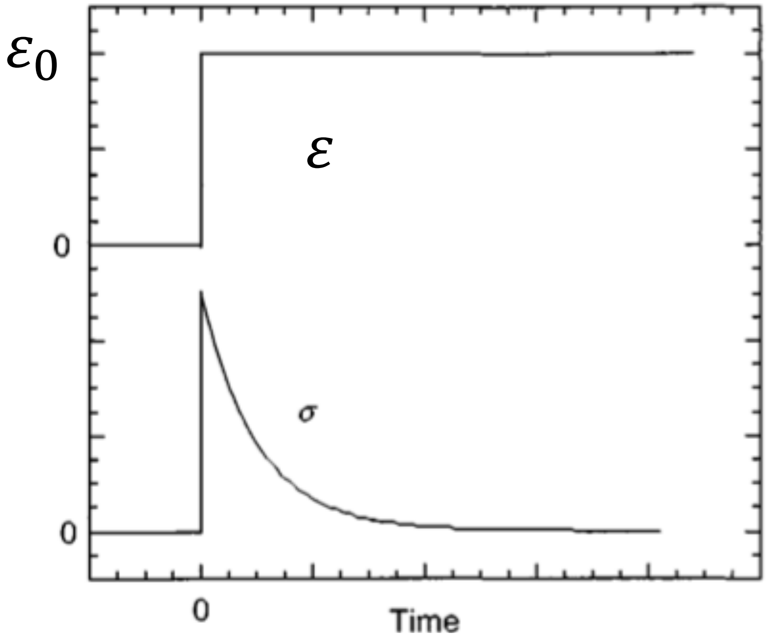
Dashpot has a viscosity η

Some key relationships

$$\sigma_s = E\varepsilon_s$$

$$\sigma_d = \eta\frac{d\varepsilon_d}{dt} = \eta\dot{\varepsilon}_d$$

What happens if we apply an instanteous strain ε_0 at t = 0



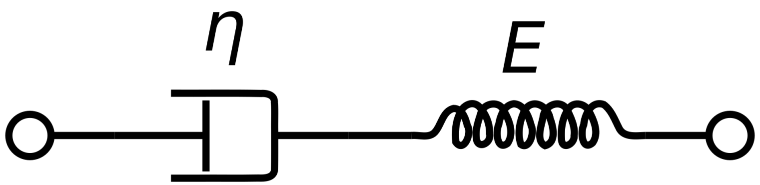
At short times, dashpot doesn't move. Strain all from spring

Stretched spring exerts a force on dashpot → Dashpot will move

Spring will relax to rest, no more stress.

Long term response is that of a liquid

Maxwell model



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Dashpot has a viscosity *η*

Some key relationships

$$\sigma_s = E\varepsilon_s$$

$$\sigma_d = \eta \frac{d\varepsilon_d}{dt} = \eta \dot{\varepsilon}_d$$

What happens if we apply an instanteous strain ε_0 at t = 0

$$\varepsilon_0 = \varepsilon_s + \varepsilon_d$$

Since strain is constant for t > 0

$$\frac{d\varepsilon_0}{dt} = \frac{d\varepsilon_s}{dt} + \frac{d\varepsilon_d}{dt} = 0$$

Substitute the key relationships

$$\frac{d\varepsilon_0}{dt} = \frac{d}{dt}\left(\frac{\sigma_s}{E}\right) + \frac{\sigma_d}{\eta} = 0$$

$$\frac{1}{E}\frac{d\sigma_s}{dt} + \frac{\sigma_d}{\eta} = 0$$

Since $\sigma(t) = \sigma_d(t) = \sigma_s(t)$

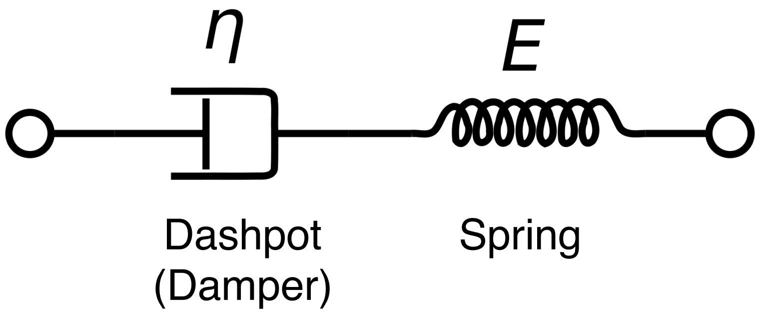
$$\frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\sigma = \sigma_0 e^{-\frac{t}{\tau}}$$

Where $\tau = \frac{\eta}{E}$

At constant strain, **stress relaxes!**

Maxwell model



Spring has an elastic constant E

Dashpot has a viscosity η

Some key relationships

$$\sigma_s = E\varepsilon_s$$

$$\sigma_d = \eta\frac{d\varepsilon_d}{dt} = \eta\dot{\varepsilon}_d$$

What happens if we apply an instanteous stress σ_0 at t = 0

$$\varepsilon = \varepsilon_s + \varepsilon_d$$

$$\varepsilon = \frac{\sigma_s}{E} + \frac{\sigma_d}{\eta}\int_0^t dt$$

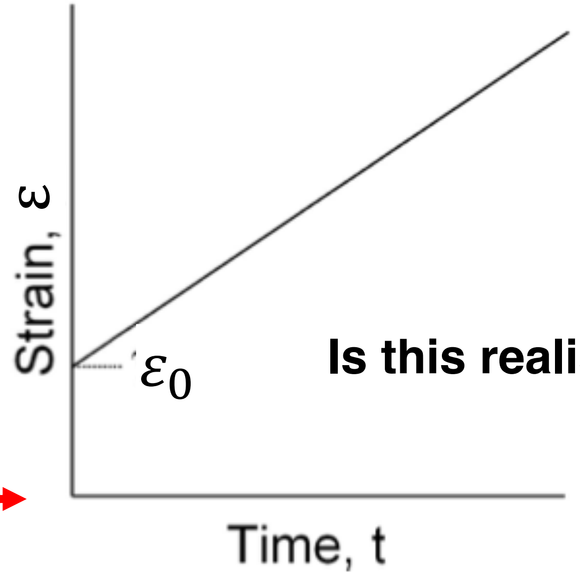
$$= \frac{\sigma_s}{E} + \frac{\sigma_d}{\eta}t$$

Since $\sigma_0 = \sigma_d = \sigma_s$

$$\varepsilon = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta}t$$

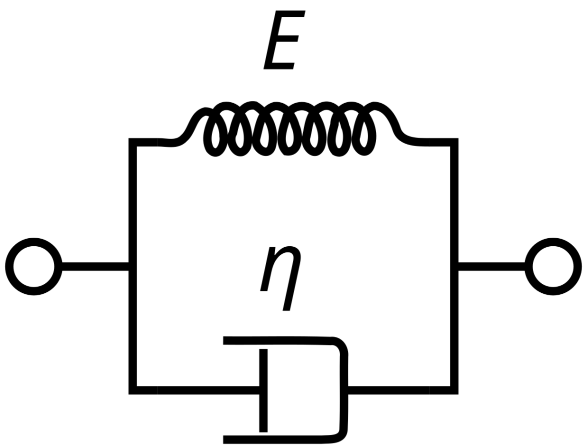
$$\varepsilon = \frac{\sigma_0}{E}(1 + \frac{E}{\eta}t)$$

$$\boxed{\varepsilon = \varepsilon_{s,0}\,(1 + \frac{t}{\tau}) \quad \text{Where } \tau = \frac{\eta}{E}}$$



Is this realistic?

Kelvin-Voigt model*

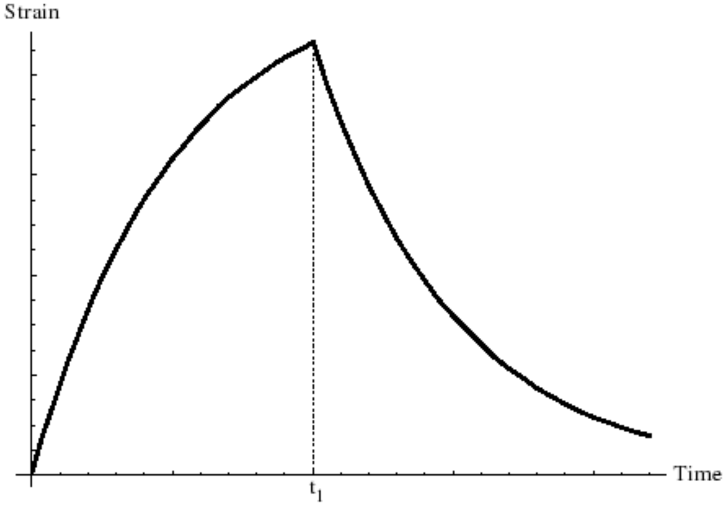


Spring has an elastic constant *E*

Dashpot has a viscosity η

Connected in parallel this time!

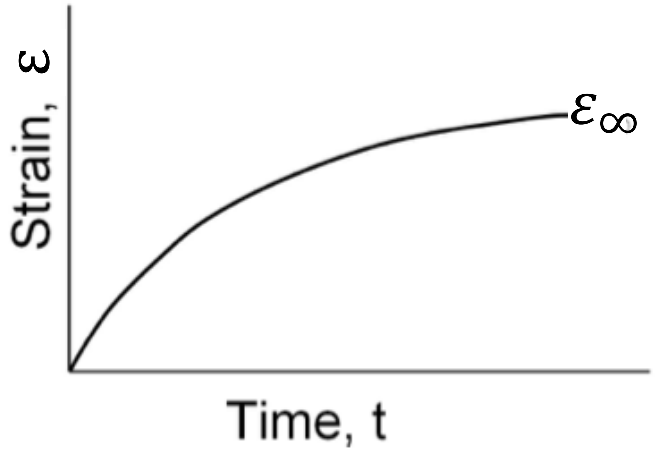
Constant stress applied up to t_1
Stress released at t_1



$$\varepsilon = \varepsilon_{s,0}\,(1 - e^{-\frac{t}{\tau}})$$

Where $\tau = \dfrac{\eta}{E}$

Constant stress applied for infinite time → approach a constant

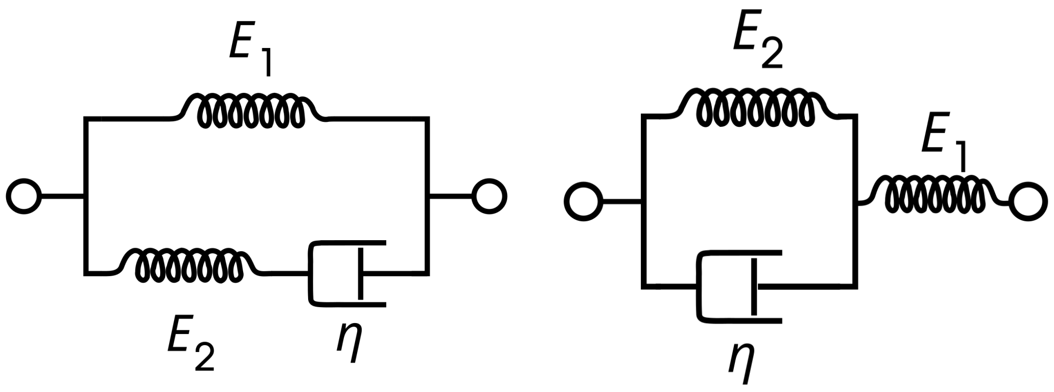


What is ε_∞?

Voigt model can demonstrate creep but not stress relaxation

*We'll derive the math in the exercise

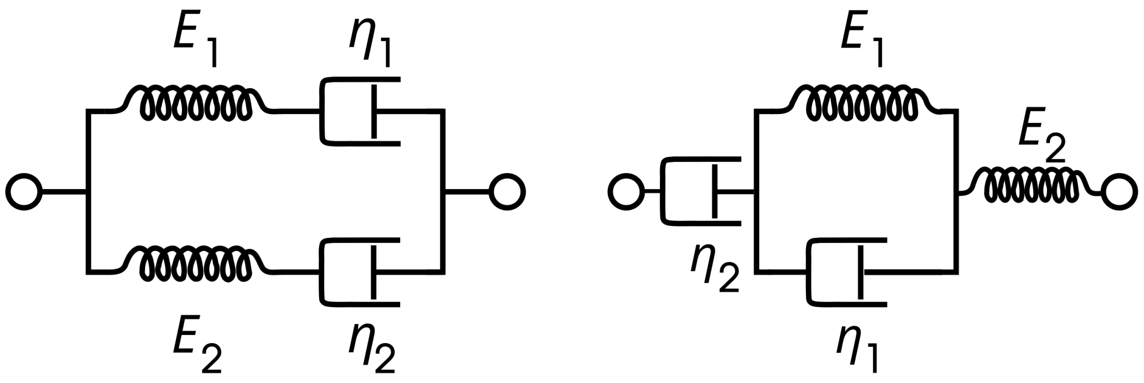
Standard linear solid model / Zener model



Maxwell representation

Kelvin representation

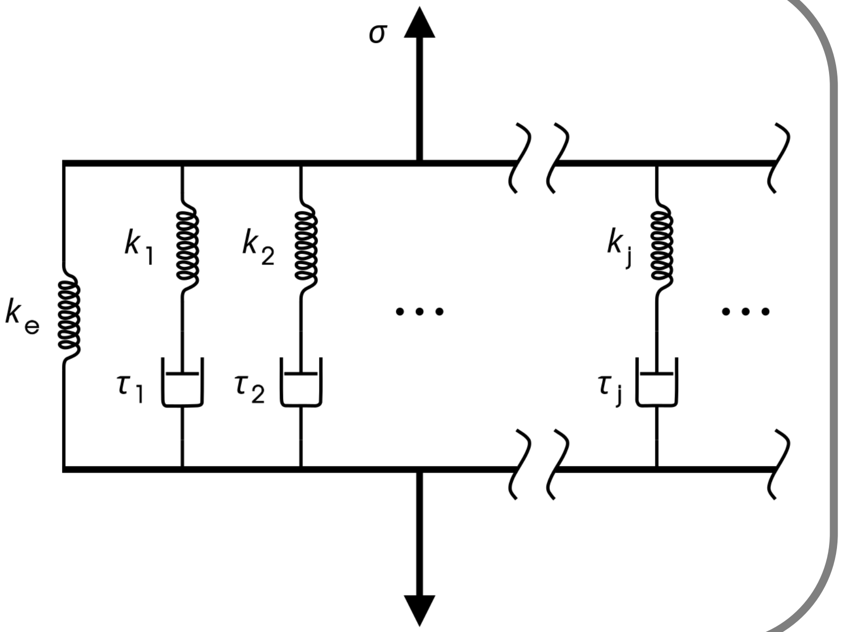
Burgers model



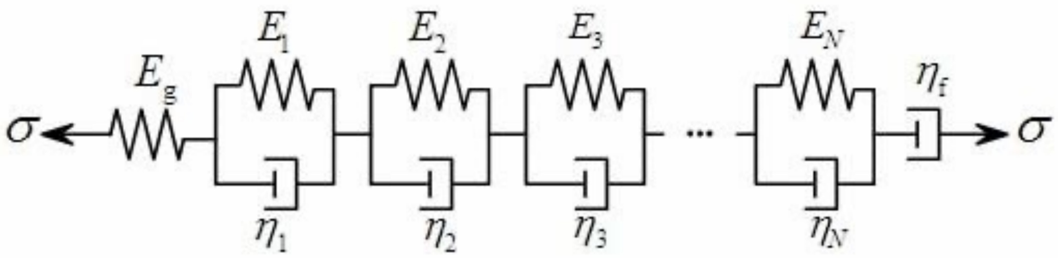
Maxwell representation

Kelvin representation

Generalized Maxwell model



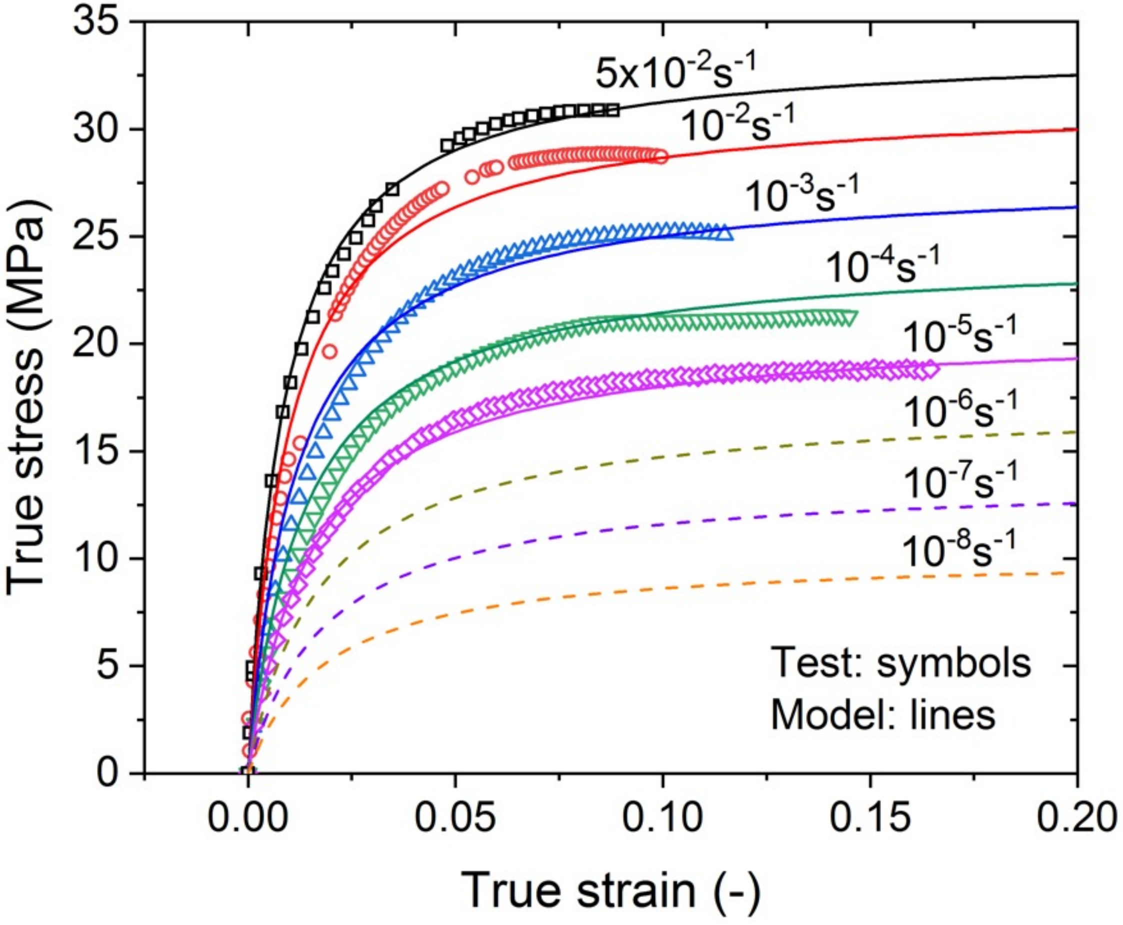
Generalized Kelvin-Voigt model



Many models exist! Used to model different viscoelastic behavior

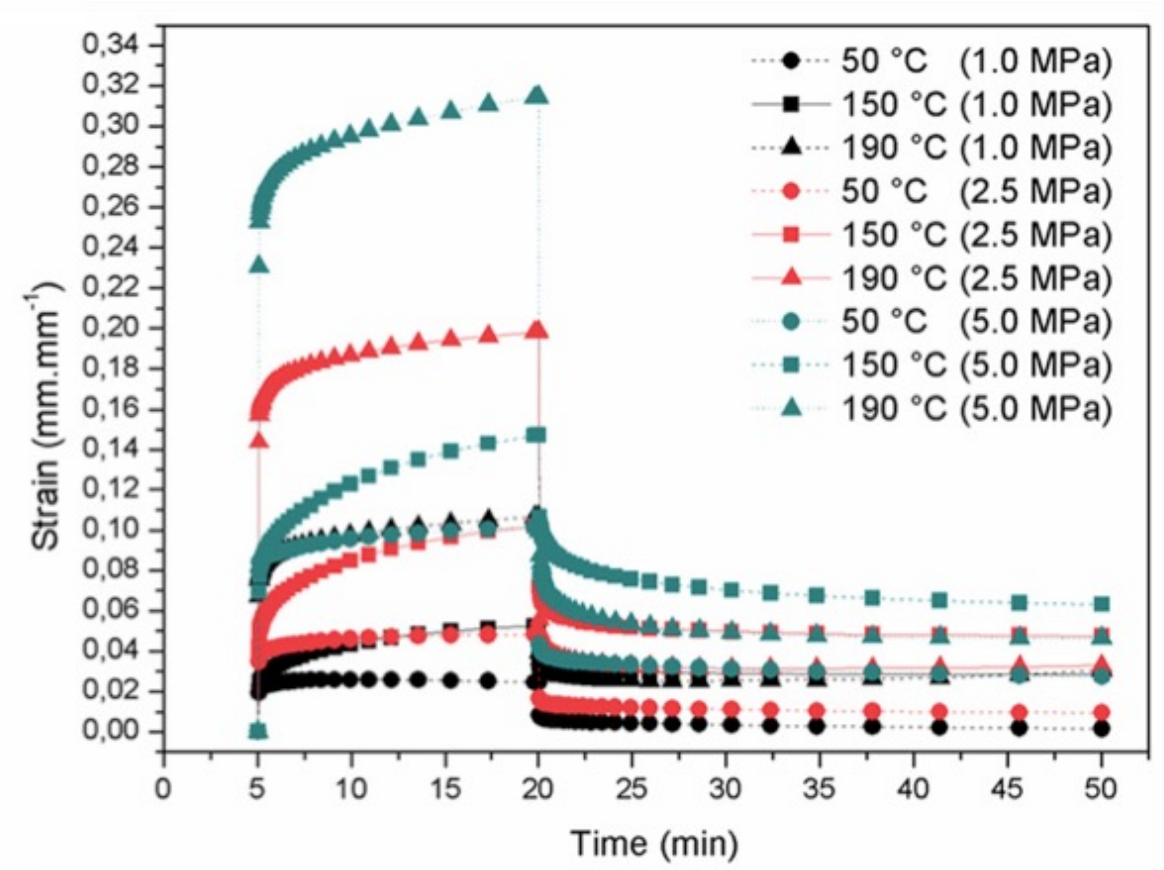
Viscoelasticity needs to be taken into consideration during operation

The strain rate at which you use/test polymers are important!



Li, Yan, et al. *Polymers* 14.7 (2022): 1357.

The temperature you test also plays a huge role!

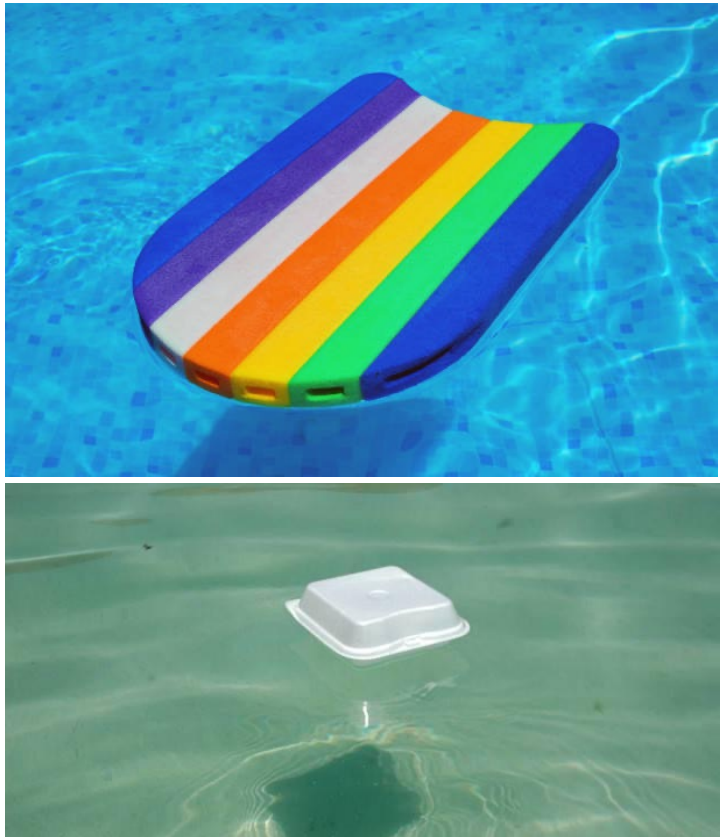


Monticeli et al. *The Journal of Strain Analysis for Engineering Design* 55 (2020): 109-117.

Polymers and Solvents

Why do some polymers dissolve in some solvents and not in others?

Polystyrene in water

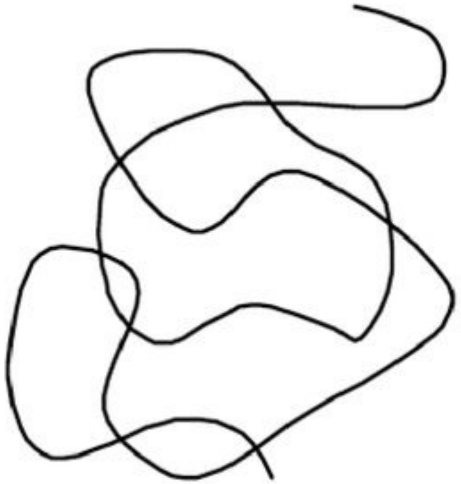


Polystyrene in acetone

Polymers and Solvents

It comes down to the quality of the solvent

Good solvent



Monomer-solvent interactions more favorable than monomer-monomer interactions

Theta solvent

Monomer-monomer interactions the same as monomer-solvent interactions

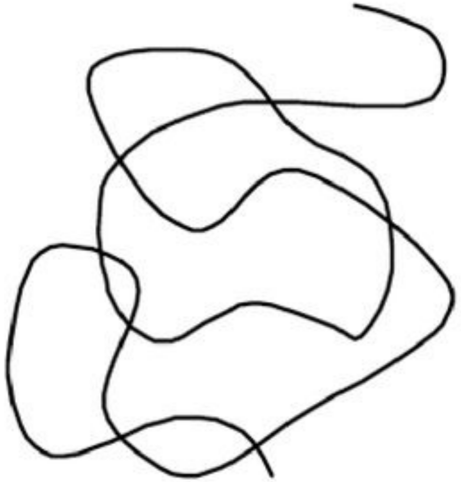
Poor solvent / Nonsolvent

Monomer-monomer interactions more favorable than monomer-solvent interactions

Solvent quality is often a function of temperature
For a polymer-solvent pair, the theta condition can be reached at the theta temperature

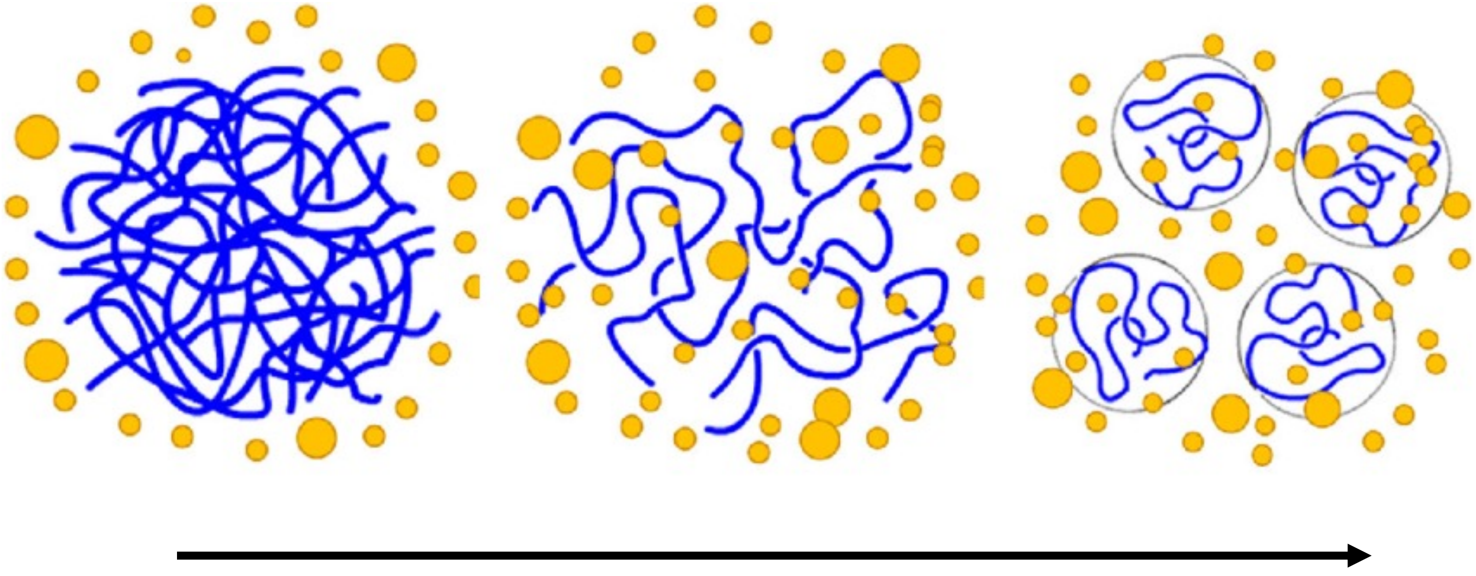
Polymers and Solvents

Good solvent



Monomer-solvent interactions more favorable than monomer-monomer interactions

Schematic of polymer dissolution



Time

Note 1: Polymer does not degrade, it dissolves. No loss of monomer!

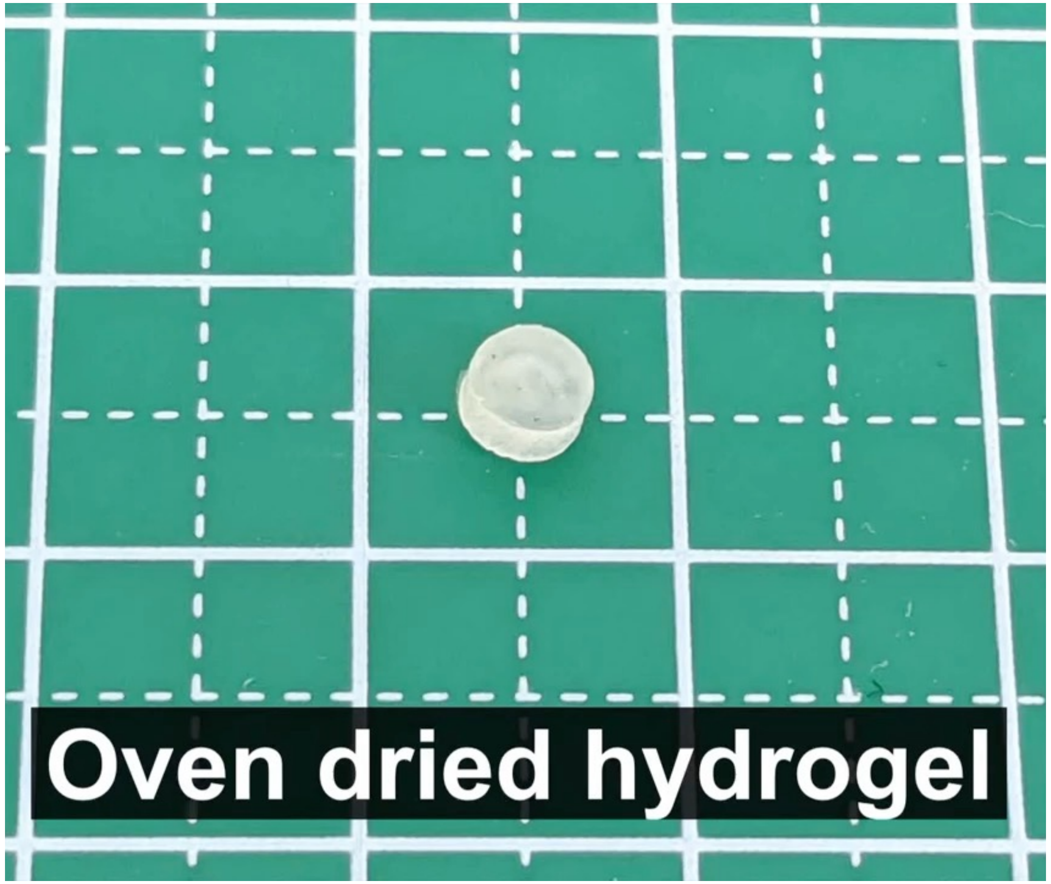
Note 2: Polymer chains remain coiled even when dissolved. Why?

Solvation and Swelling

Assuming a good solvent, why do some polymers dissolve and some swell?

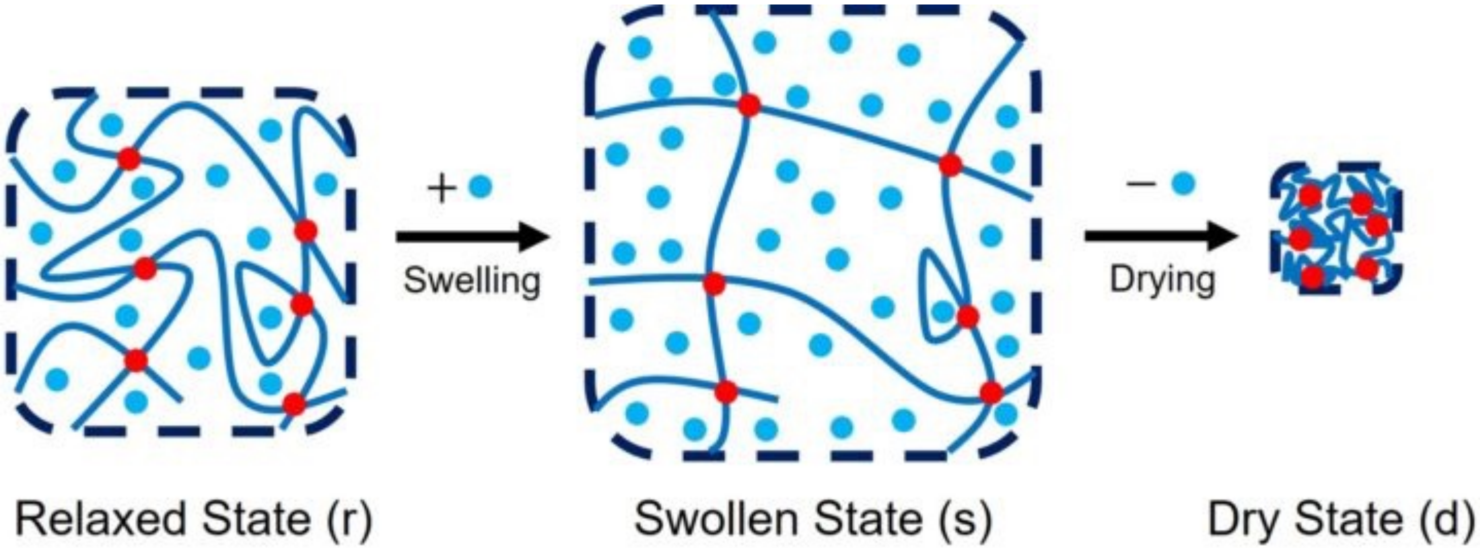
Polymer dissolves

Polymer swells



Solvation and Swelling

The presence of crosslinks prevents dissolution and results in swelling

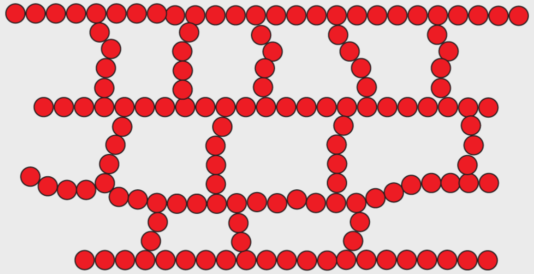


- 🔴 Crosslink points
- 🔵 Good solvent

Crosslink: A bond or short sequence of bonds that links one polymer chain to another

Chemical Crosslinks

Chemical crosslinks



Covalent chemical bonds between polymer chains

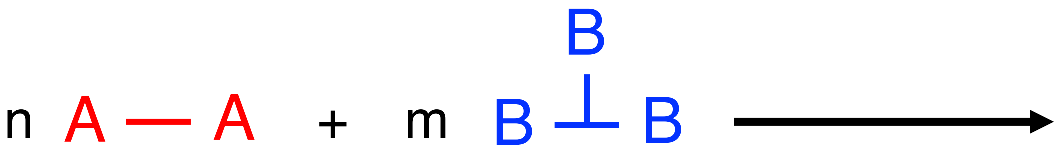
Strength of covalent bonds are strong!

Covalent bonds are permanent. Not transient

Often depends on the number of polymerizable groups on the monomers

Step Growth:

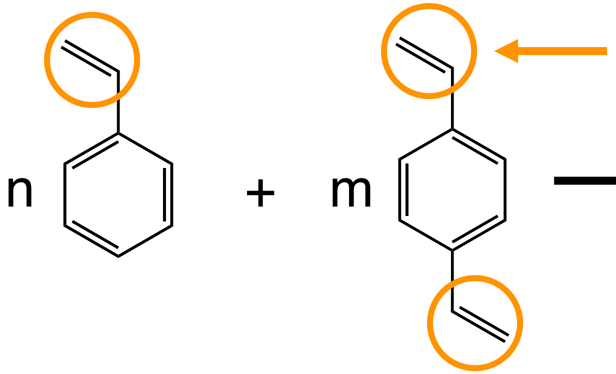
Monomers needs to have functionality* > 2



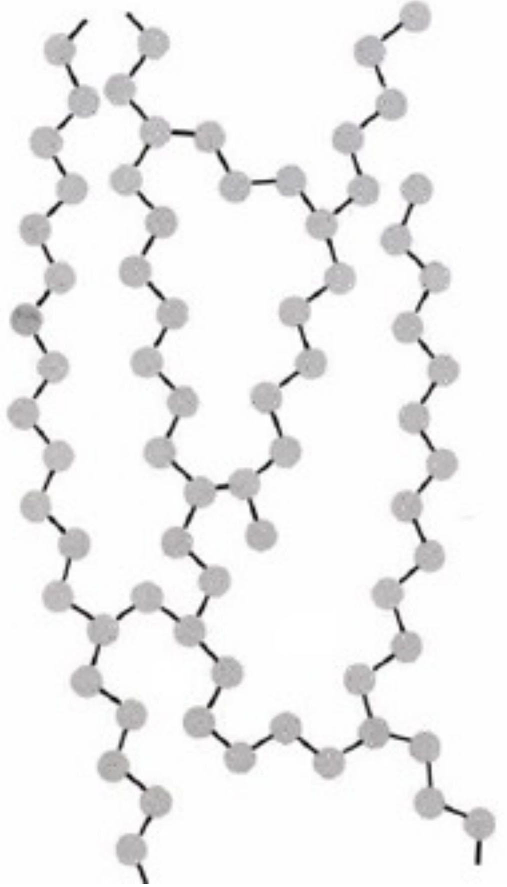
$n\ \text{A—A} + m\ \text{B}\overset{\text{B}}{\perp}\text{B} \longrightarrow$

Chain Growth:

Monomers needs to have functionality* > 1



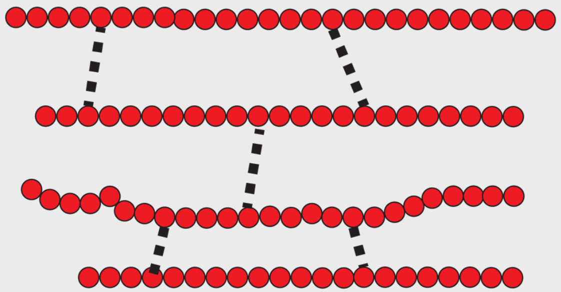
Chain propagates using these functional groups



*Recap: Functionality (f) = # of polymerizable groups

Physical Crosslinks

Physical crosslinks



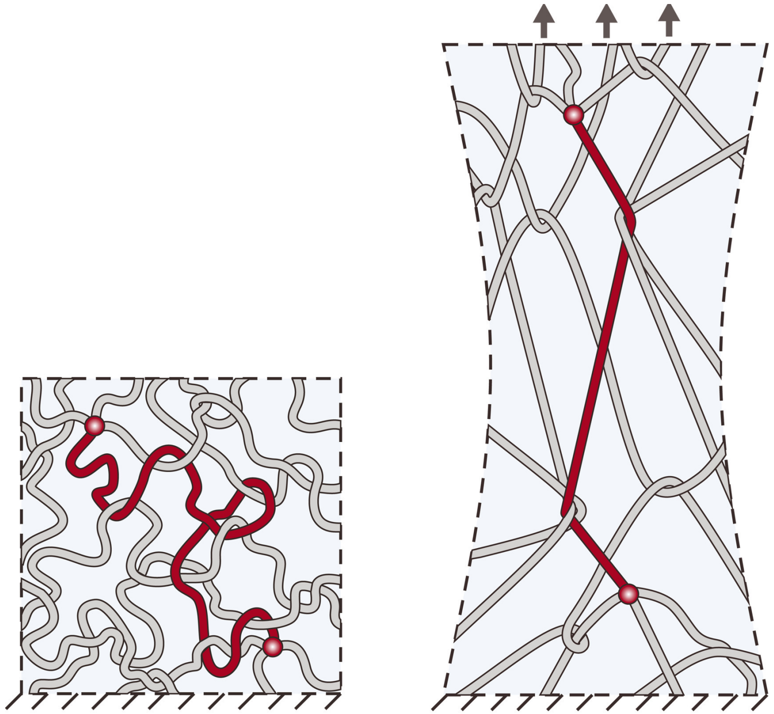
Non-covalent bonds between polymer chains

Strength of noncovalent bonds are weak!

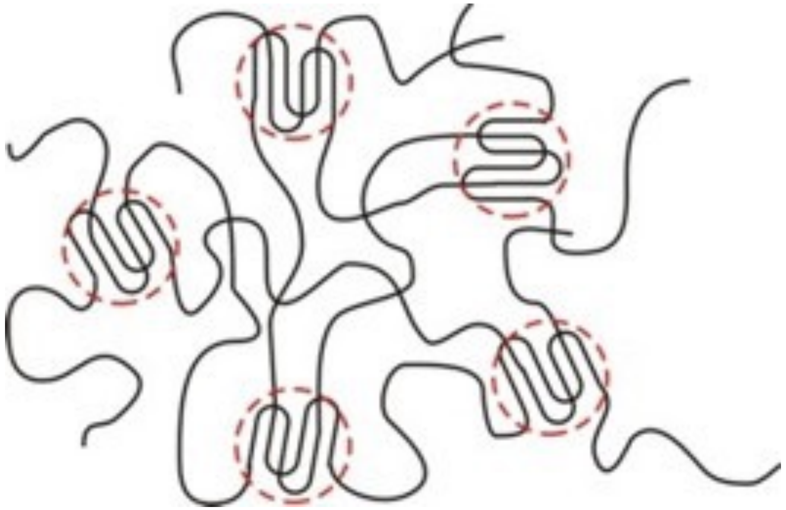
Noncovalent bonds are transient. Often time-dependent

Many different kinds of physical crosslinks!

Chain entanglements

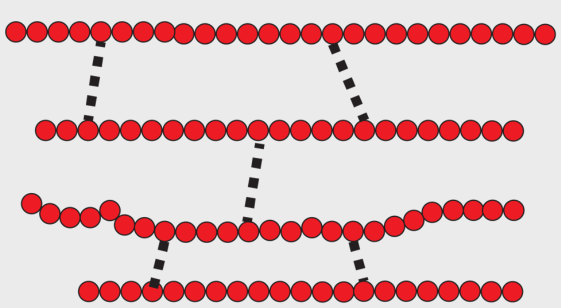


Crystallite crosslinks



Physical Crosslinks

Physical crosslinks



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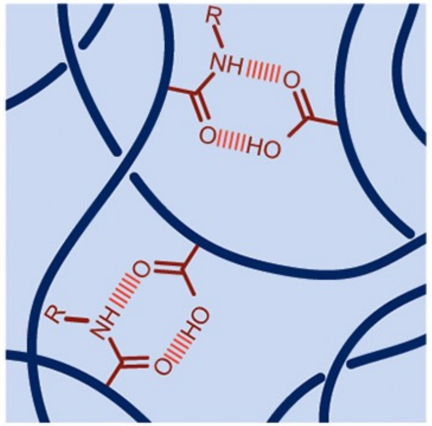
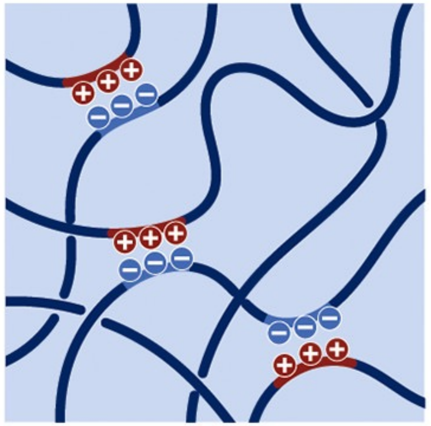
Noncovalent bonds are transient. Often time-dependent

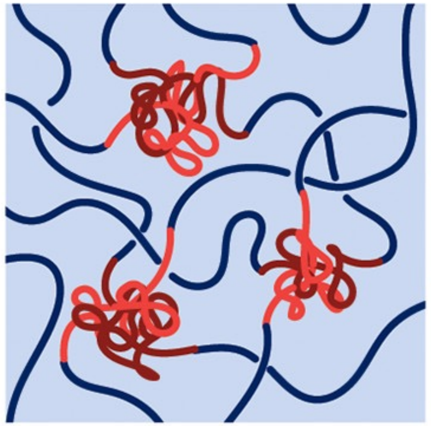
Many different kinds of physical crosslinks!



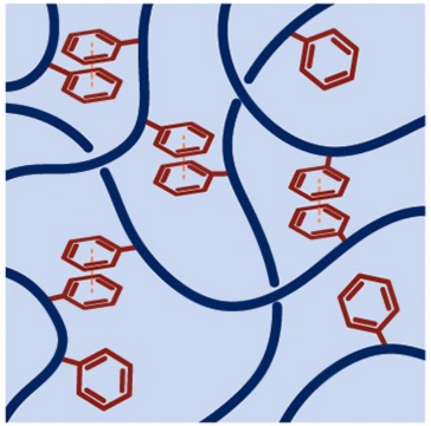
Hydrogen bond



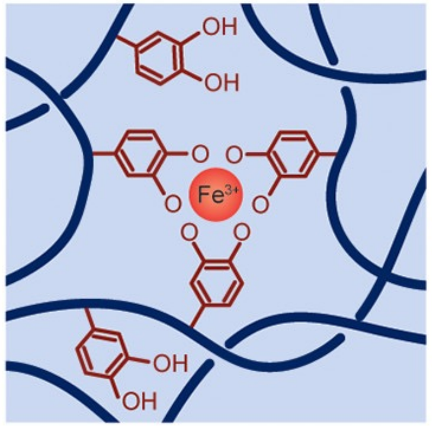
Electrostatic interactions



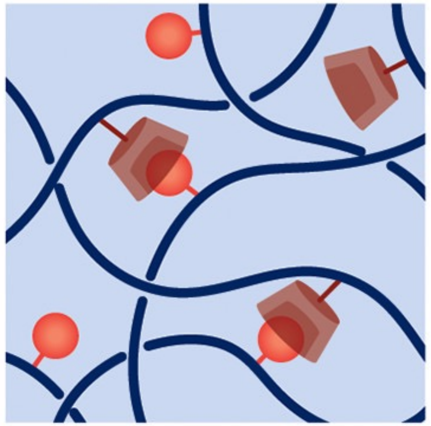
Hydrophobic association



π-π interaction



Coordination complex

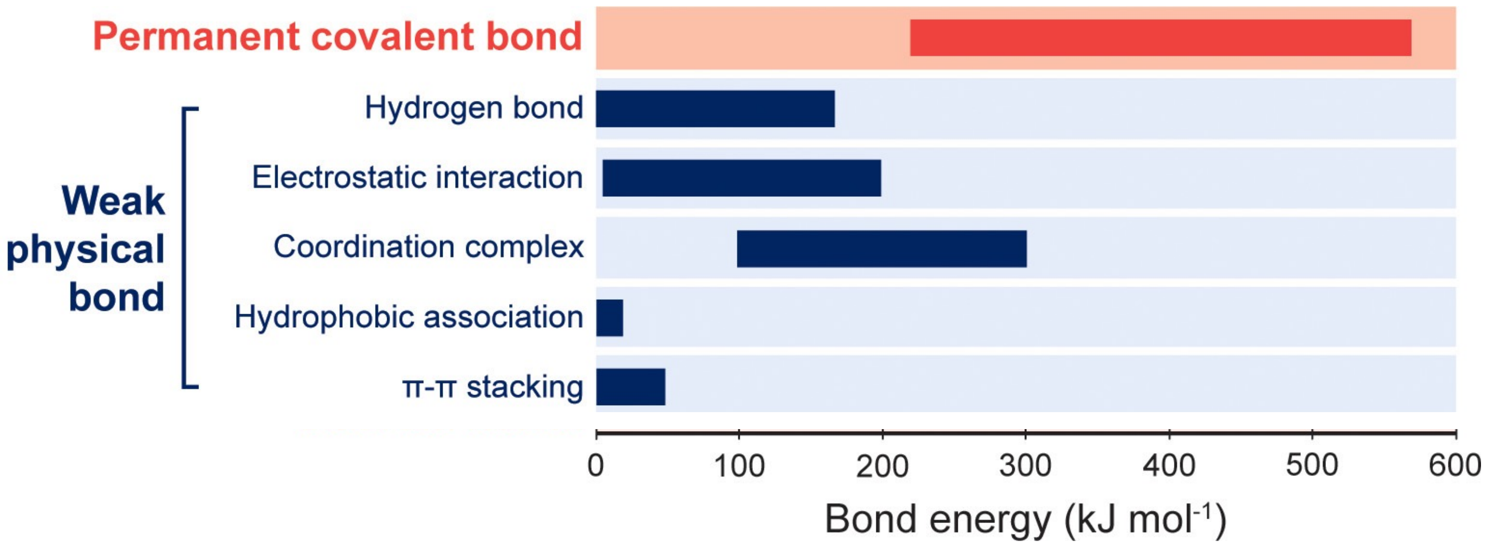


Host-guest interaction

The types of physical crosslinks possible is often based on the composition of the monomer

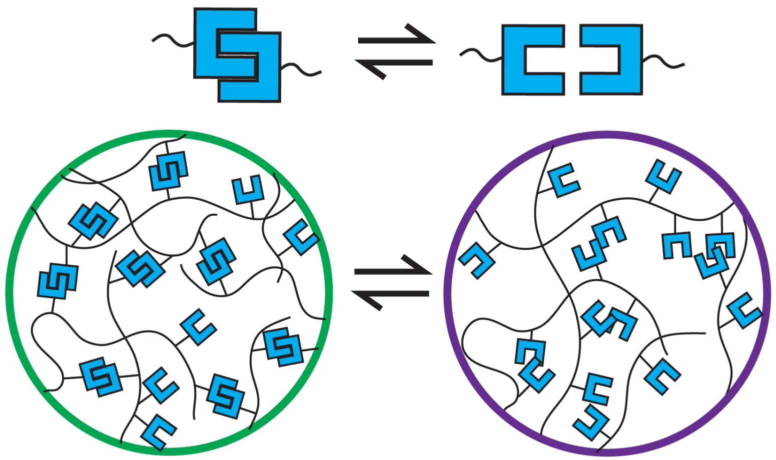
Zhao et al. *Chem. Rev.* 2021, 121, 8, 4309–4372

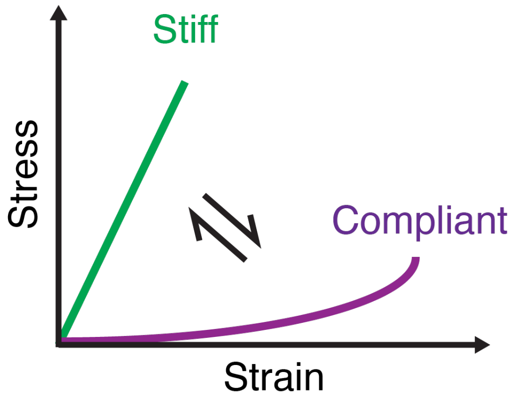
Chemical vs Physical Crosslinks



Chemically crosslinked polymers are often stronger

Common to have both chemical and physical crosslinks!



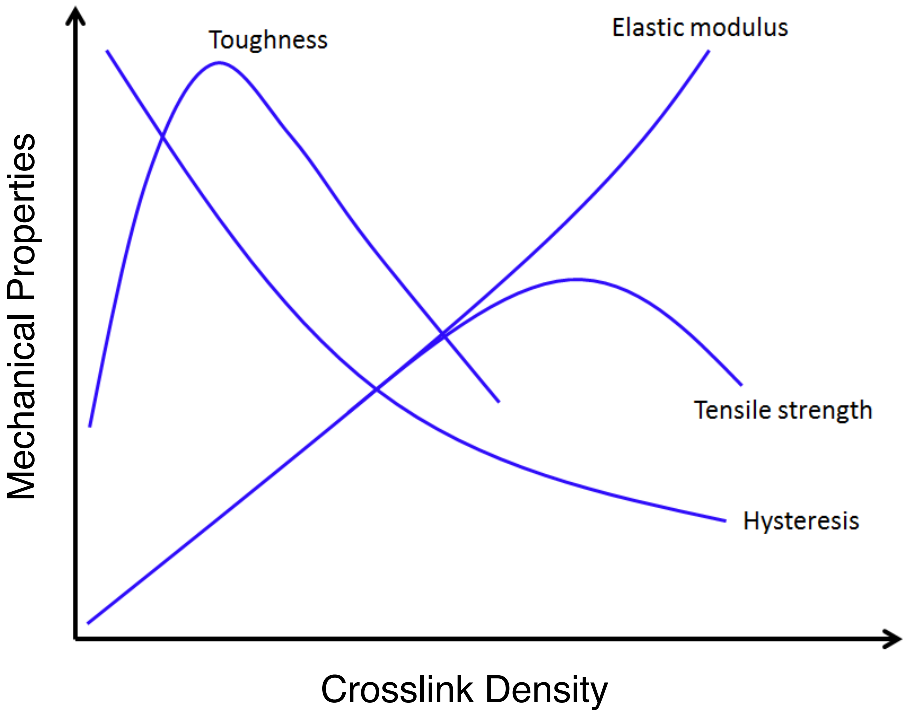


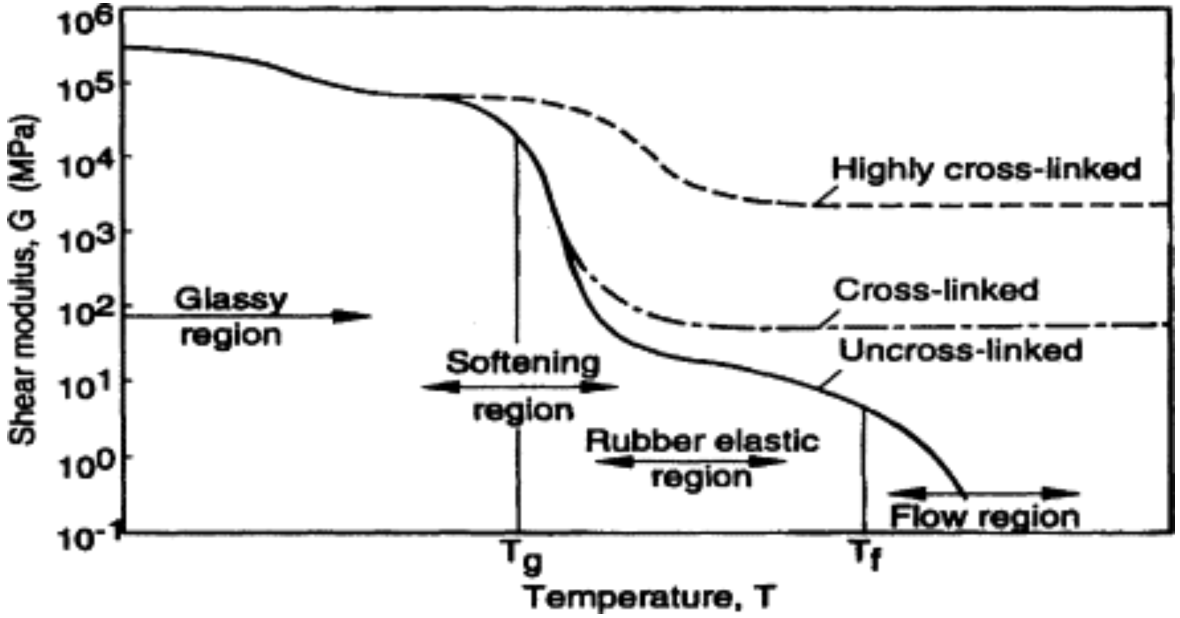
Physically crosslinked polymers are stimuli-responsive

Zhao et al. *Chem. Rev.* 2021, 121, 8, 4309–4372

Crosslinking improves stability and mechanical properties

Degree of crosslinking impacts mechanical properties





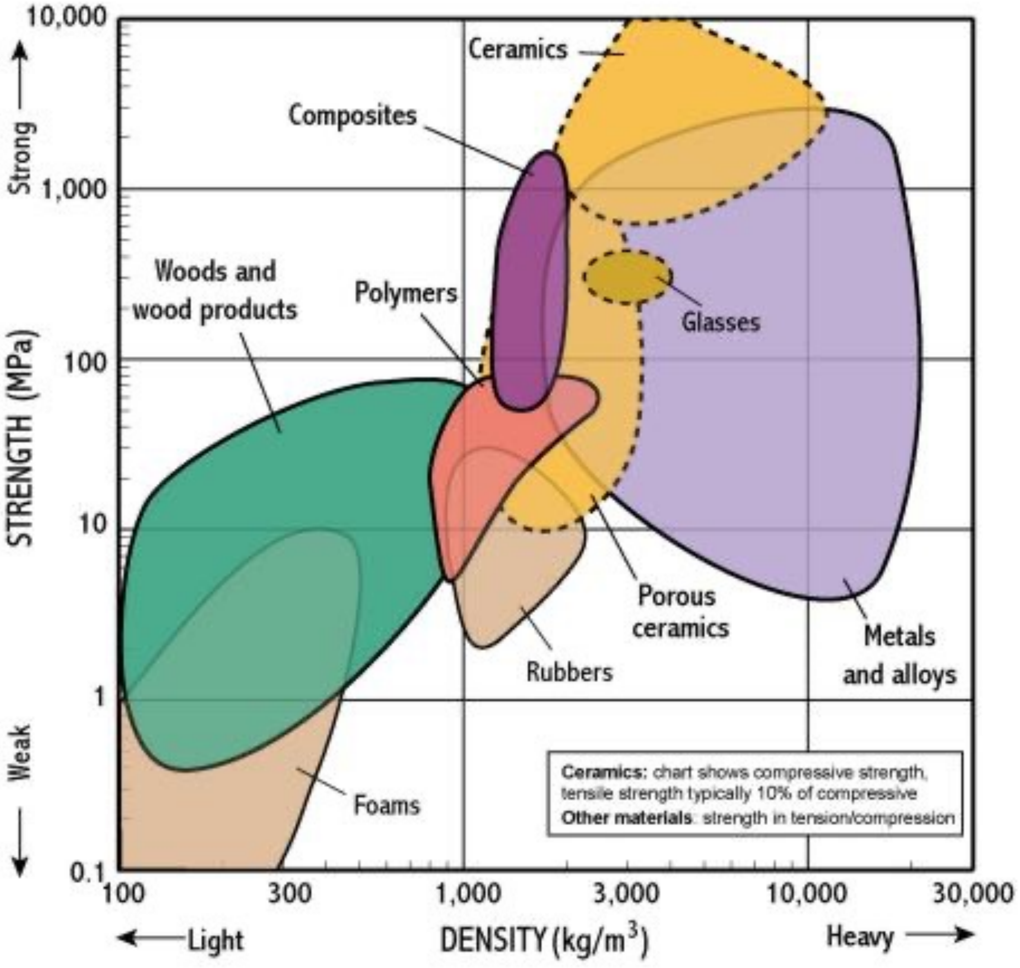
Chemically crosslinked polymers are often stable at high temperatures

Chemically crosslinked polymers cannot be dissolved

Crosslinking negatively impacts the ability to crystallize

General Polymer Properties — Lightweight

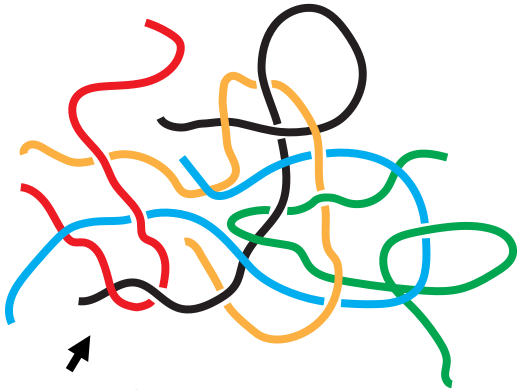
Polymers are very light for their properties



Reason 1: Polymers typically consist of light elements such as C, O, N, H.

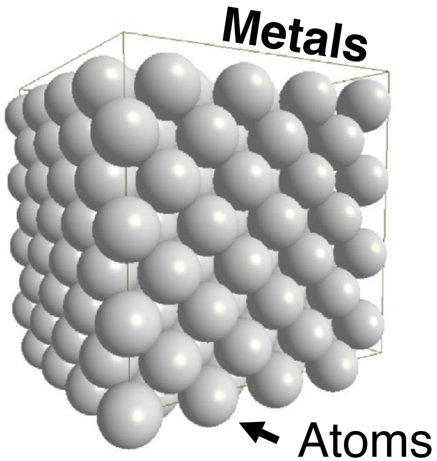
Element	Molar mass (g/mol)
C	12
O	16
Fe	56
Ti	48

Reason 2: Polymers are not very dense since they don't pack well



Chains of atoms

vs

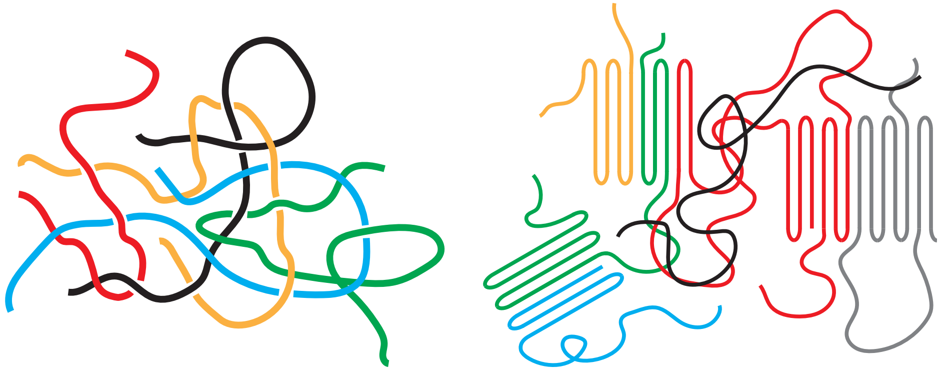


General Polymer Properties — Soft

Partially adapted from Teo et al. *ACS Biomater. Sci. Eng*. 2016, 2, 454

Polymer	***E* (MPa)**	**(Stress at Failure) (MPa)**	**Strain at Break**
LDPE	200 – 400	8 – 12	6 – 6.5
HDPE	600 – 1400	20 – 32	1.8 – 10
Nylon 66	1700 – 2000	80 – 85	0.12 – 3
PDMS	360 – 870	2.24	4.3 – 6.4
Rubber	4	28	7
Epoxy Resin	3000 – 6000	35 – 100	0.01 – 0.06
Carbon Steel	190000 – 210000	276 – 1882	0.1 – 0.32

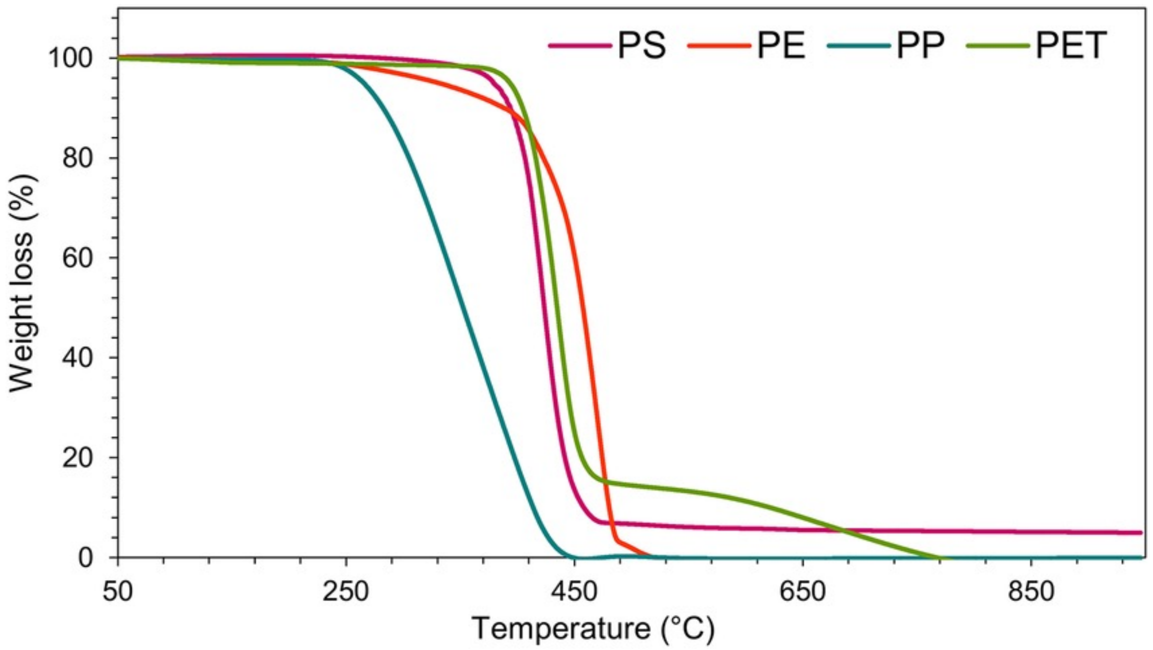
Chains can slide and move past each other to accommodate deformation



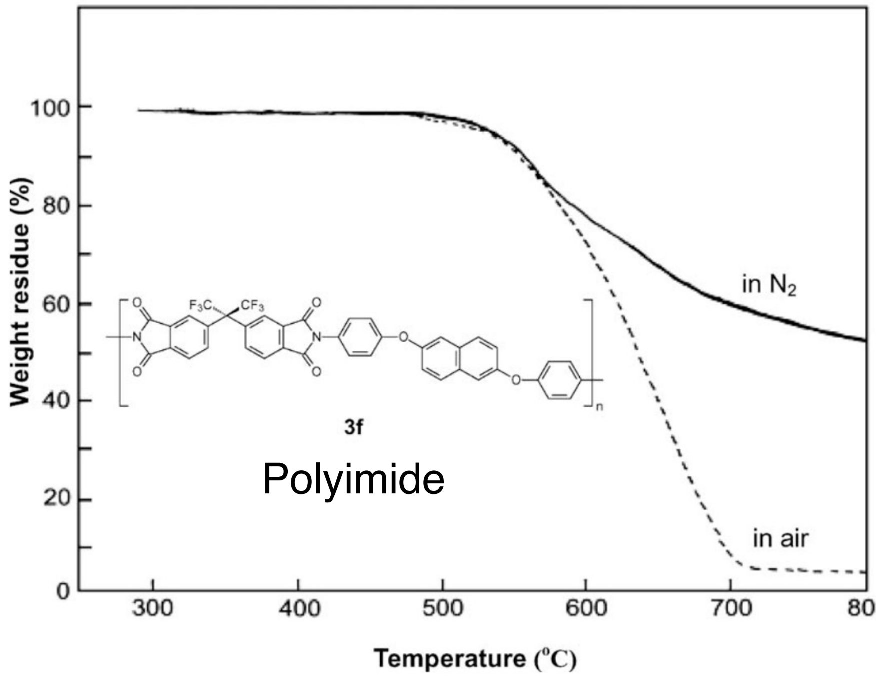
Polymers are flexible and soft compared to ceramics and metals

General Polymer Properties — Low Thermal Stability

Most commodity polymers degrade by 500˚C



Our best high-T polymers degrade by 700˚C



Polymers are often unusable before they reach their degradation temperature! → **Polymers lose strength beyond their T_g and T_m!**

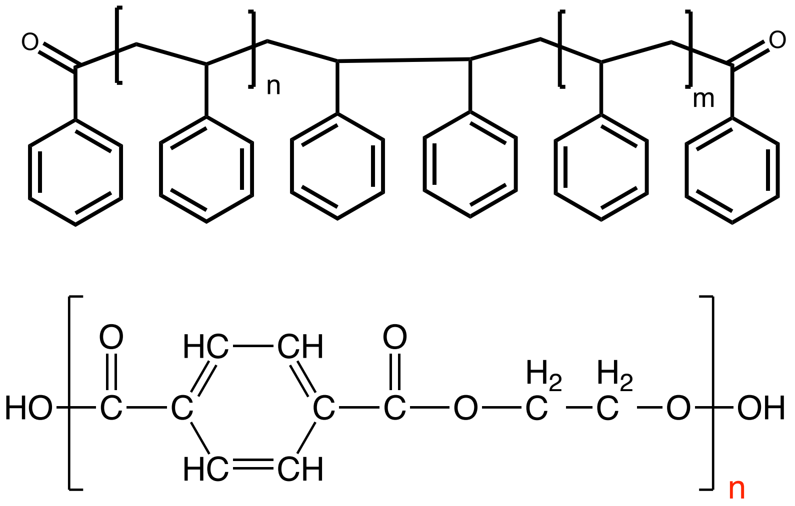
In contrast, metals melt around >1000˚C

Miandad, Rashid, et al. *Frontiers in energy research* 7 (2019): 437000.

Yang et al. *Journal of Polymer Research* 11 (2004): 23-29.

General Polymer Properties — Others

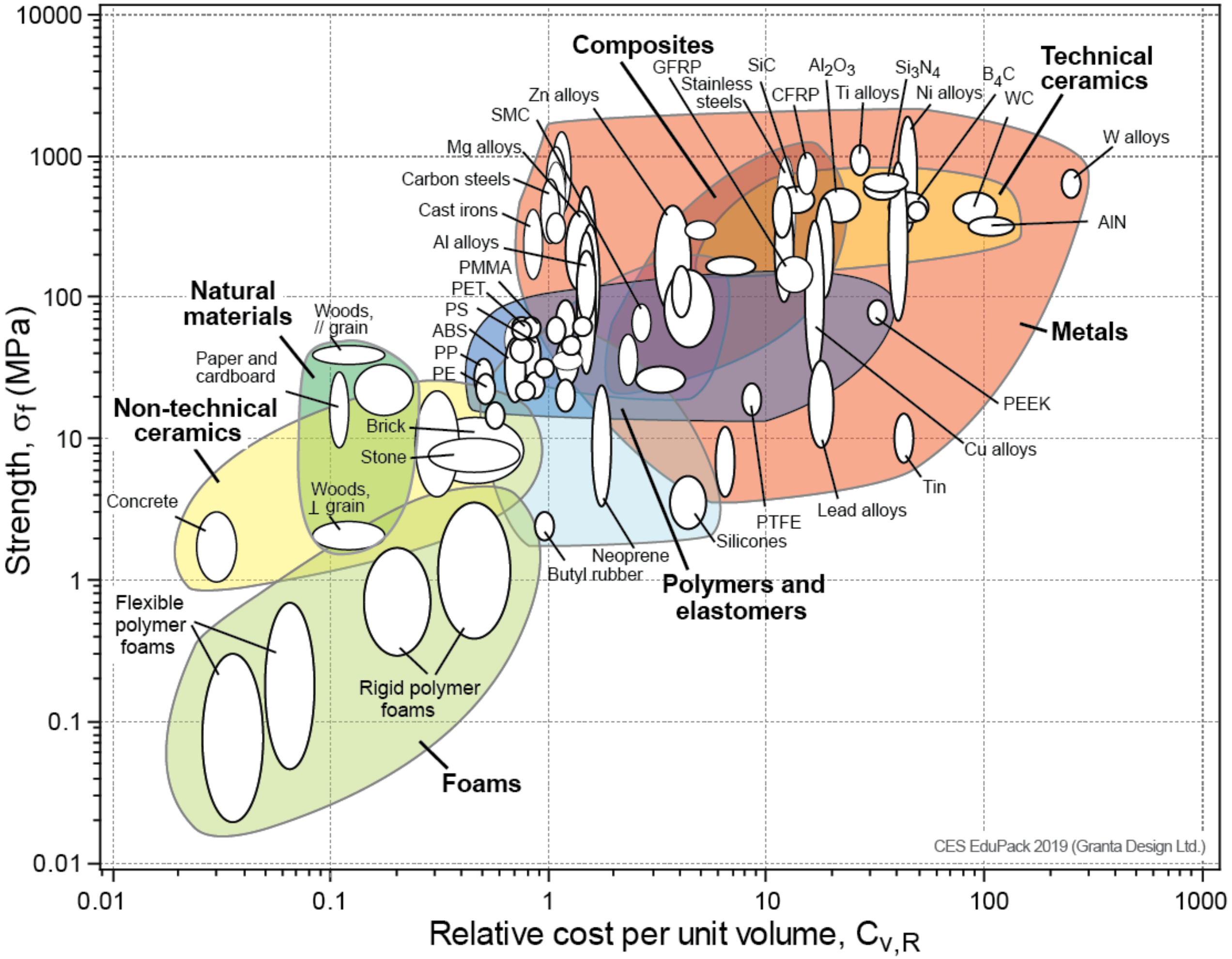
Often electrically insulative*



Covalent bonds keep electrons tightly bound to their atoms

No free electrons to carry an electrical current

Low cost**



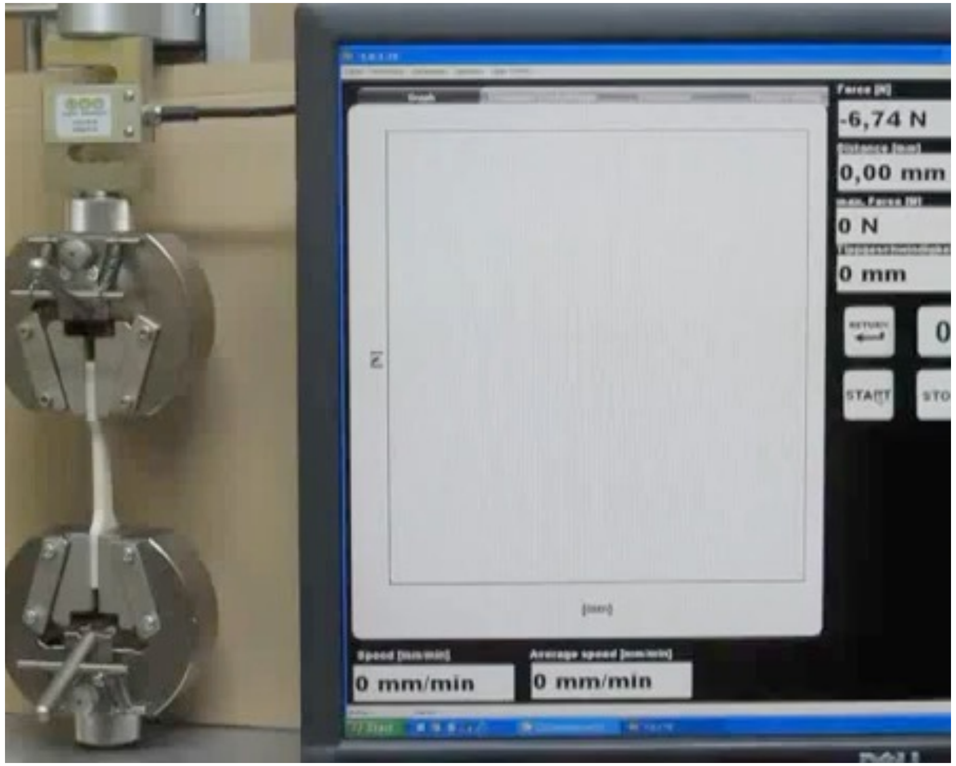
*conductive polymers do exist though. How does that work?

**To be discussed next lecture

HOW DO WE MEASURE POLYMER PROPERTIES?

Mechanical Properties — Common tests

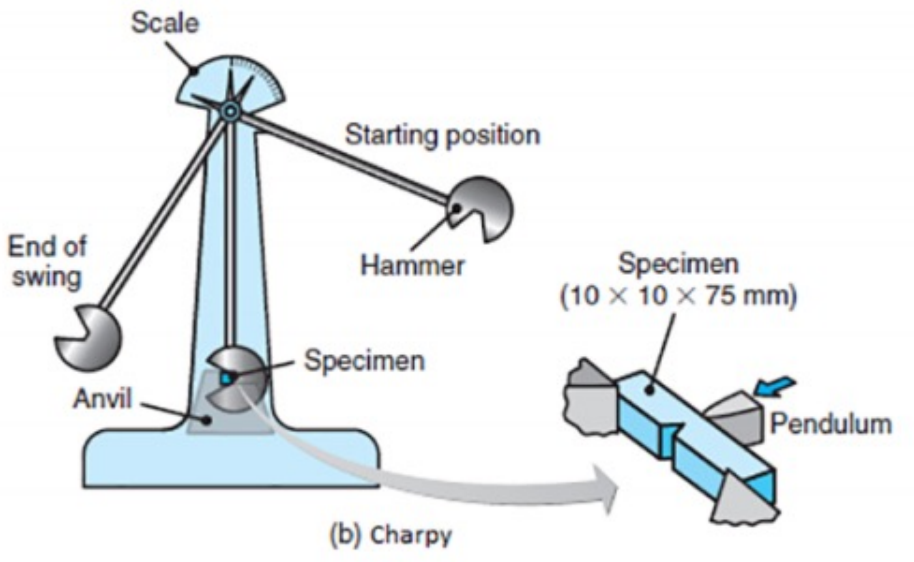
Tensile test



Measures:

Tensile strength,
Young's modulus, Ductility

Charpy impact test



www.green-mechanic.com

Measures:

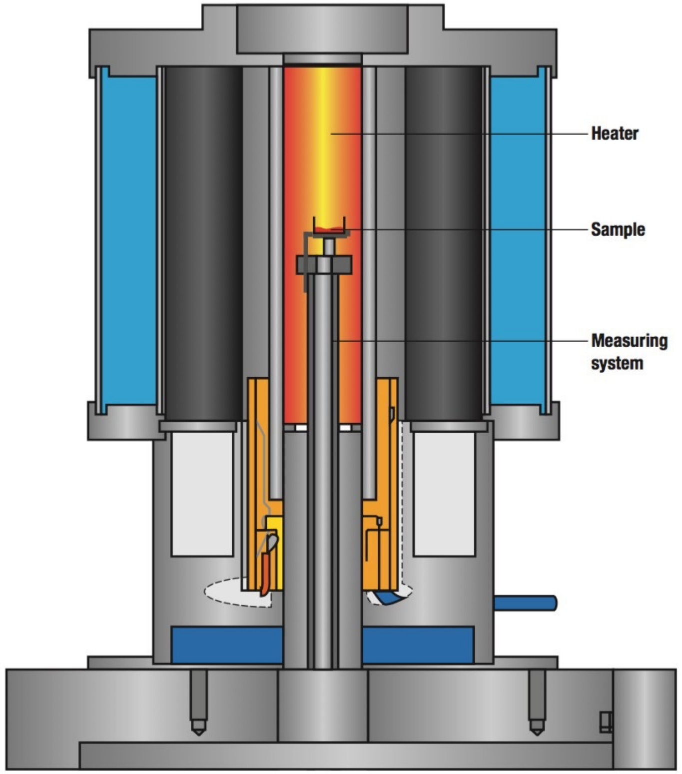
Toughness

Other tests

Compression
Flexural
Hardness
Creep
Stress relaxation
Fatigue
Tear resistance
Etc.

Thermal Properties — Common tests

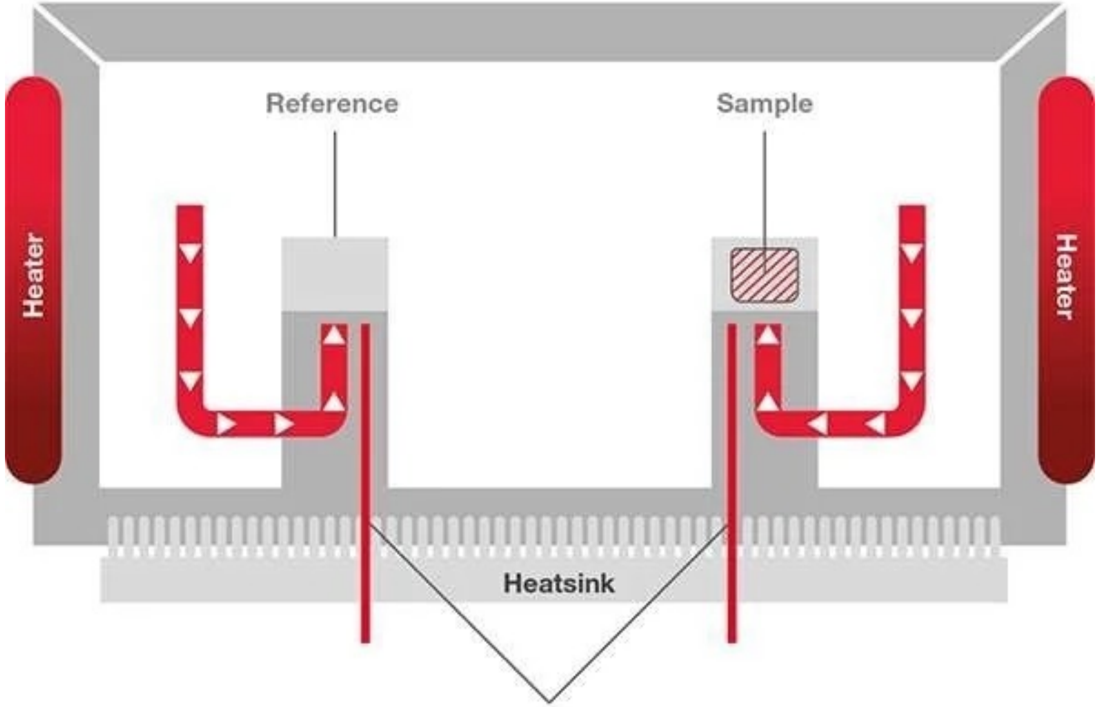
Thermogravimetric Analysis



Measures:

Mass change as a function of temperature

Differential Scanning Calorimetry



Measures:

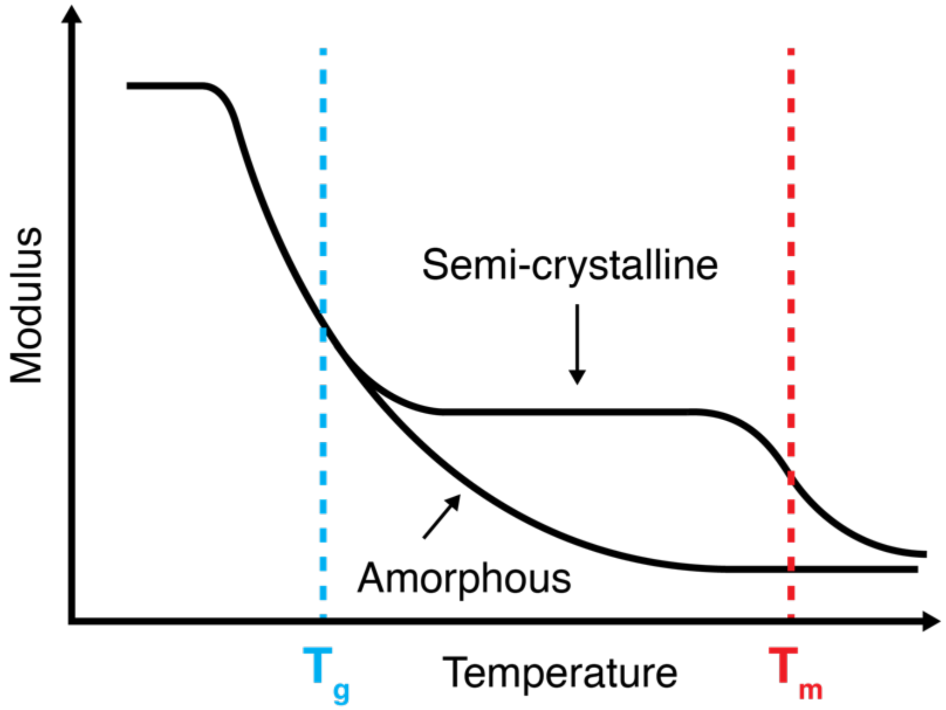
Amount of heat released or absorbed during heating or cooling

LET’S TALK ABOUT MANUFACTURING

Manufacturing

Polymers are one of the easiest materials to manufacture*:

- Relatively low synthesis temperatures (< 150˚C) compared to metals and ceramics
- Relatively low processing temperatures (< 300˚C) compared to metals and ceramics



T_g or T_m can be tuned via polymer synthesis

↓

Polymers can be shaped and deformed easily above T_g or T_m

↓

Readily accessible thermal processing window
Lower operating costs

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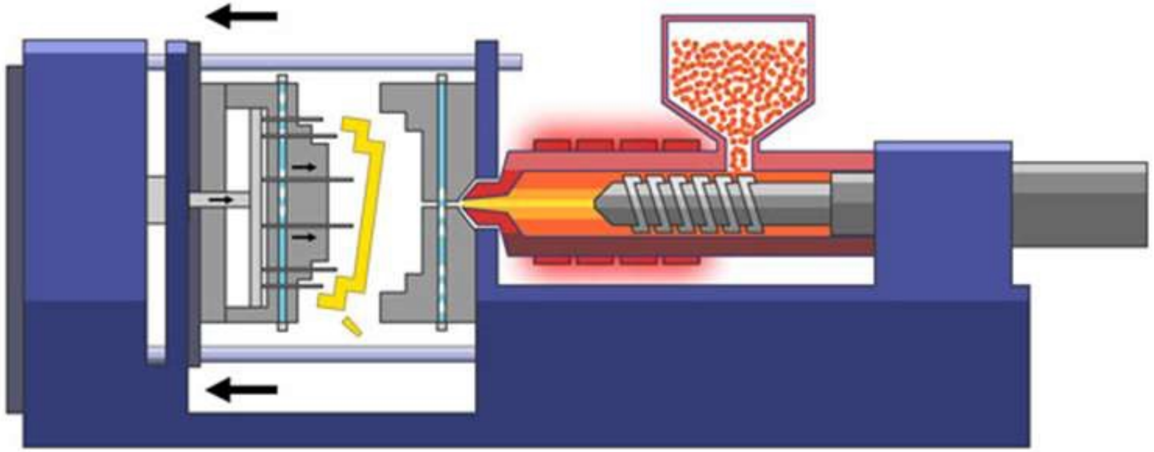
*other factors favor the manufacturing of polymers, such as low cost of feedstock, ease of transportation since polymers are light, etc.

SOME CLASSICS

Injection Molding



Polymer pellets are heated until they can flow and then fed into the machine where they are further heated till liquid

The polymer melt is then injected into a mold at high pressure and temperature.

The melt solidifies in the mold to give the shaped part → Complex shaped parts possible!

Injection Molding

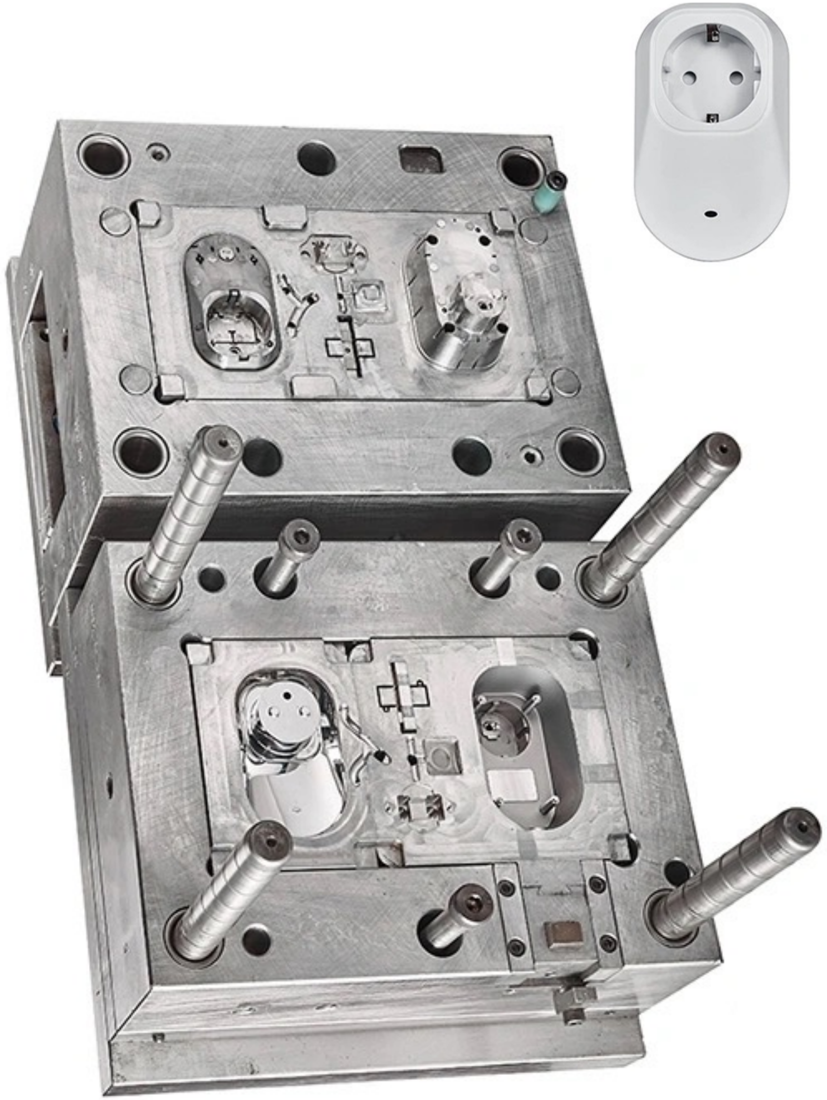
Advantages

- Compatible with all thermoplastics, some thermosets, and some elastomers
- Highly cost-competitive — high-volume production brings down cost-per-unit
- Highly repeatable with tight tolerances

Disadvantages

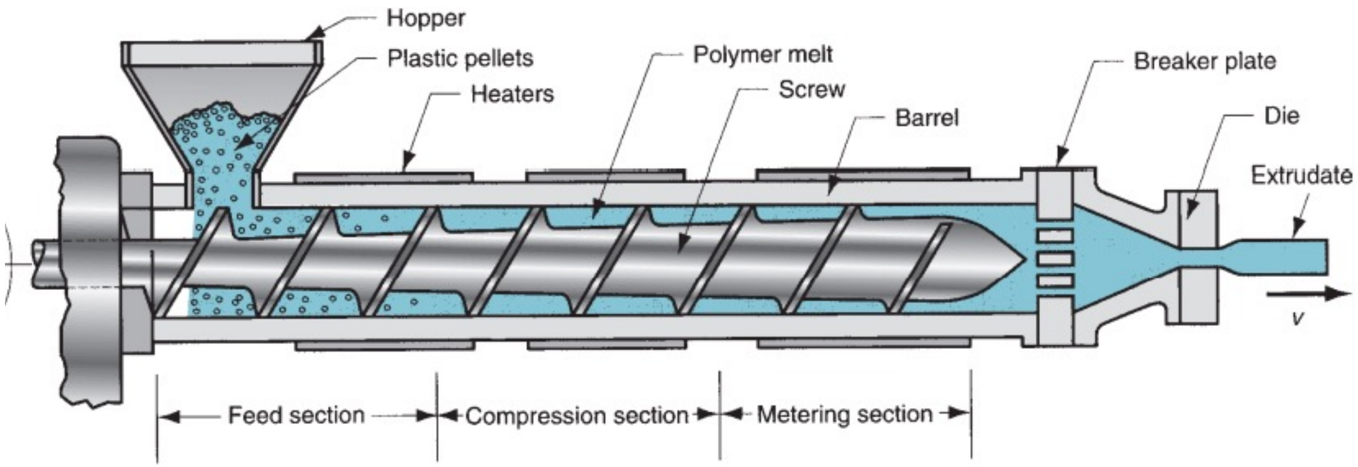
- Start up cost high — making the mold is very expensive!
- Design changes are costly — expensive to modify the mold.
- Long lead times — need time to make the mold

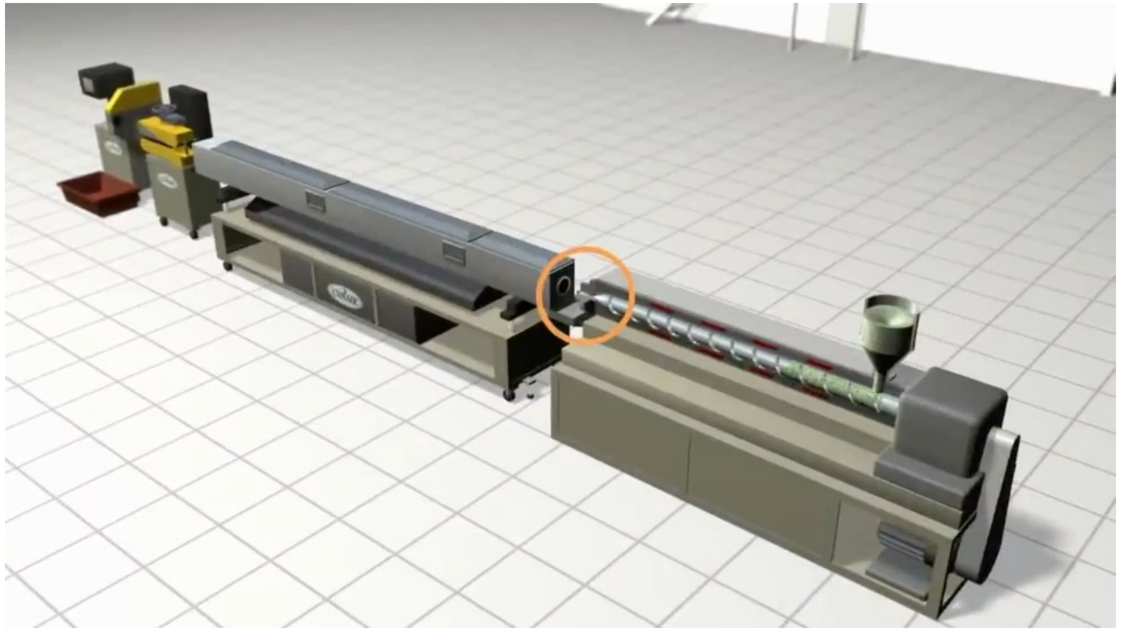
Parts made with Injection Molding



Many of the items you use in your daily life are injection molded!

Extrusion





Conceptually similar to injection molding:

1. Polymer melt is forced through a die to form the desired shape
2. Polymer is continually pushed through the die
3. Cooling of the polymer results in solidification and hardening into the shape

Extrusion

Advantages

- Compatible with all thermoplastics, some thermosets, and some elastomers
- Highly cost-competitive — high-volume production brings down cost-per-unit
- Continuous production

Disadvantages

- Dimensional inaccuracies — polymers are squeezed into the die; when polymers exit the die, they relax and change shape
- Constant cross-section products: Complex shapes not possible with extrusion

Parts made with Extrusion

Many of the items you use in your daily life are extruded!

Other Classic Polymer Manufacturing Processes

- Thermoforming
- Blow Molding
- Compression Molding
- Transfer Molding
- Vacuum Casting
- Rotational Molding

Typically used for large-volume production

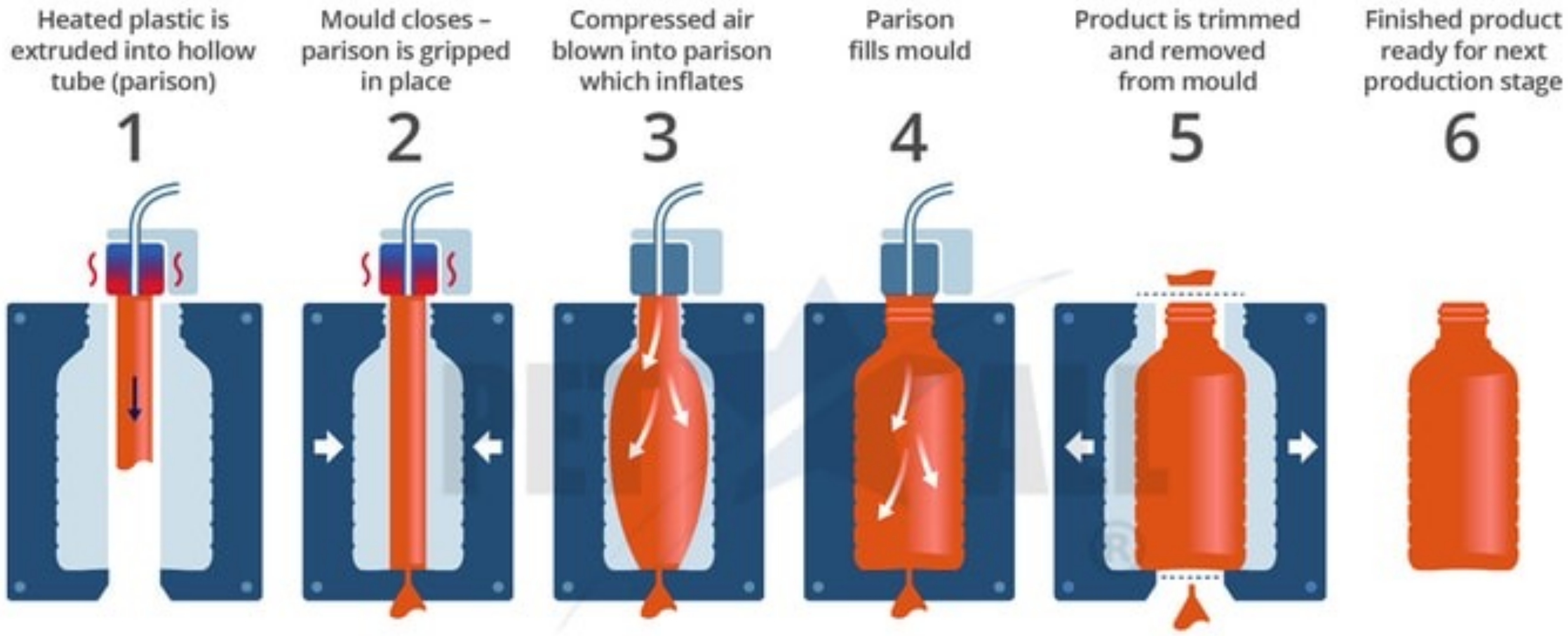
General concept for many of these processes:

1. Heat up polymer feedstock to a liquid state or to a softened state
2. Deform softened polymer or fill mold with liquid polymer
3. Cool polymer down to solidify it.

The devil is in the details! — The challenge comes down to making sure the desired part has the right **dimensions**, right **tolerances**, and right **properties**.

Understanding the chemistry and the processing is key

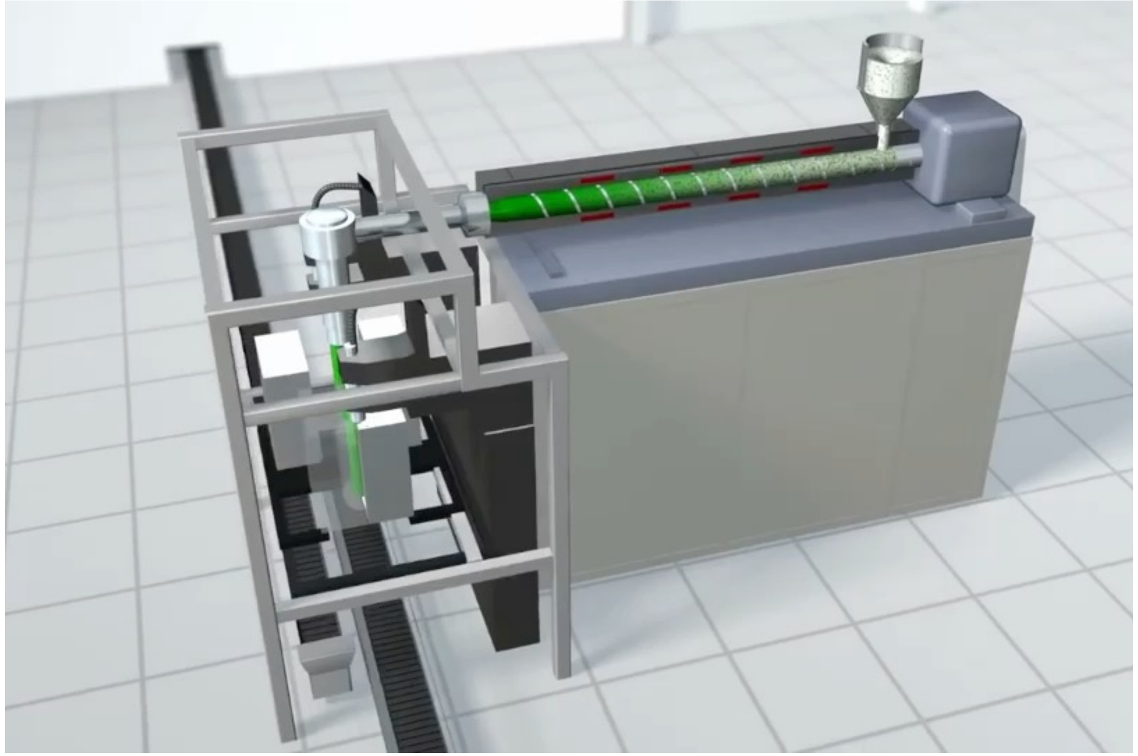
Blow Molding



Used to make hollow products

Extuded hollow tube → Goes into mold → Pressurized air expands the hollow tube to fit the mold

Blow Molding



- Low cost
- Fast production rates
- Limited in part design
- Blown parts require trimming → Material waste

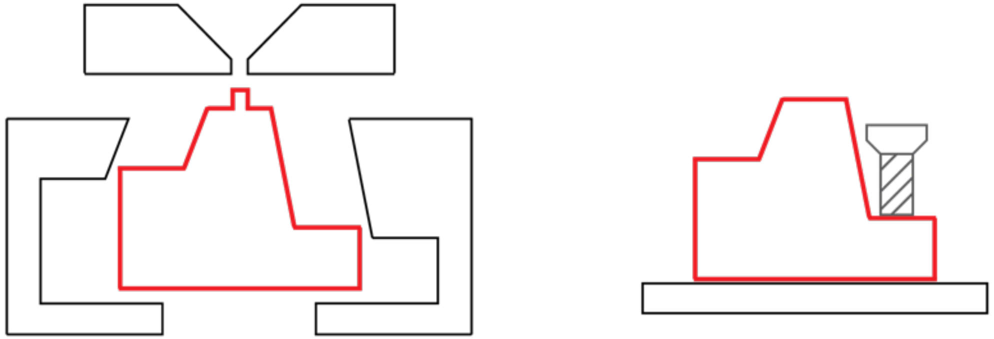
Many of the items you use in your daily life are blow molded!

THE LESS CLASSIC

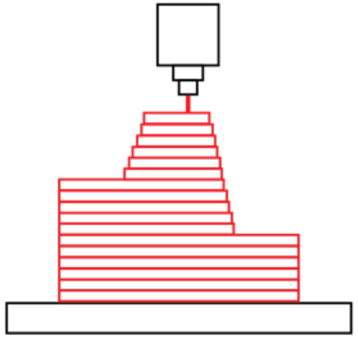
Additive Manufacturing (AM)

Some challenges with ”traditional” polymer manufacturing approaches:

- Limited part complexity
- Difficult to pivot between part designs
- Optimized for scale — start up cost is very high
- Subtractive approaches* can be wasteful



Additive Manufacturing



Part is built in a layer-by-layer^ manner

- ”Complexity for free”
- Easy to pivot between multiple designs
- Can be more material efficient
- Small-scale

---

^This definition is evolving with volumetric methods

*we didn’t cover this but an example is machining

Additive Manufacturing — Versatile, On-demand manufacturing

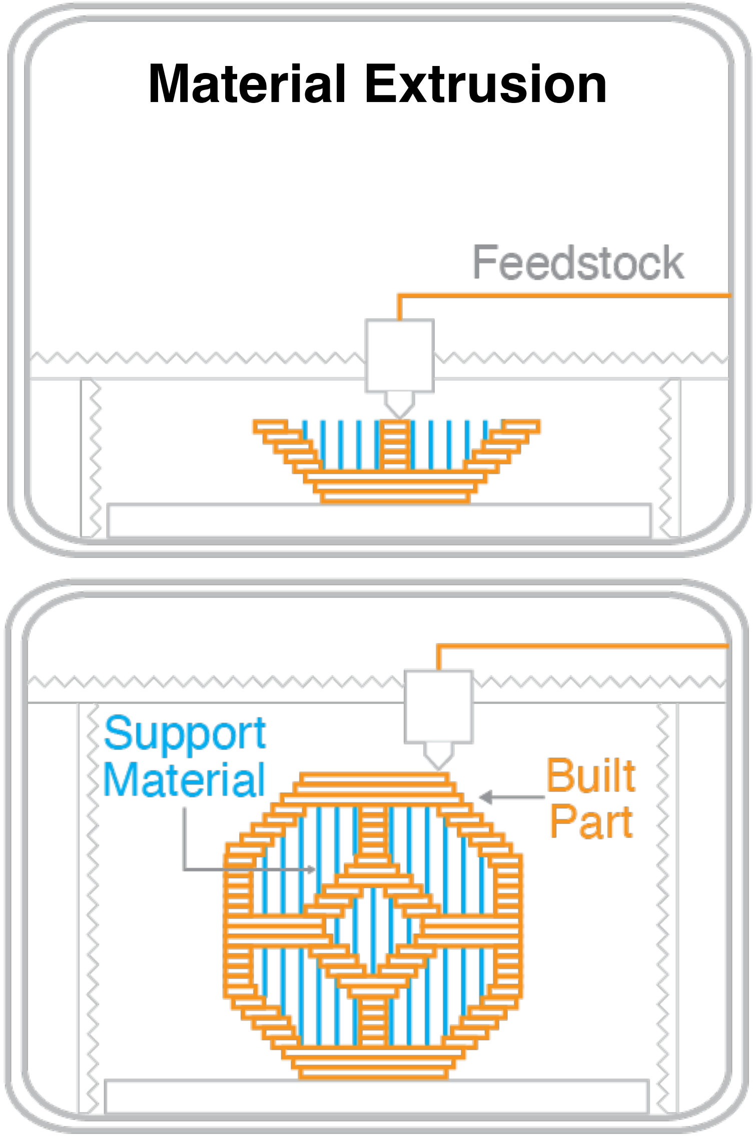
Injection Molding

High throughput
Rapid
High startup cost
Not easy to pivot to different part
Not suited for small-medium production volume

Additive Manufacturing

Low throughput
Slow
Low startup cost
Easy to pivot to different parts
Suited for small-medium production volume

Polymer Additive Manufacturing: Material Extrusion

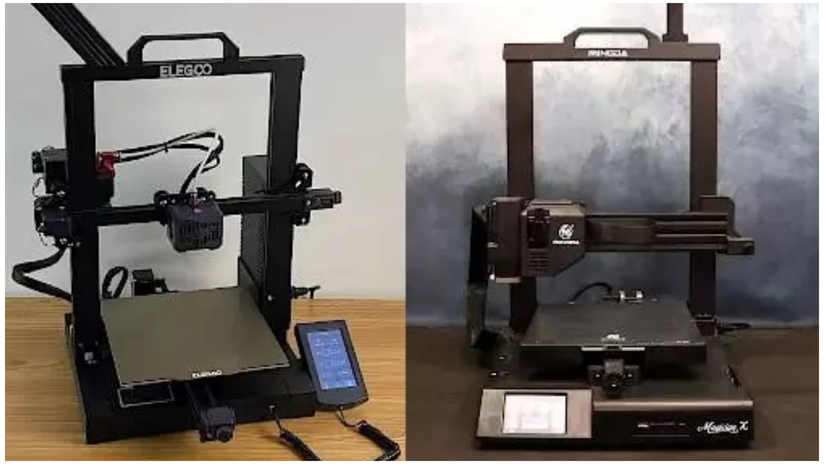


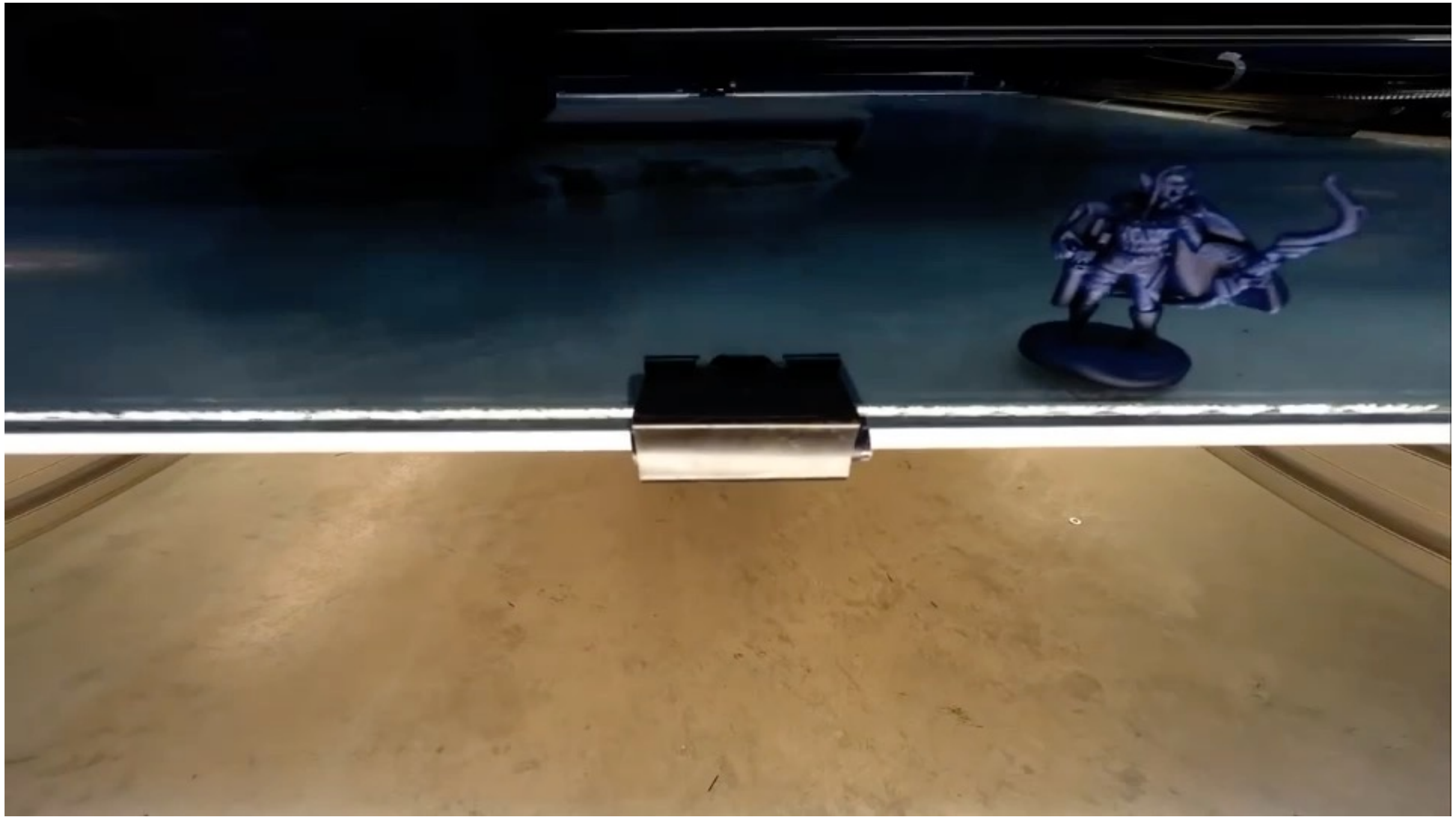
Family of AM techniques where a material is deposited through a nozzle onto a substrate

Often confused with “Fused Deposition Modeling (FDM)” or ”Fused Filament Fabrication (FFF)”.

FDM and FFF belong to the family of techiques called Material Extrusion

Polymer Additive Manufacturing: Material Extrusion

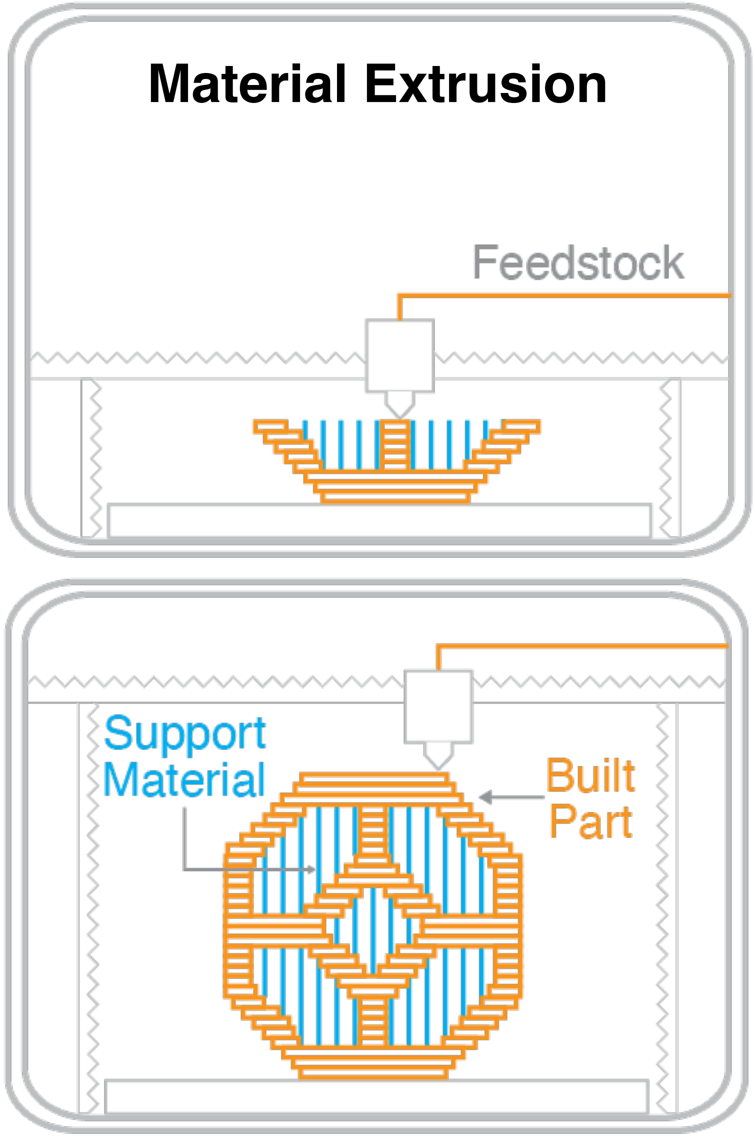




Polymer Additive Manufacturing: Material Extrusion

Jennifer Lewis, Harvard University

Polymer Additive Manufacturing: Material Extrusion



Operating Principle

Feedstock: Polymer, polymer composite, nanoparticle dispersions

Heat and/or pressure is used soften the material and allow it to flow through the nozzle

Material is deposited spatially

Material solidifies after deposition

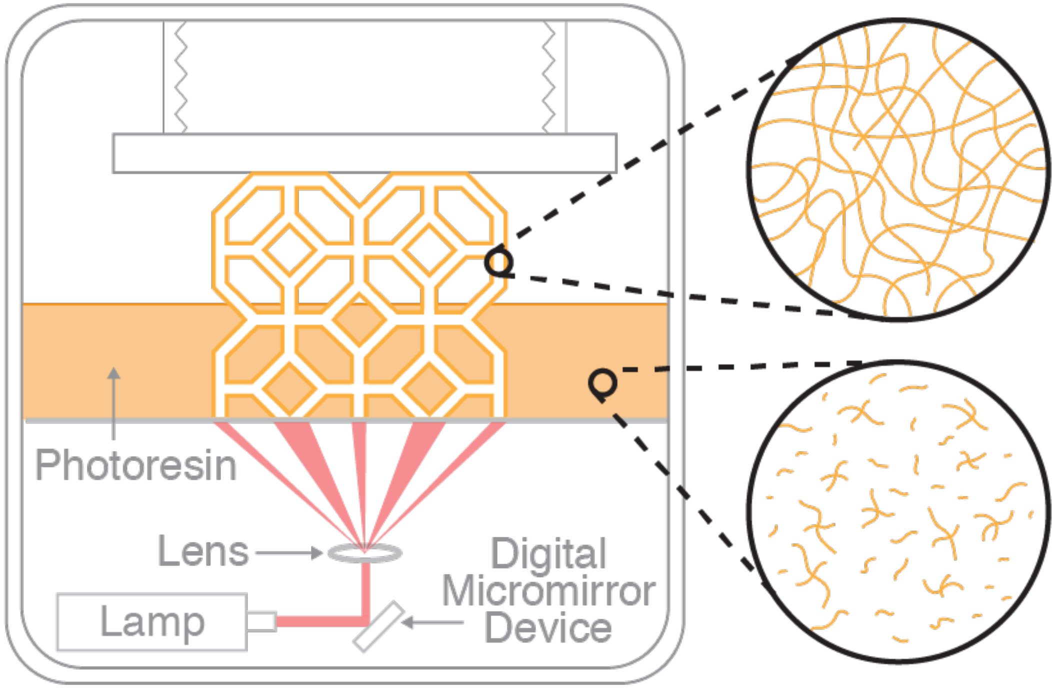
Pros

- Simple and inexpensive
- Low toxicity
- Ease of multimaterial

Cons

- Supports needed for complex geometries
- Warping due to thermal gradients
- Anisotropic properties
- Best used with thermoplastics

Polymer Additive Manufacturing: Vat Photopolymerization



Often confused with “stereolithography”.
Stereolithography is a subset of vat photopolymerization

Family of AM techniques where a liquid photopolymer in a “vat” is cured via photopolymerization

Often termed as “resin printing”

Form 3

Azul 3D

Polymer Additive Manufacturing: Vat Photopolymerization

Operating Principle

<u>Resin</u>: Monomer, oligomer, photoinitiator, solvent, etc.

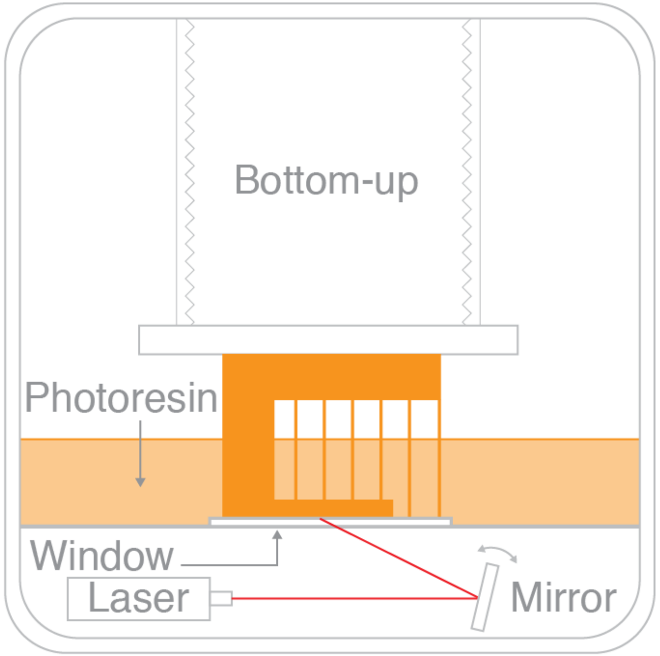
Light is used to spatially photopolymerize the monomer and form the polymer solid

Usually chain-growth polymerization

Different techniques apply light in different ways

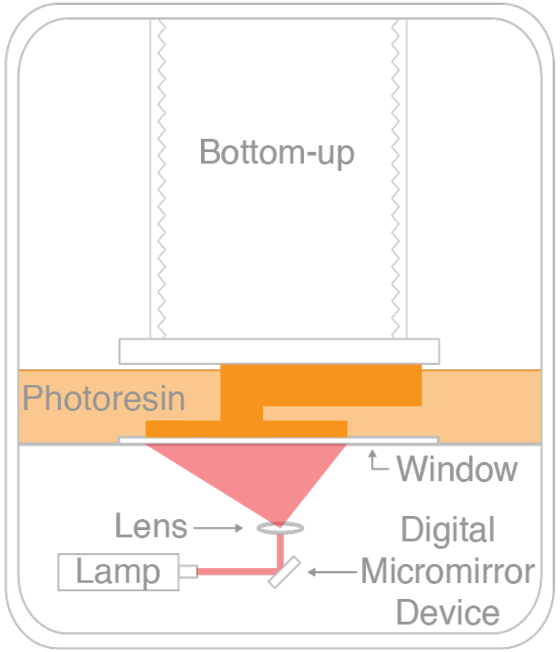
Stereolithography

Laser is rastered on resin



Digital Light Processing Printing

Pattern is projected onto resin



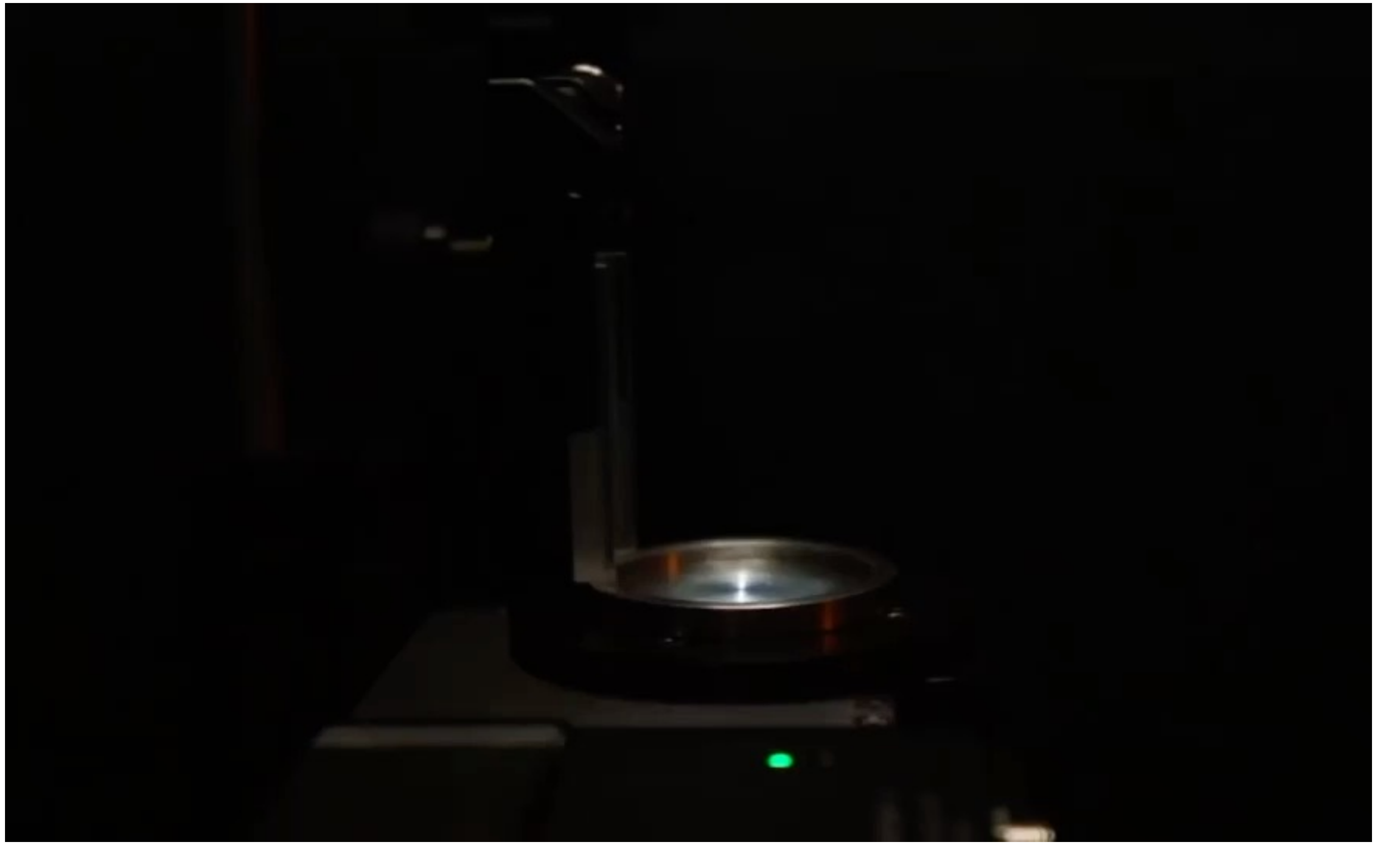
<u>Other techniques in this family</u>: LCD printing, multiphoton lithography, microstereolithography, continuous liquid interface production, volumetric printing, etc.

Polymer Additive Manufacturing: Vat Photopolymerization

Two Photon Lithography

Capable of ~100-150nm resolution

Volumetric Printing



Pioneered by Prof. Christophe Moser at EPFL!

Polymer Additive Manufacturing: Vat Photopolymerization

Pros

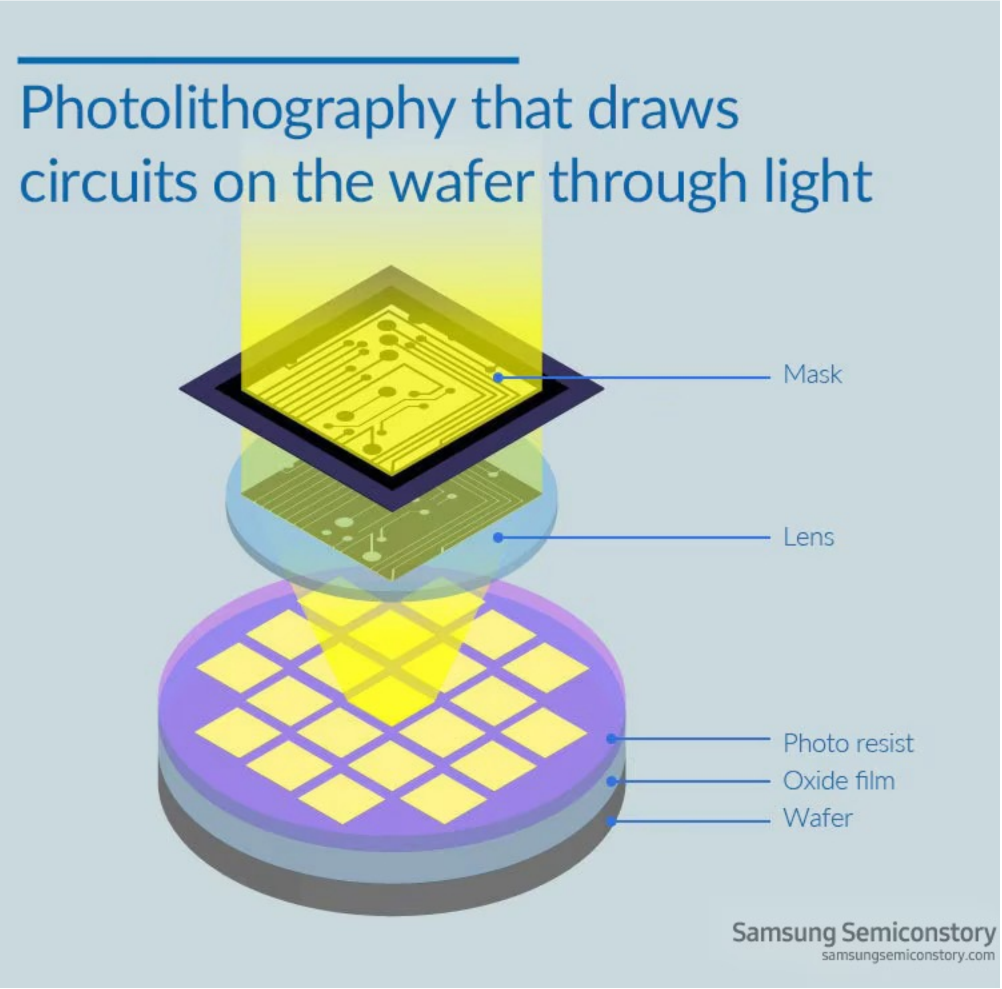
- Simple and inexpensive
- High resolutions (as low as 100 nm. Typically ~30 μm)
- Complex geometries easily achievable
- Rapid printing (especially with projection methods)

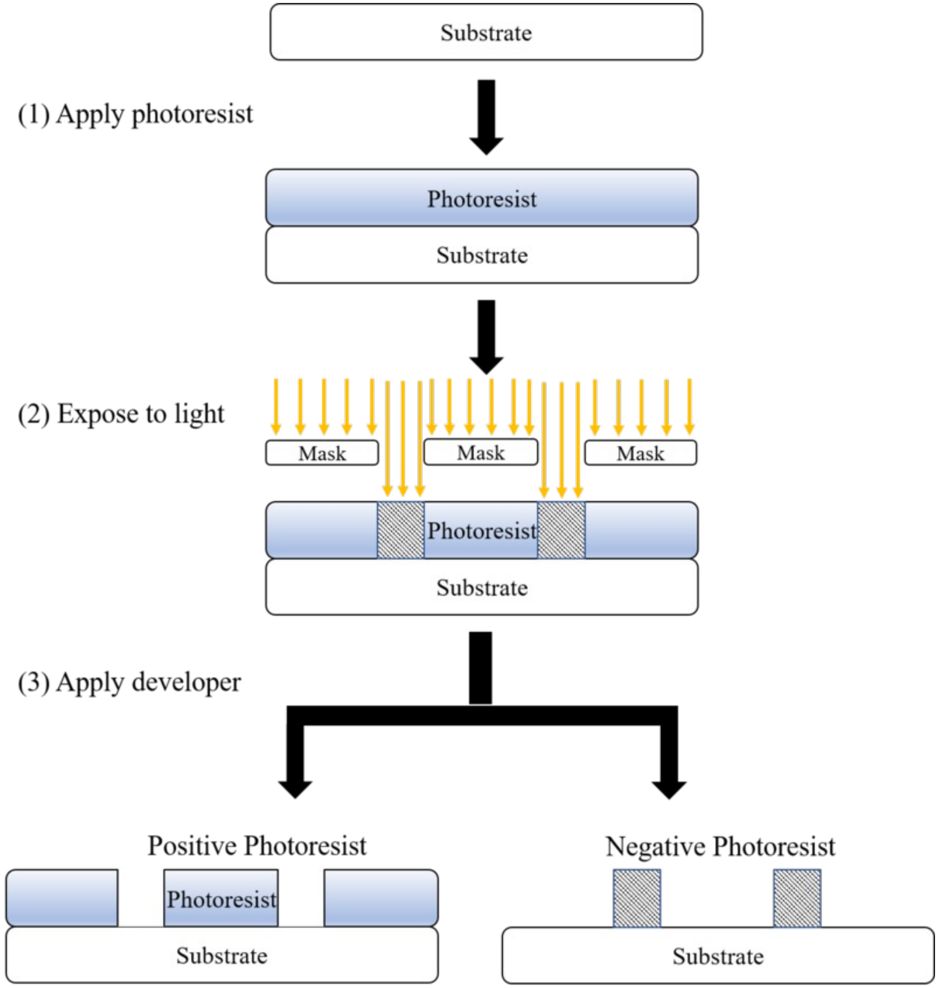
Cons

- Resin is often toxic. Difficult to handle at home
- Multimaterial is challenging to achieve
- Best used with thermosets
- Anything that scatters light will make the print difficult
- Polymer needs to be compatible with photopolymerization

SOME MICROENGINEERING RELEVANT POLYMER PROCESSING

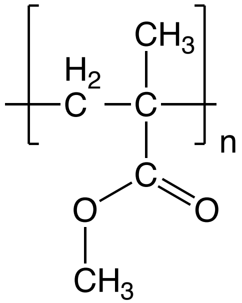
Photolithography





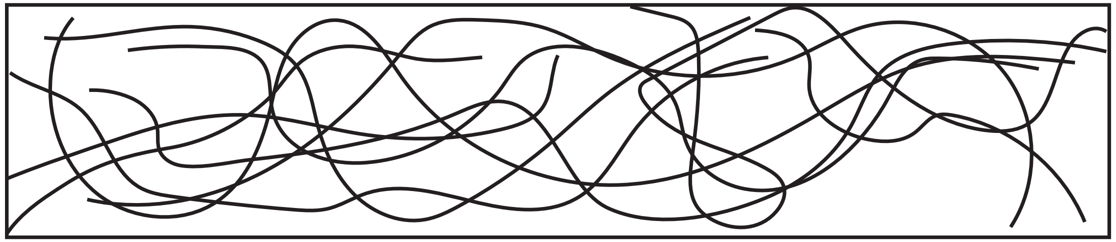
Positive Resist: Exposed = Dissolve

Poly(methyl methacrylate)

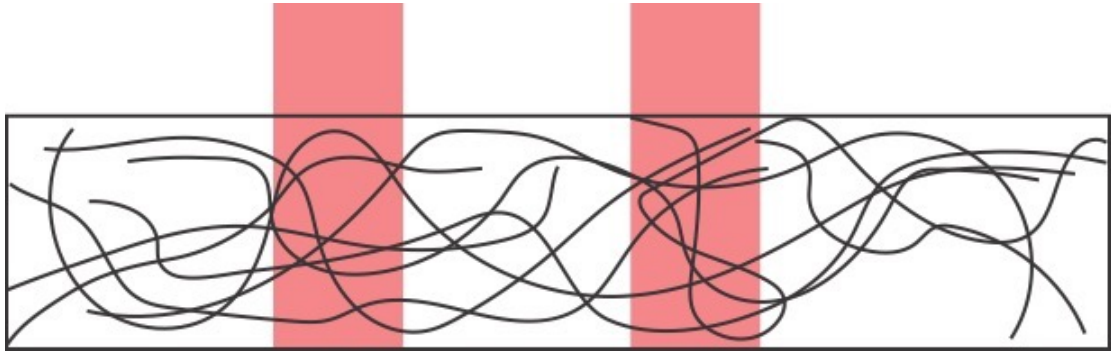


PMMA is commonly used as a high resolution positive resist for electron beam, deep UV, and X-ray lithography

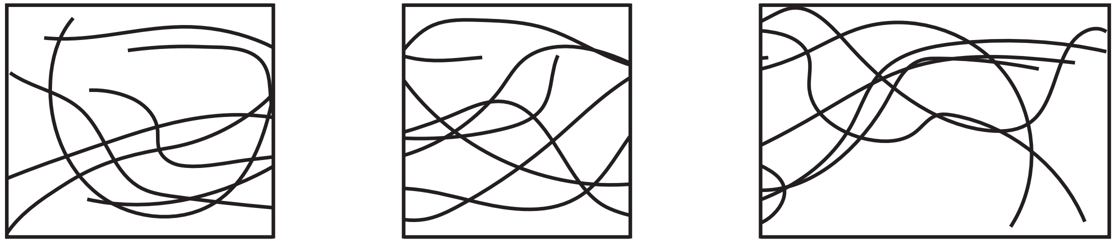
The coating, exposure, and dissolution process parameters are all impacted by the molecular weight!



PMMA film coated onto substrate



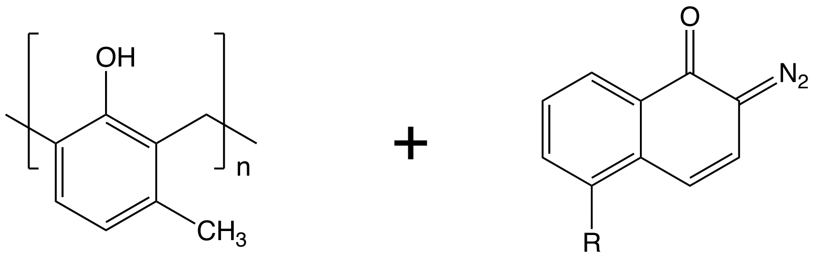
Exposure causes chain scission, lowering molecular weight



Lower molecular weight regions can be dissolved away

Positive Resist: Exposed = Dissolve

Novolac-DNQ

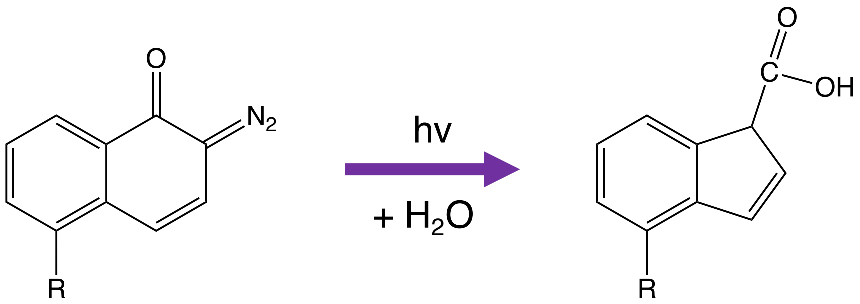


Novolac resin

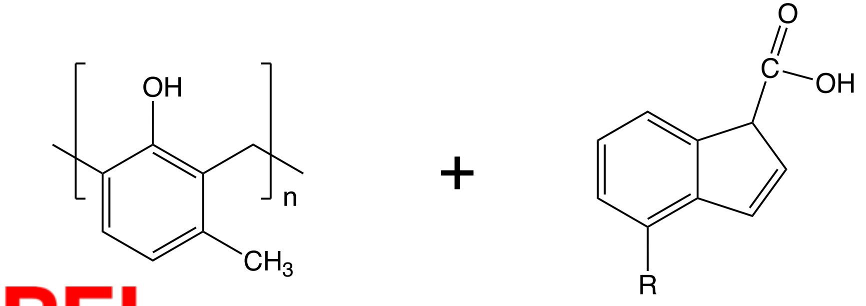
Diazonaphthoquinone (DNQ)

DNQ is a dissolution inhibitor

Slow dissolution

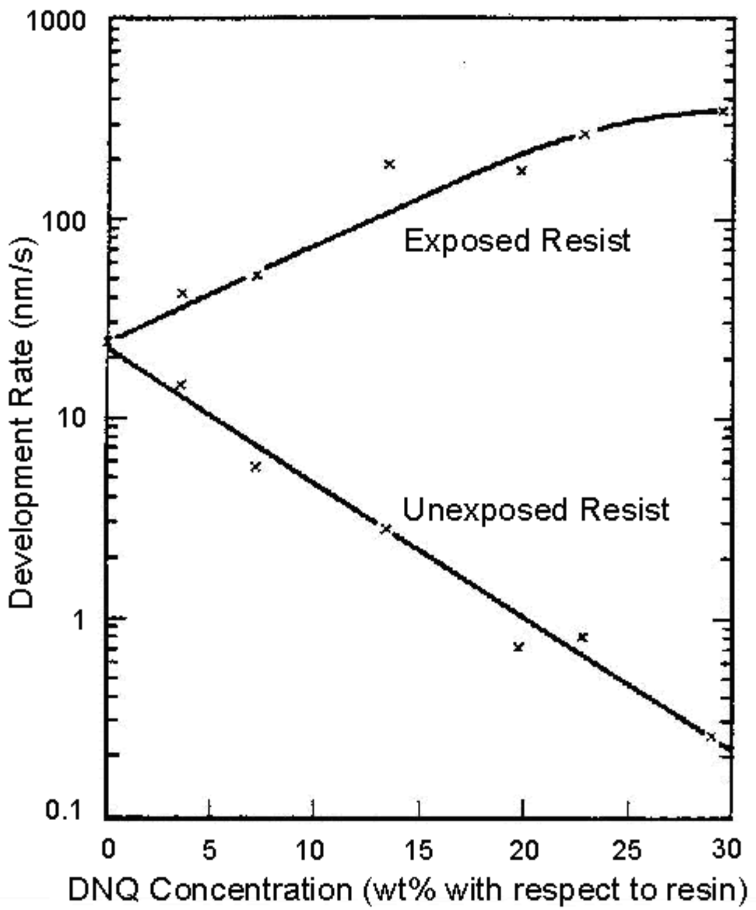


Indene-Carboxylic acid Photoproduct (ICA)



ICA is a dissolution promotor

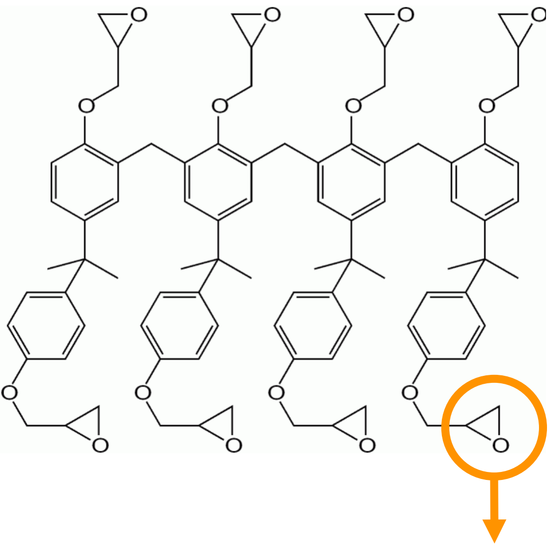
Fast dissolution



Design of polymer impacts the rate of dissolution

Negative Resist: Exposed = Stay

SU-8



Epoxide functional group

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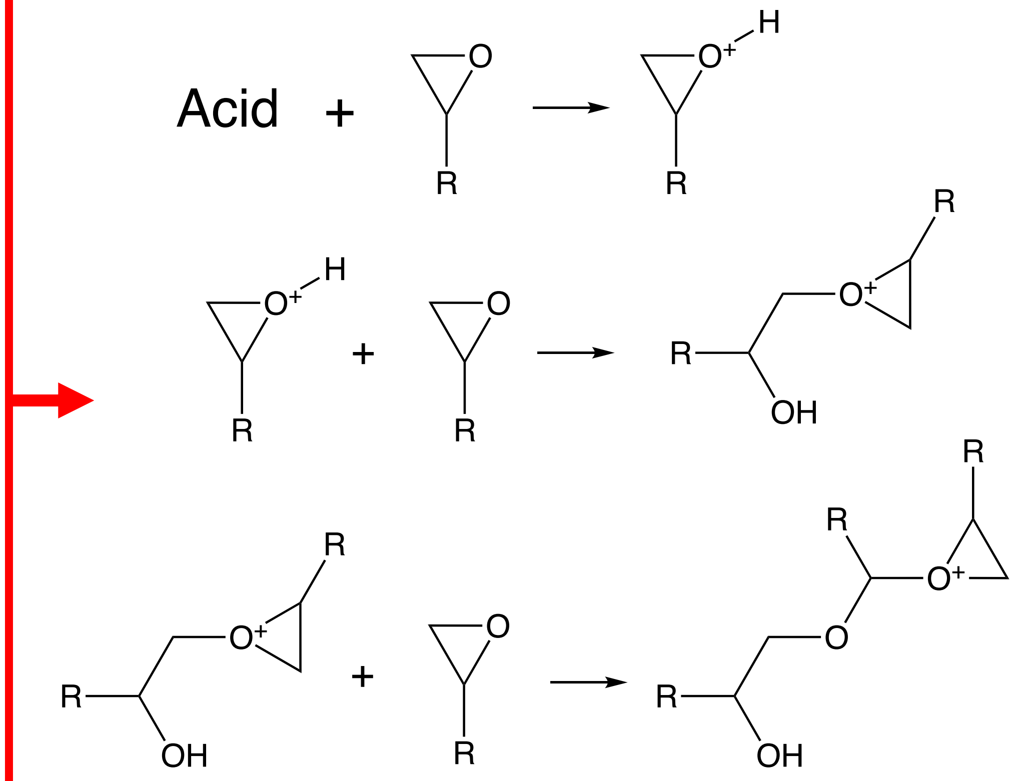
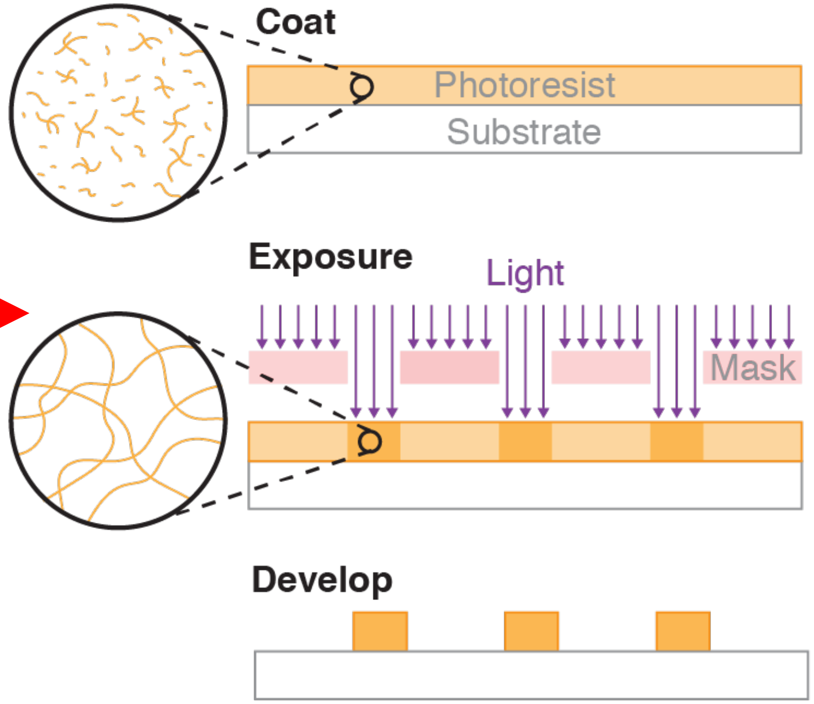
Photoacid Generator* (PAG)

PAGs react with light to generate acids
Epoxides can react with acids!



Chain-growth polymerization!

Areas exposed with light crosslink and become insoluble



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*if you're interested, the PAG for SU-8 is triarylsulfonium/hexafluoroantimonate salt

Short Summary about Manufacturing

- Polymers are easy to manufacture! — Relatively low processing temperatures compared to metals and ceramics

- Traditional polymer manufacturing is optimized for high-volume production

- Additive manufacturing an emerging alternative manufacturing method for small/medium volume production

- Polymer processing and manufacturing is relevant to microengineers as well!

- Polymers are cheap!