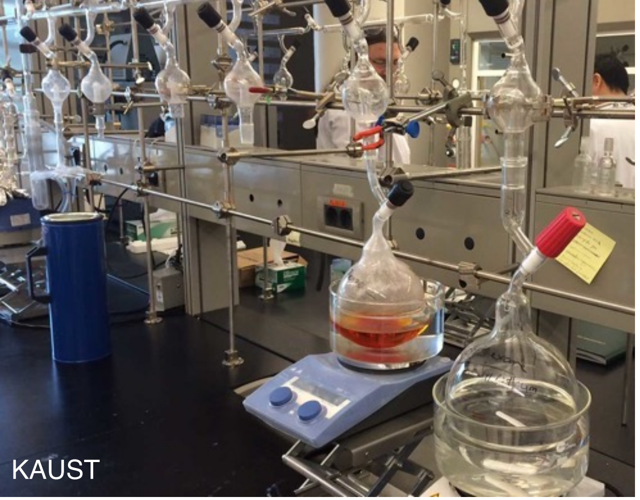
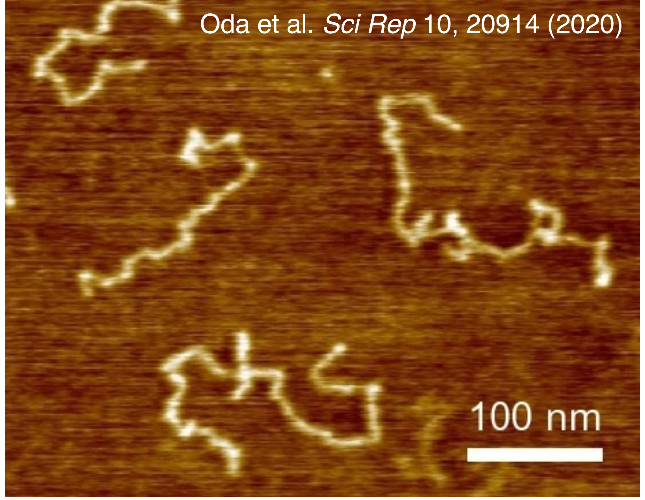




Materials Engineering I (MSE 214)

Lecture 4: Microstructure + Properties

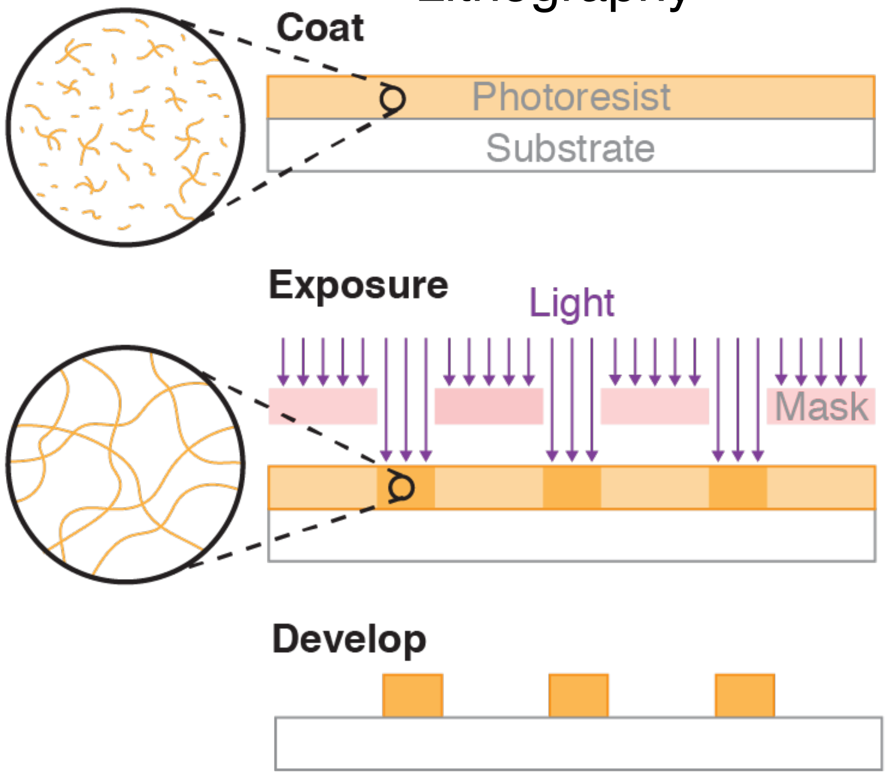
Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

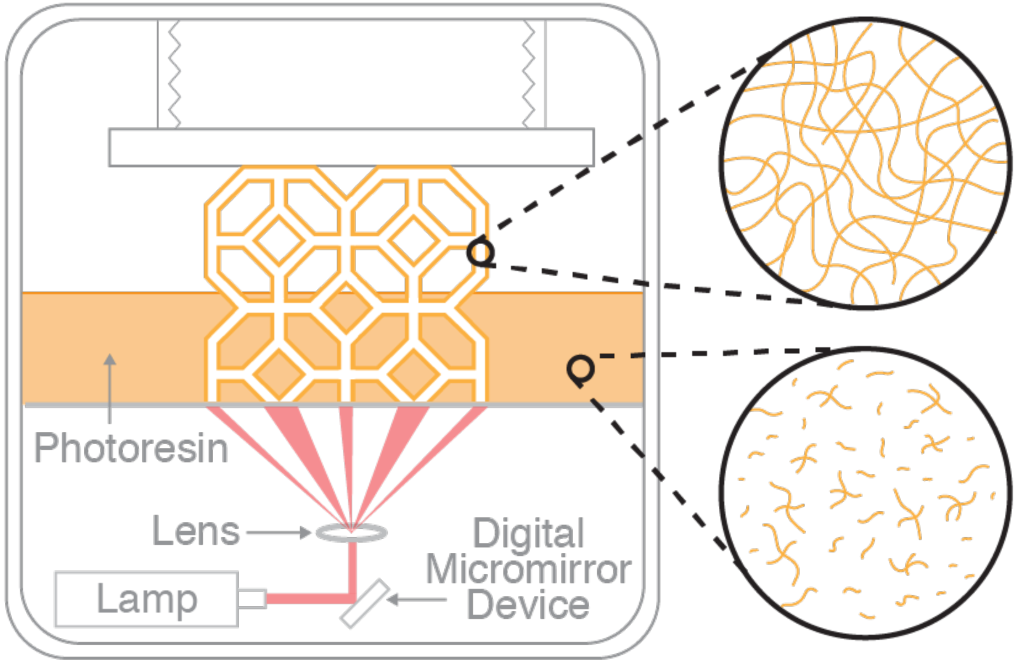
EPFL

Polymer Synthesis in Microengineering and Advanced Manufacturing

Lithography



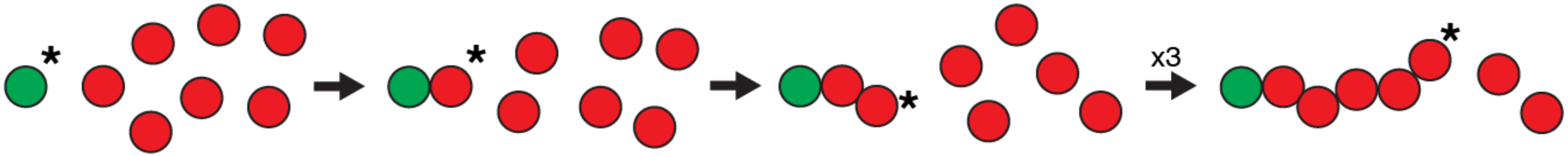
Additive Manufacturing



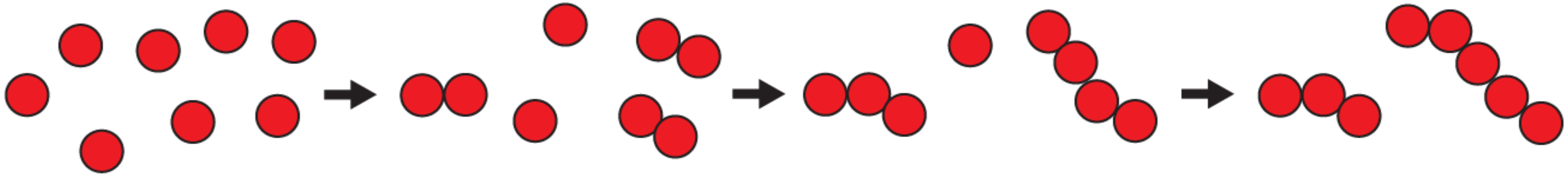
Learning polymer synthesis → Understand manufacturing
+ Understand how to tune their properties

Week 2 + 3 Recap

Chain-growth*: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain
Active site(s) regenerated at the end of each growth step



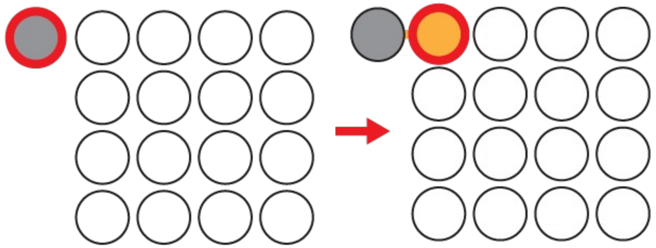
Step-growth*: Polymer grows via the reaction between any pairs of reactive species



*Deprecated by IUPAC but still very very widely used. Taught here so you'll be familiar with the literature.

Chain-growth Polymerization: The Three Phases

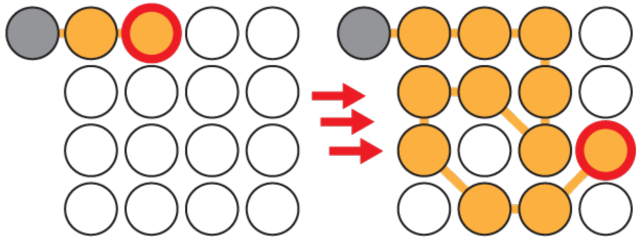
Initiation



$I \longrightarrow I^*$

$I^* + M \longrightarrow I\text{-}M^*$

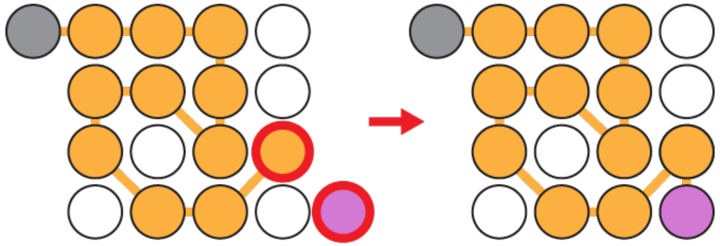
Propagation



$I\text{-}M^* + M \longrightarrow I\text{-}M\text{-}M^*$

$I\text{-}M\text{-}M^* \xrightarrow{M} I\text{-}M\text{-}(M)_n\text{-}M^*$

Termination



$I\text{-}M\text{-}(M)_n\text{-}M^* + Y^* \longrightarrow I\text{-}M\text{-}(M)_n\text{-}M\text{-}Y$

Note: Color here is just a guide to the eye, color is not used normally to denote different phases

Chain-growth Polymerization: Molecular Weight

Number average degree of polymerization $\bar{X}_n$ is related to $\boldsymbol{v}$

Let ***a*** be the fraction of chains that terminate by coupling
→ (***1 – a***) is the fraction of chains that terminate by disproportionation

Let ***b*** be the average number of initiator fragments per polymer → $b = \frac{Total\ number\ of\ initiator\ fragments}{Total\ number\ of\ polymer\ molecules}$

b is a value between 1 and 2 and represents the extent of mixed mode termination

$$\overline{X_n} = bv = \frac{2v}{2-a} = \frac{2R_p}{(2-a)R_t} = \frac{2\,k_p[\,M\,]}{4-2a\,(f\,k_d\,k_t\,[\,I\,])^{\frac{1}{2}}}$$

$$R_p = k_p[\,M\,]\left(\frac{f k_d[\,I\,]}{k_t}\right)^{\frac{1}{2}}$$

Two Problems:

1. Degree of polymerization and rate of polymerization are coupled
2. Experimental degree of polymerization observed to be lower than predicted

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Chain-growth Polymerization: Chain Transfer

Premature termination via transfer of radical to another species

$$M_n\bullet + XA \xrightarrow{k_{tr}} M_n{-}X + A\bullet$$

(k_{tr} is the chain-transfer rate constant)

XA could be monomer, initiator, solvent, polymer, or other substance.
X is the atom or species transferred to the chain

$$A\bullet + M \xrightarrow{k_a} M\bullet$$

(k_a is the reinitiation rate constant)

Chain transfer results in the production of a new radical $A^{\bullet}$, which reinitiates polymerization

Chain transfer ≠ termination of radical

Chain transfer just causes a premature decrease in the size of the propagating polymer chain

EPFL

Chain Transfer and Branching

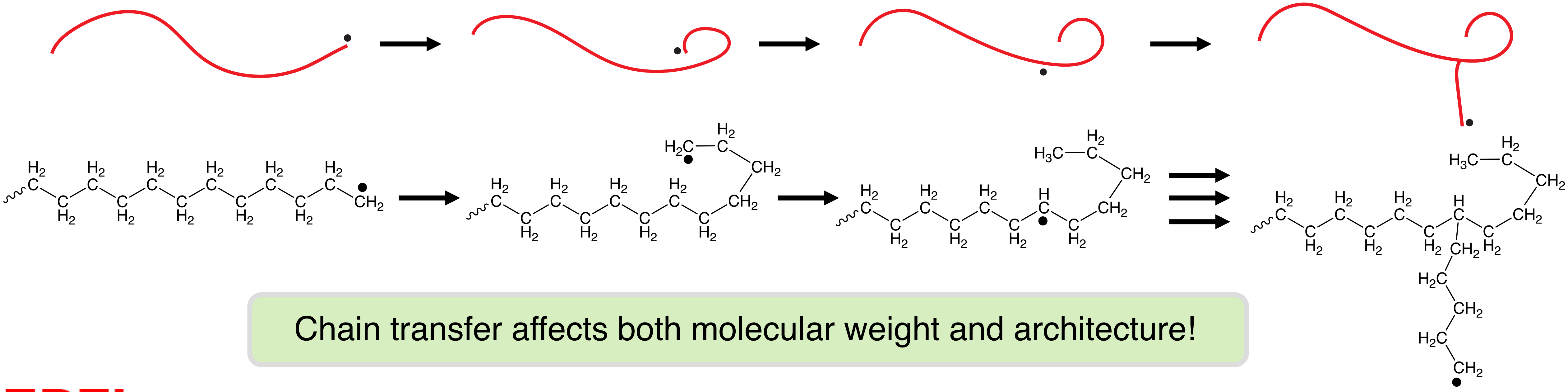
If chain growth can be summed up as:

$$\text{I-M-M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{I-M-M-M}^{\bullet}$$

How do we get non-linear polymers?

Ans: At high conversions, chain transfer to polymer is possible!

Short branches* via "Backbiting"



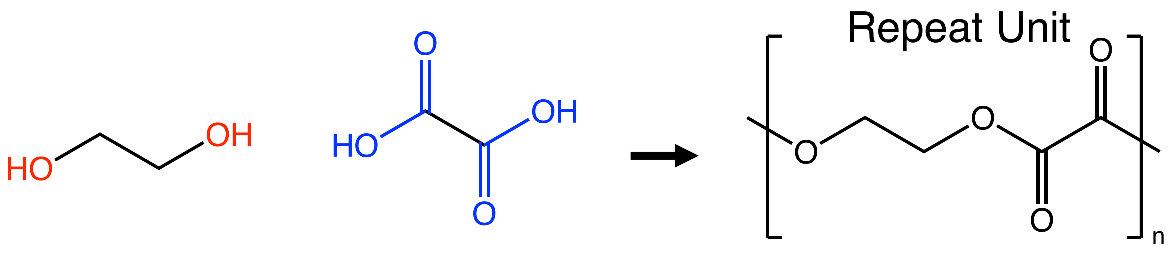
Chain transfer affects both molecular weight and architecture!

*Long branches will be covered in the exercise

A note about Step Growth

- It is much easier to abstract it like this:

Example system:
(Polyester)



+ (2n-1) H_2O

n Monomer A-A n Monomer B-B

-AB-

Structural/ Monomeric Unit from A-A

Structural/ Monomeric Unit from B-B

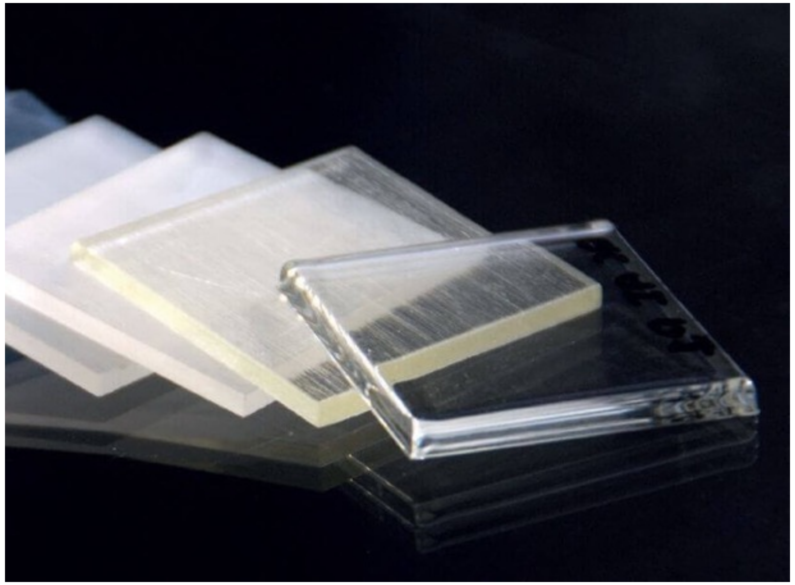
A — A + B — B → A — AB — B

AB is its own thing!

You will not be asked to memorize any structures.
All in As or Bs

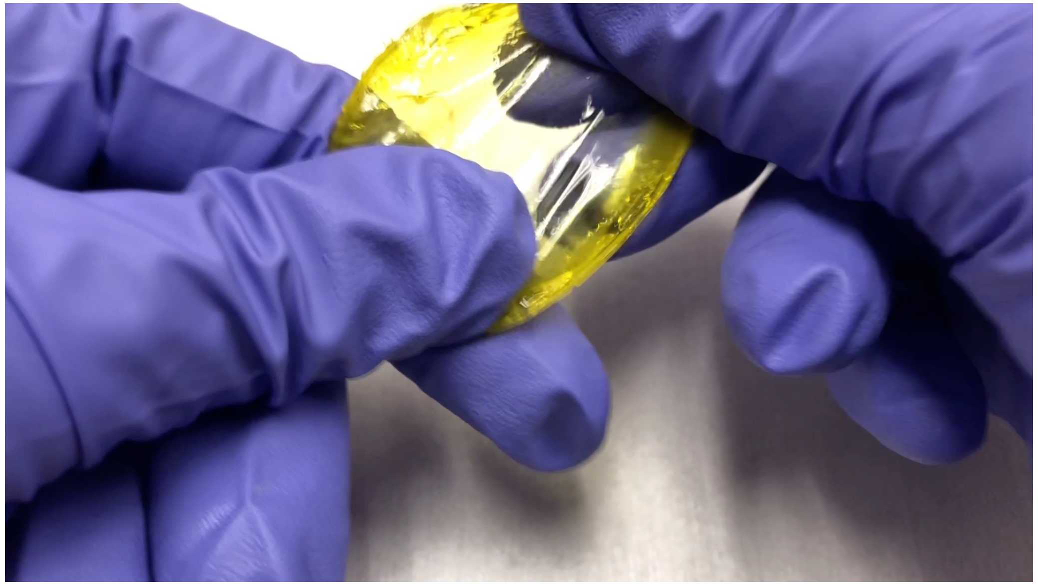
From Synthesis to Properties

Optical



Thermal

Mechanical



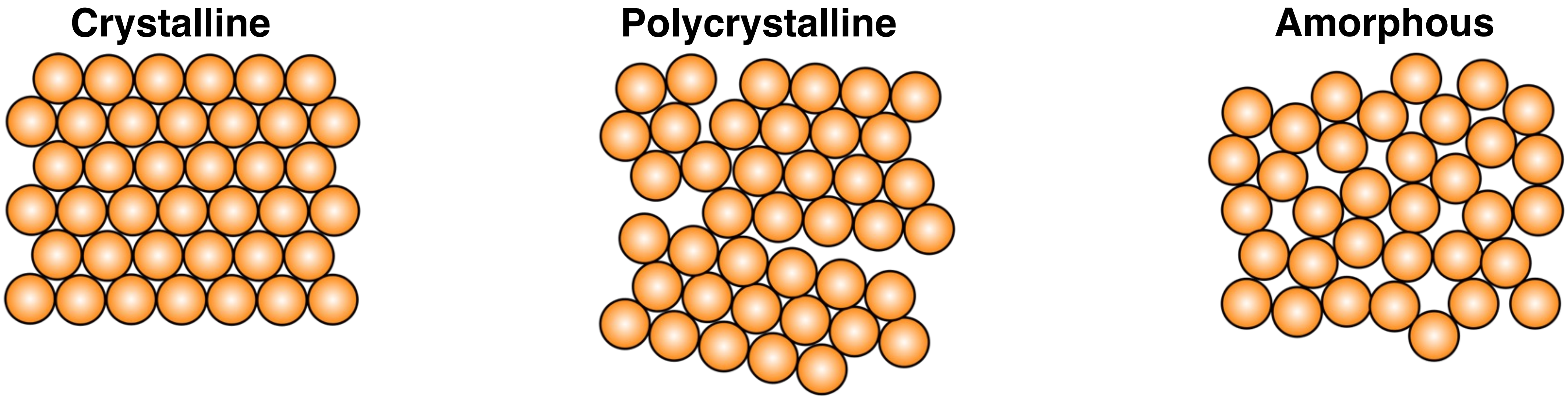
How can we understand the properties of polymers?

How does synthesis affect the properties?

Week 5 Learning Objectives

- **Understand the difference between amorphous, semi-crystalline, and crystalline polymers**
- **Understand the factors that favors polymer crystallization**
- **Understand what the glass transition temperature is and how it differs from the melting temperature**
- **Understand the factors that impact the T_g and T_m temperature**
- **Understand the impact that T_g and T_m has on material properties and behavior**

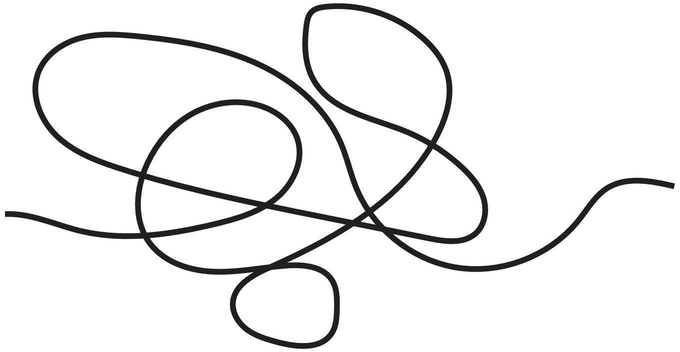
Recall from MSE 101b: Crystalline vs Amorphous



Simplest definition of cystallinity: Material whose constituents are arranged in a highly ordered manner

We've been representing polymers like this →

How do polymers crystallize?



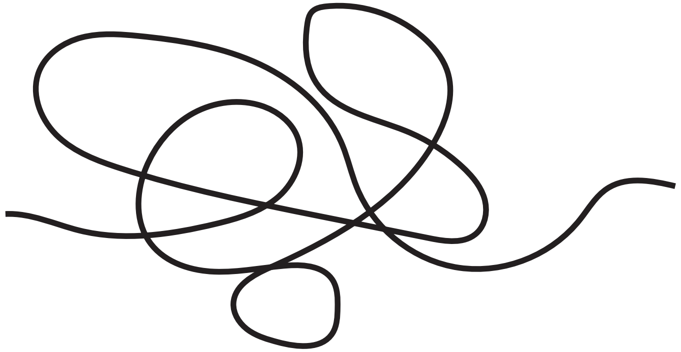
Single chain

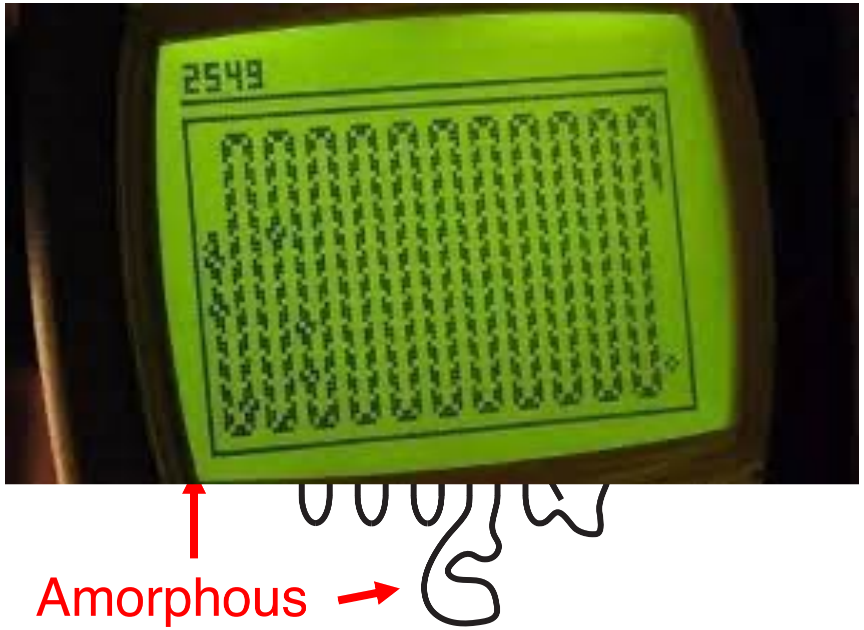
Multiple chains!

How do polymers crystallize?

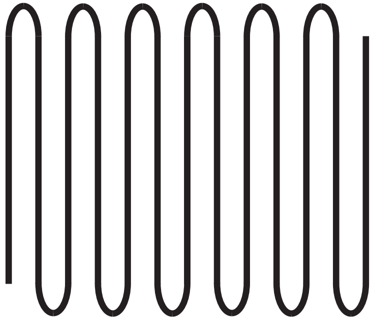
Basically a game of “snake”*

Amorphous





Crystalline



Crystallization is thermodynamically favorable!

Lowers energy state of the polymer

Polymers states:

Can be completely amorphous

Can be semi-crystalline

Can never be 100% crystalline

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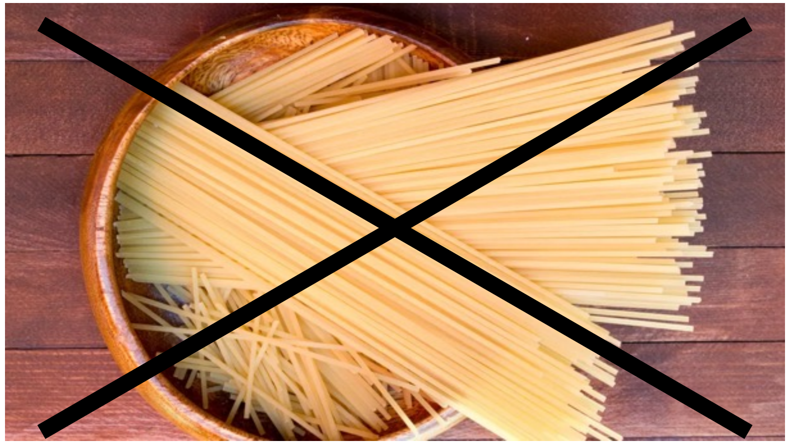
*You might be too young for this…

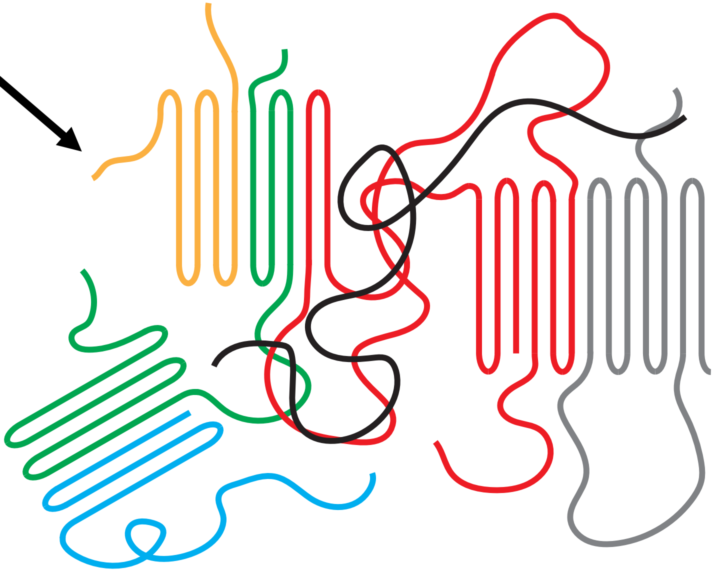
How do polymers crystallize?

For a system with multiple chains, how does crystallization happen?



Interactions between polymer chains prevent 100% crystallinity

Polymers that *can* crystallize only forms semi-crystalline polymers

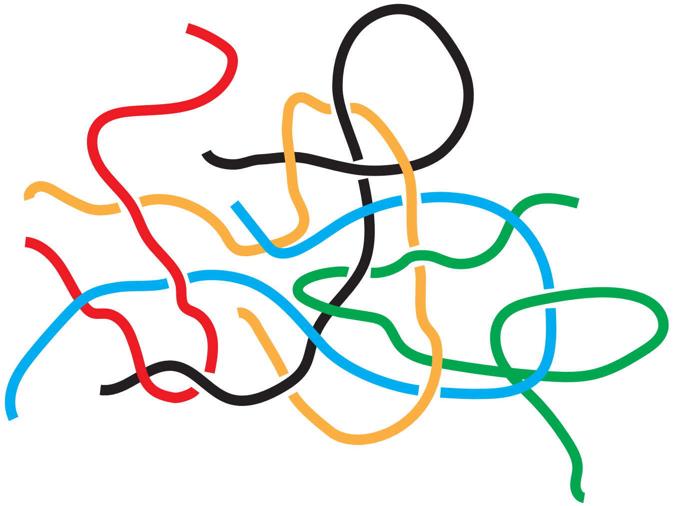


Polymer crystals surrounded by an amorphous matrix

A single chain can be involved in zero/one/multiple crystals

How do polymers crystallize?

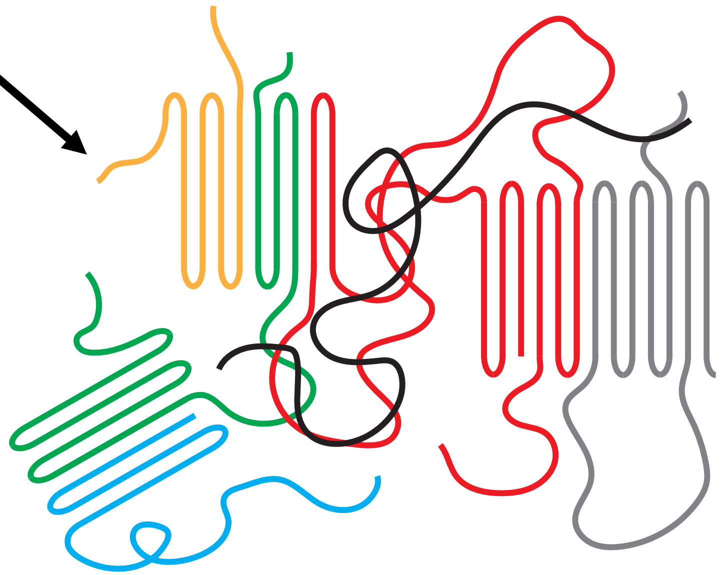
For a system with multiple chains, how does crystallization happen?



Long chains tend to get entangled and make crystallization difficult

Entanglements prevent 100% crystallinity and result in semi-crystallinity

Interactions between polymer chains prevent 100% crystallinity



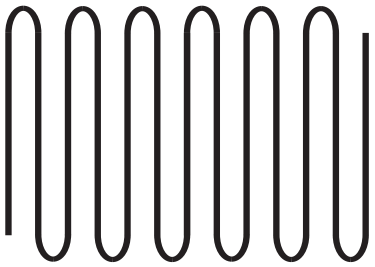
Polymers that *can* crystallize only forms semi-crystalline polymers

Polymer crystals surrounded by an amorphous matrix

A single chain can be involved in zero/one/multiple crystals

What favors crystallization of polymers?

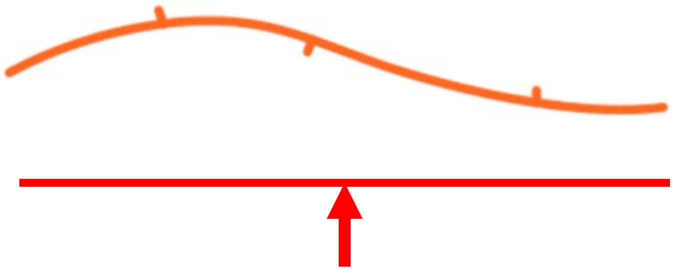
<u>Polymer Crystallite</u>

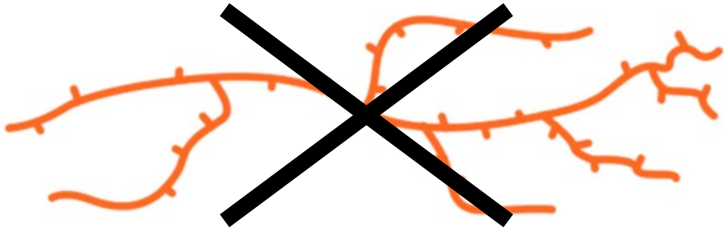


Chain needs to pack together

Regularity of polymer structure
+
Processing

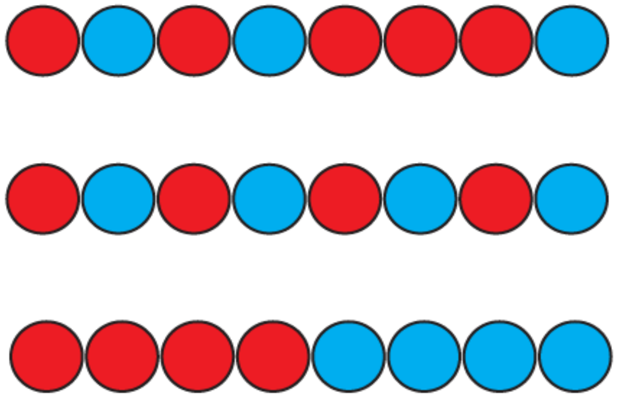
<u>Degree of branching</u>





Low or no branching favors crystallization

<u>Regularity of polymer composition</u>

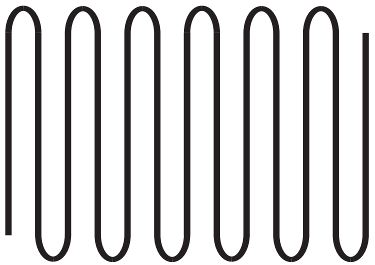


Statistical copolymers are usually amorphous

Block and alternating copolymers can crystallize

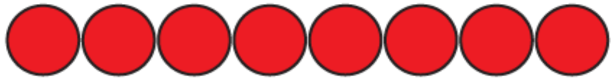
What favors crystallization of polymers?

Polymer Crystallite



Chain needs to pack together

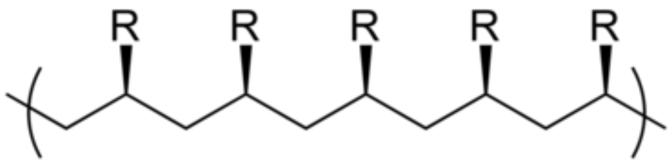
Regularity of polymer structure
+
Processing



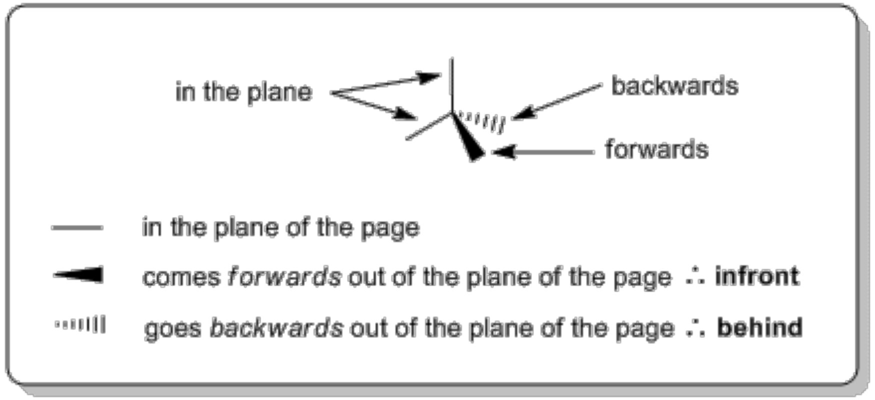
If regular composition is needed, why don't all homopolymers crystallize?

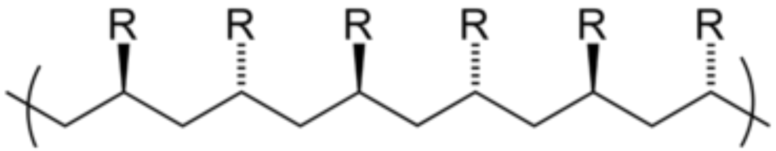
Tacticity

Can think of this as regularity of the side groups on the backbone

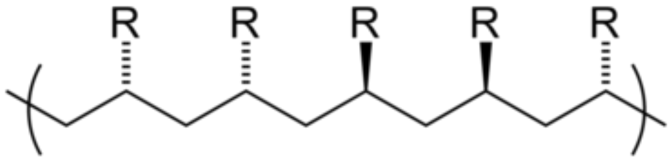


Isotactic





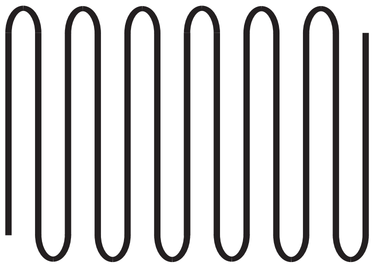
Syndiotactic



Atactic

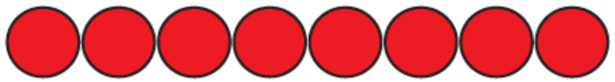
What favors crystallization of polymers?

Polymer Crystallite



Chain needs to pack together

Regularity of polymer structure
+
Processing



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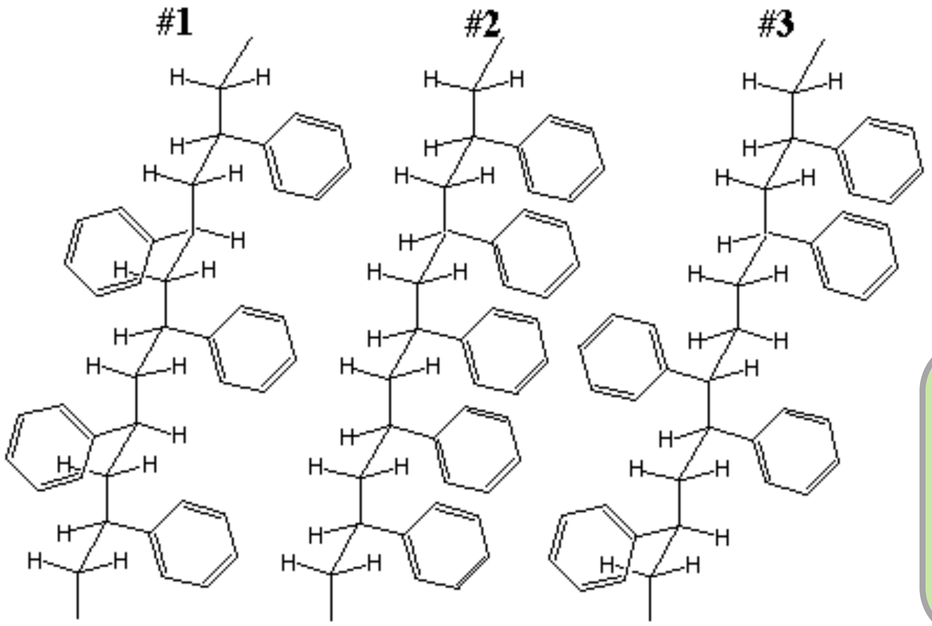
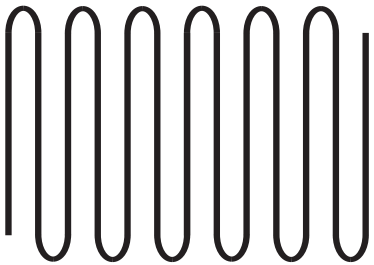


1. Syndiotactic
2. Isotactic
3. Atactic

Syndiotactic and isotactic polymers favor crystallization

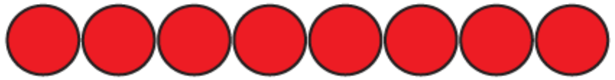
What favors crystallization of polymers?

<u>Polymer Crystallite</u>



Chain needs to pack together

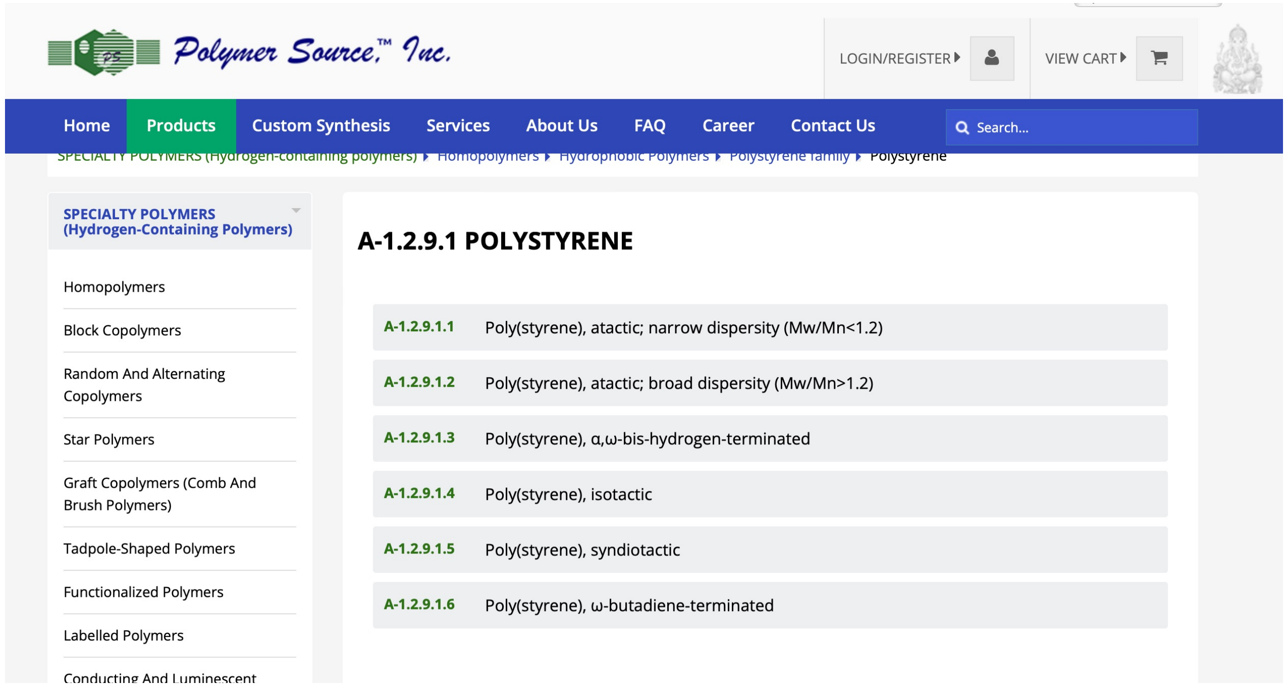
Regularity of polymer structure
+
Processing



If regular composition is needed, why don't all homopolymers crystallize?

<u>Tacticity</u>

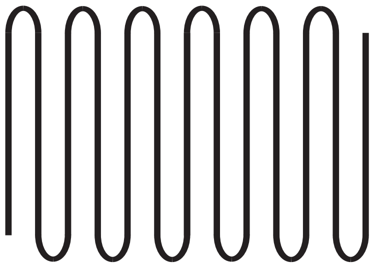
Can think of this as regularity of the side groups on the backbone



When you source polymers, you need to think about this!

What favors crystallization of polymers?

Polymer Crystallite



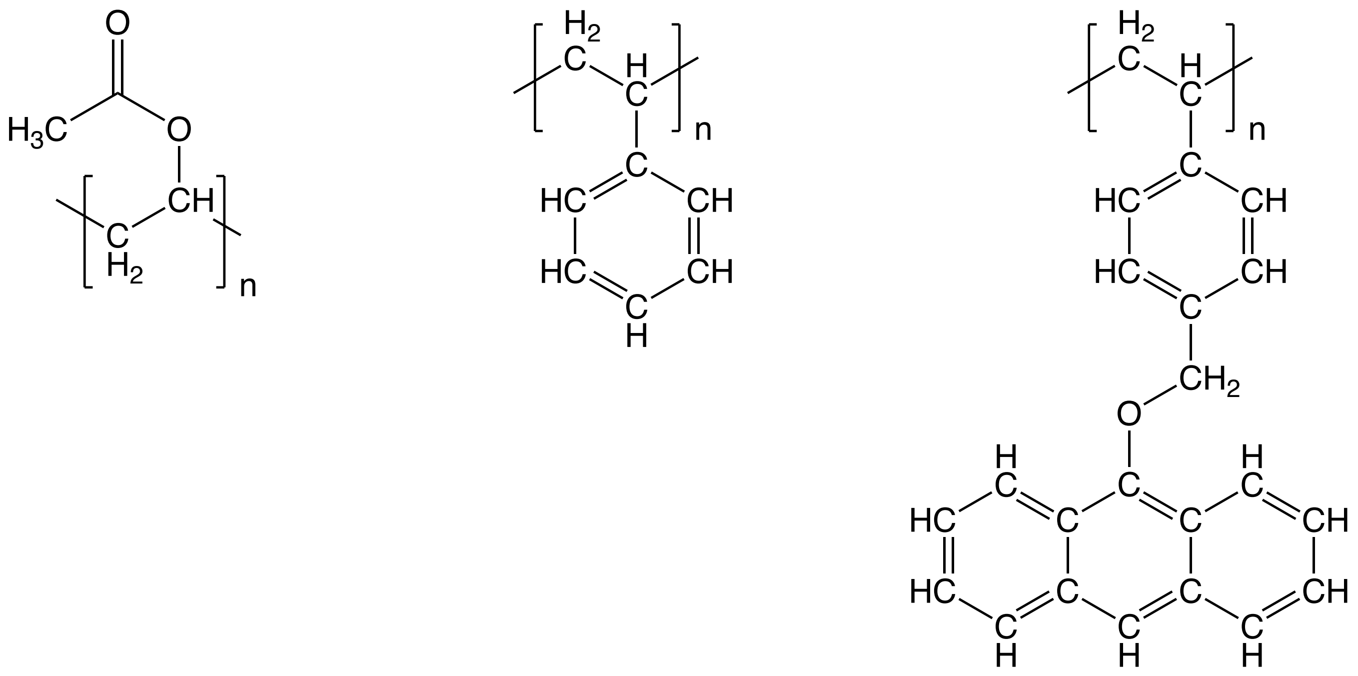
Chain needs to pack together

Regularity of polymer structure

+

Processing

Size of side groups



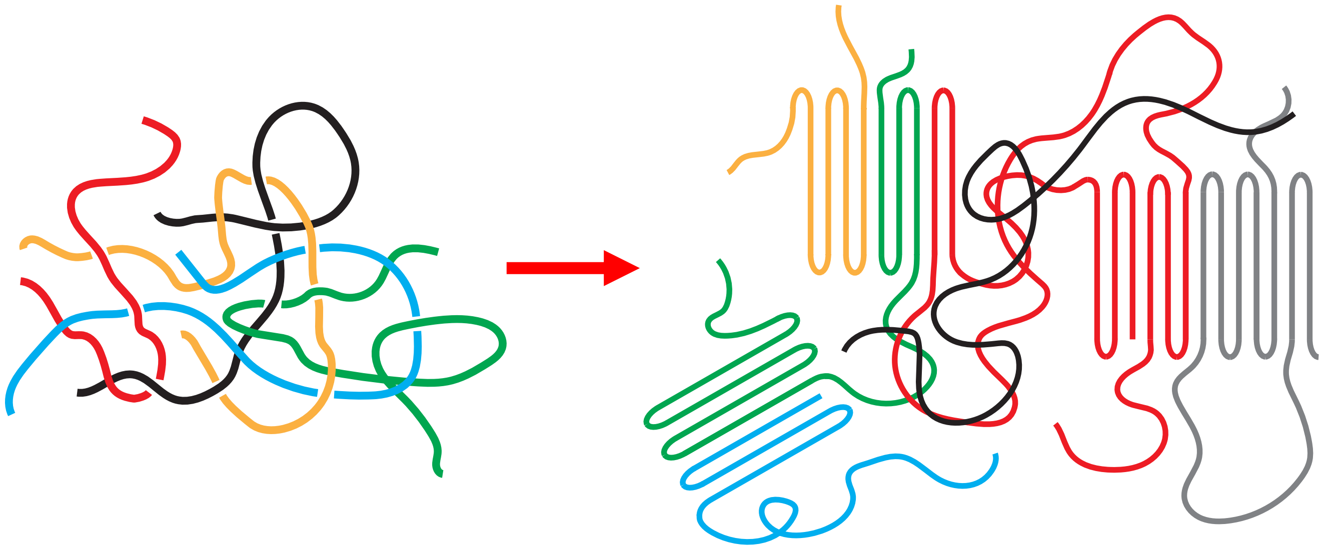
Crystallization difficulty

Fun fact: Atactic polymers with very small side groups can still crystallize

How do polymers crystallize?

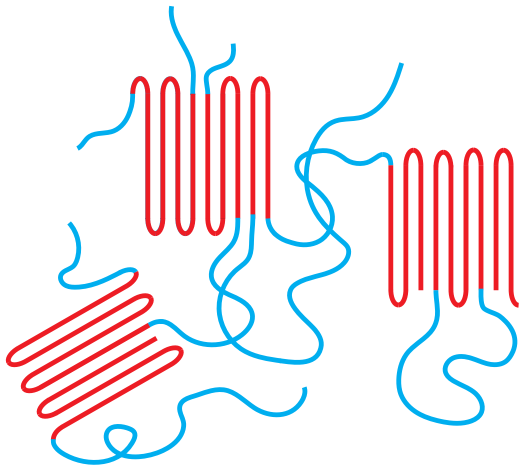
For crystallization to happen, the polymer chains need to be able to get themselves into the right configurations

Amorphous | Semi-crystalline



To understand crystallization, we first need to know about polymer phase transitions

Two key temperature transitions



Glass transition temperature (T_g)
→ Temperature range where amorphous regions starts to move

Melting temperature (T_m)
→ Temperature range where crystalline regions starts to move

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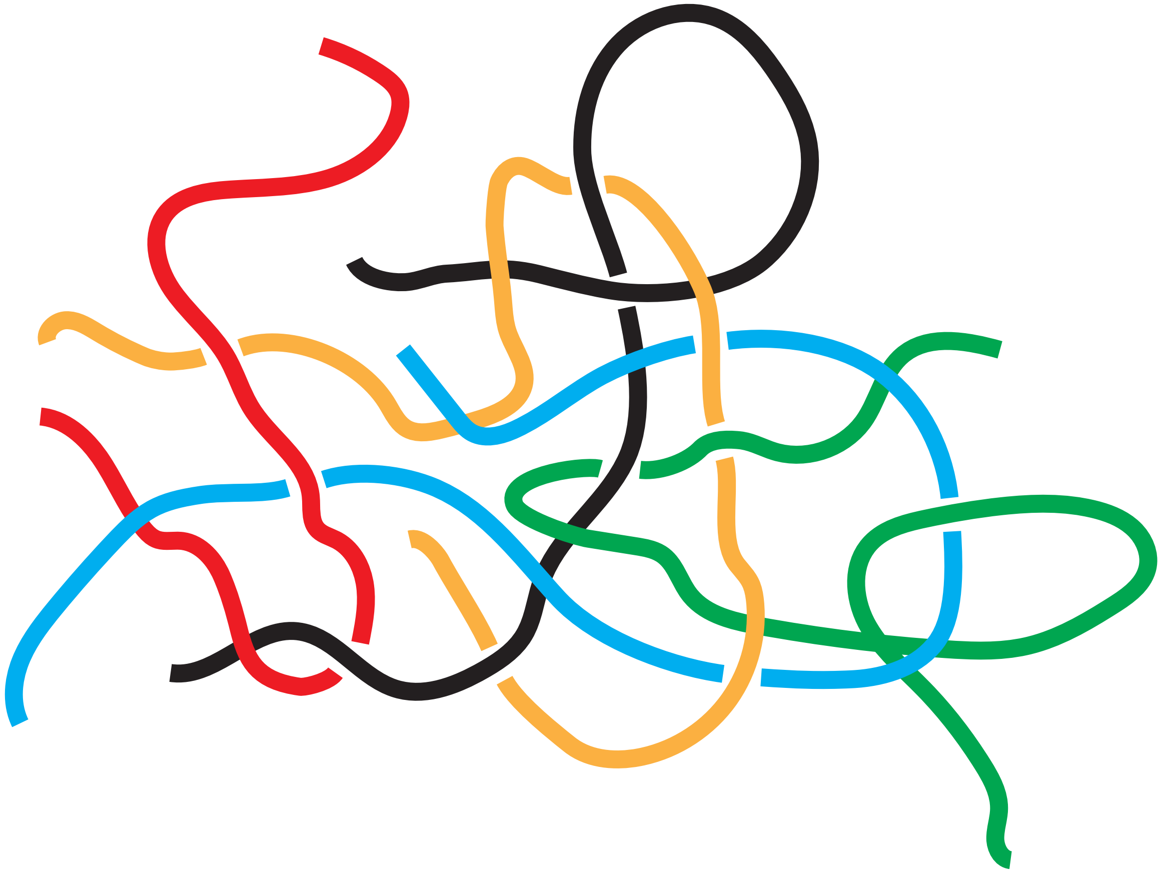
Glass Transition Temperature (T_g)



You can think of polymers as a mess of wires/cables/noodles

It's hard for one chain to "escape" from the rest → Entangled with each other

Need to provide energy for the chains to be able to "move" out of the mess

The temperature where there starts to have enough energy is the glass transition temperature

Glass Transition Temperature (T_g)

Rubbery State
($T > T_g$)

Polymer chains have enough energy to move around and slide past each other quickly*

Freshly cooked hot spaghetti can flow easily!

→

Cooling
to T_g

Chains start to lose energy and move slower; hard to move them around

Spaghetti getting cold and clumpy

→

Glassy State
($T < T_g$)

Chains do not have energy to move around or move extremely slowly

Spaghetti frozen and stuck together!

*to be precise, polymer chains can undergo long range segmental motion

Glass Transition Temperature (T_g)

Can think of T_g as the temperature range where the polymer starts to soften

- $T > T_g$ → Soft and deformable
- $T < T_g$ → Brittle and hard

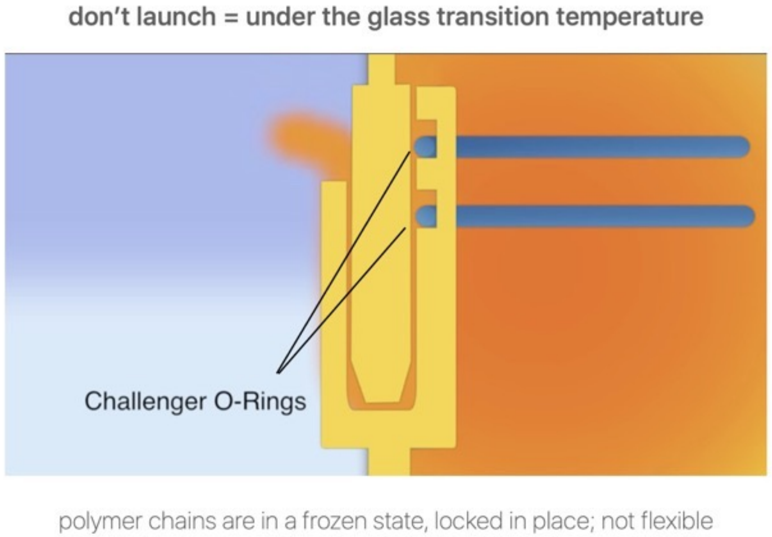
Depending on their design and processing history, the T_g of polymers can range from -100 to 200˚C

- Temperatures easily accessible to humans and also within seasonal variations

Challenger Disaster

Cold day before launch

O-rings were in the glassy state and could not seal



Glass Transition Temperature (T_g)

Can think of T_g as the temperature range where the polymer starts to soften

$T > T_g$ → Soft and deformable
$T < T_g$ → Brittle and hard

Important to know the T_g so that the operating temperatures of the polymer can be established!

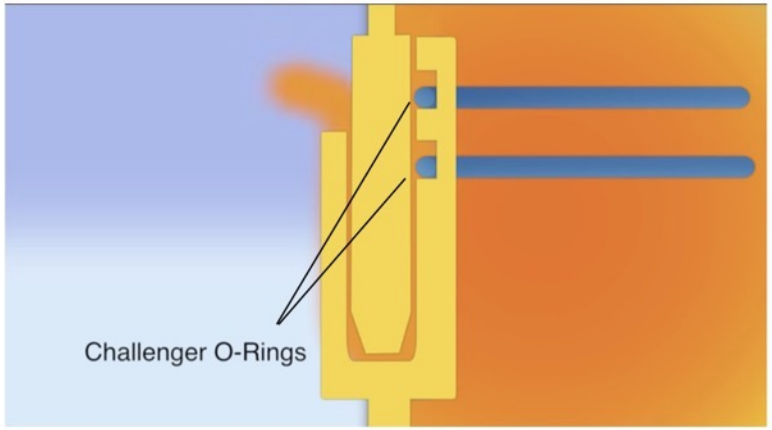
Critical for polymers used in critical applications or functions

Challenger Disaster

Cold day before launch

O-rings were in the glassy state and could not seal

don't launch = under the glass transition temperature



polymer chains are in a frozen state, locked in place; not flexible

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States of Amorphous Polymers

$T < T_g$
Glassy state

- Polymer behaves like a stiff and brittle solid
- Polymer chains are effectively rigid
- Small scale motion*

$T > T_g$
Rubbery state

- Polymer behaves like a soft and easily deformed solid
- Polymer chains are mobile
- Long range motion*

$T >> T_g$
Fluid state

- Polymer behaves like a liquid

Polymers are often used based on how their glass transition temperature compares to room and operating temperature

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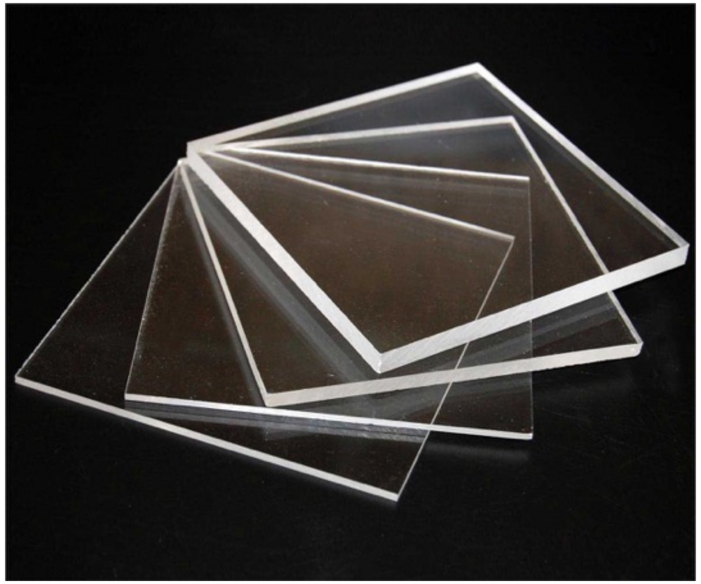
*additional information

States of Amorphous Polymers

$T < T_g$
Glassy state



Plexiglass has a T_g ~100˚C

$T > T_g$
Rubbery state

Low density polyethylene has a $T_g \sim -100$˚C

$T >> T_g$
Fluid state*

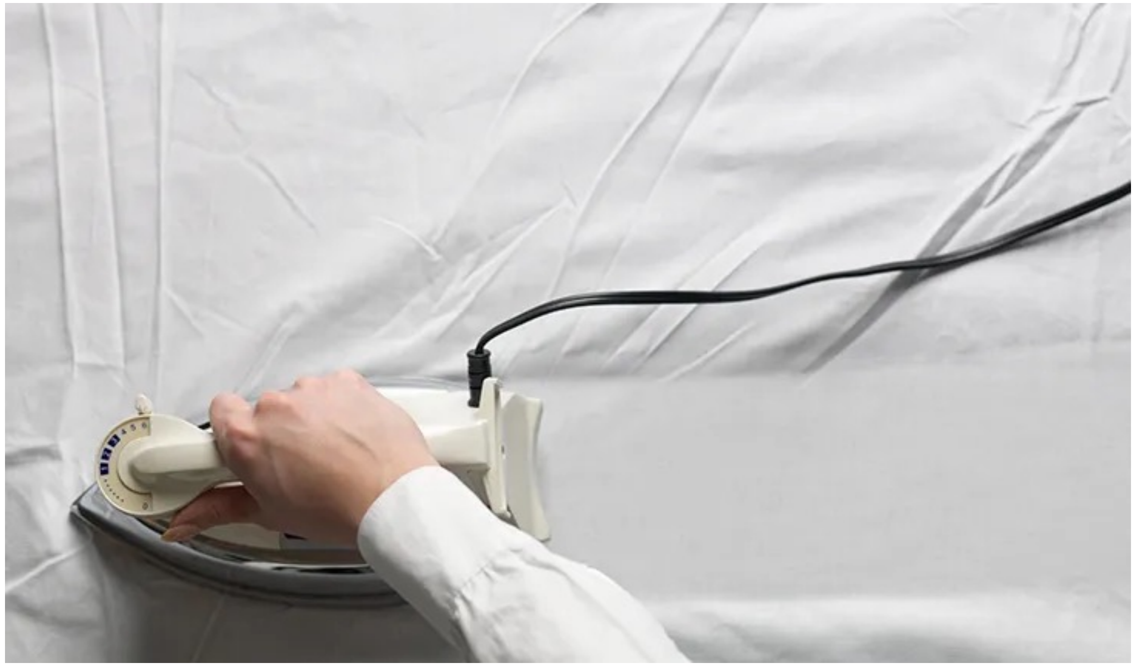
Polymers are often used based on how their glass transition temperature compares to room and operating temperature

*this is often referred to as a polymer melt…

Where have we used T_g in our daily lives before?

Shaping plexiglass/acrylics

Ironing



Heating a polymer past the glass transition allows us to manipulate its shape!

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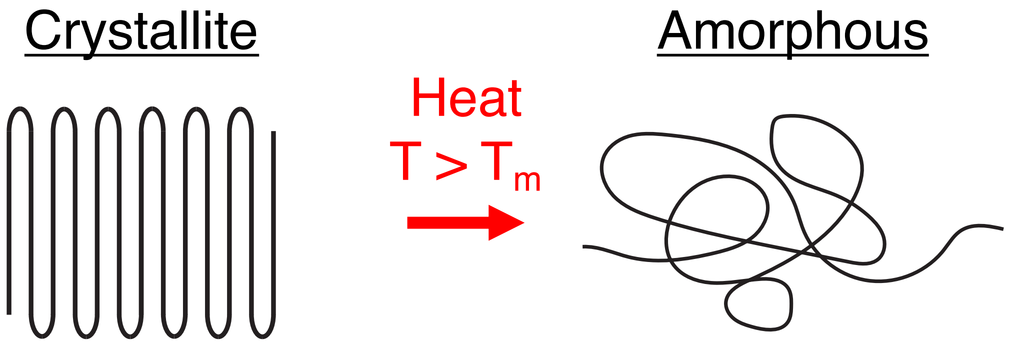
Melting Temperature (T_m)

Temperature range where crystalline regions starts to move and break apart



In the polymer sciences, melting temperature is specifically for the crystalline domains in semi-crystalline polymers

Polymers are messy:

Polymer melt is used to refer to polymers that have been heated until they flow like a liquid, regardless if they have a melting temperature or not

Similar in concept to T_g but for the crystalline regions

Chains are tightly packed together in crystalline domains

↓

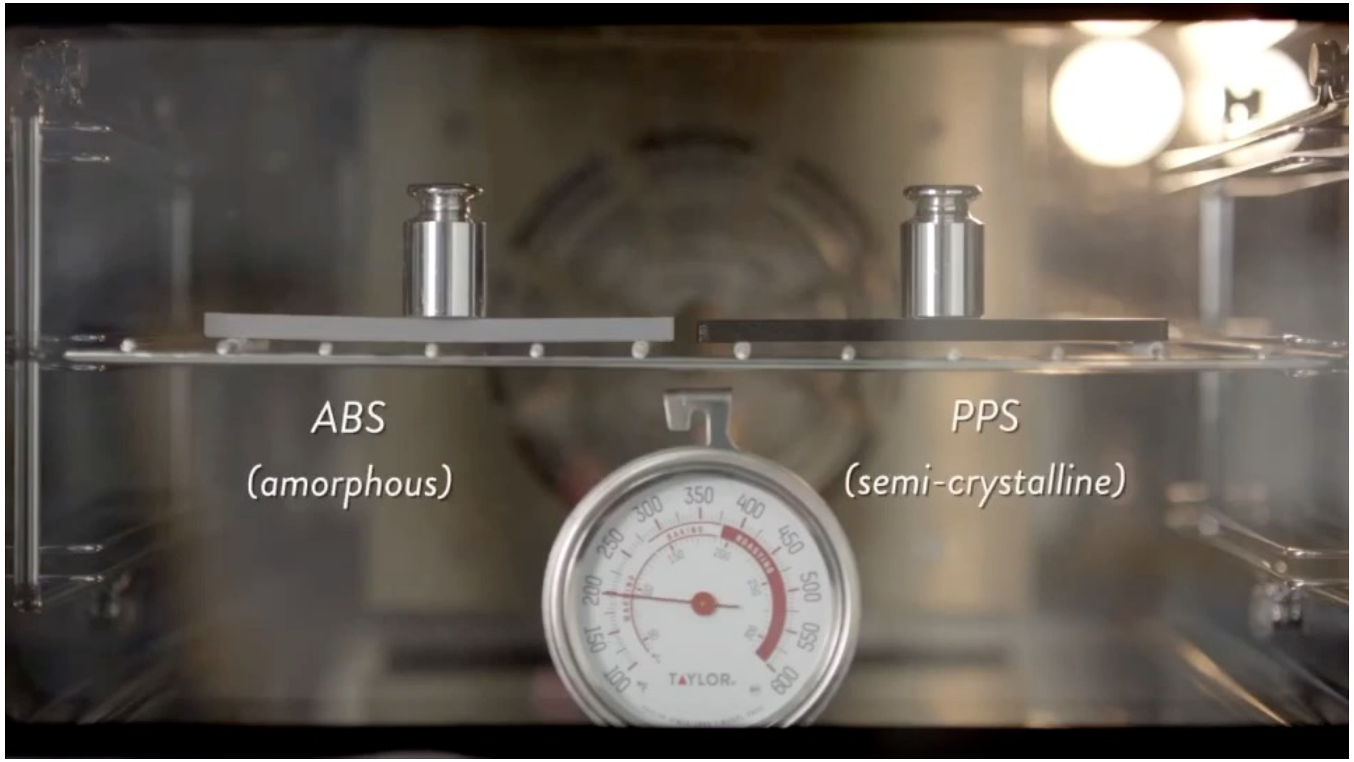
More energy needed to break them apart compared to amorphous chains

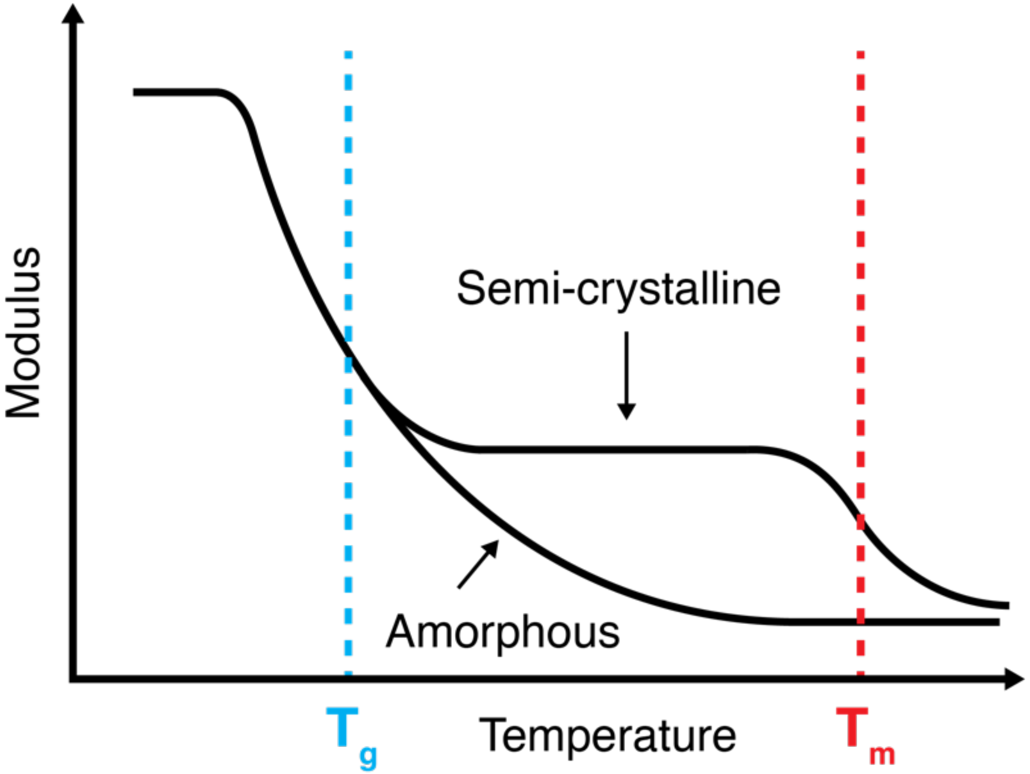
↓

$T_m > T_g$

$T_m > T_g$ → Semi-crystalline polymers can operate at higher temperatures

Numbers shown here are in Fahrenheit





ABS: Beyond T_g, all the chains can move

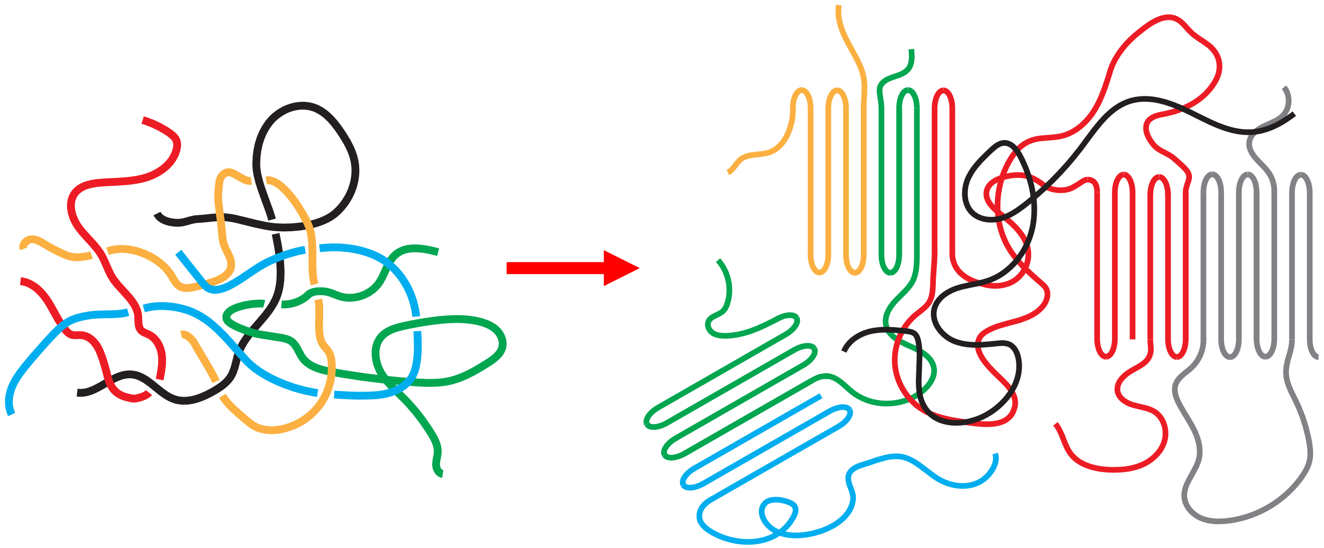
PPS: Beyond T_g, crystallites can't move still

You'll see variations of this plot but the main takeaway is that semi-crystalline regions have better mechanical properties beyond T_g.

How do polymers crystallize?

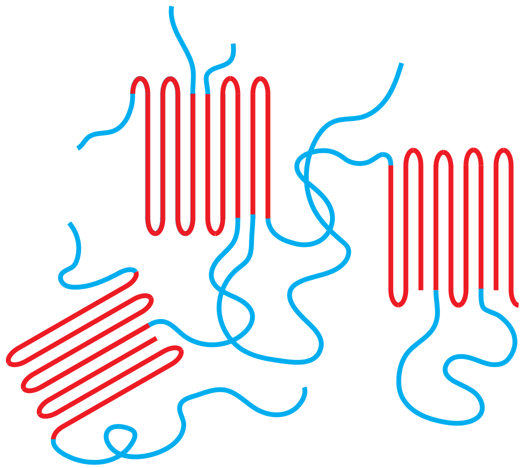
For crystallization to happen, the polymer chains need to be able to get themselves into the right configurations

Amorphous | Semi-crystalline



To understand crystallization, we first need to know about polymer phase transitions

Two key temperature transitions



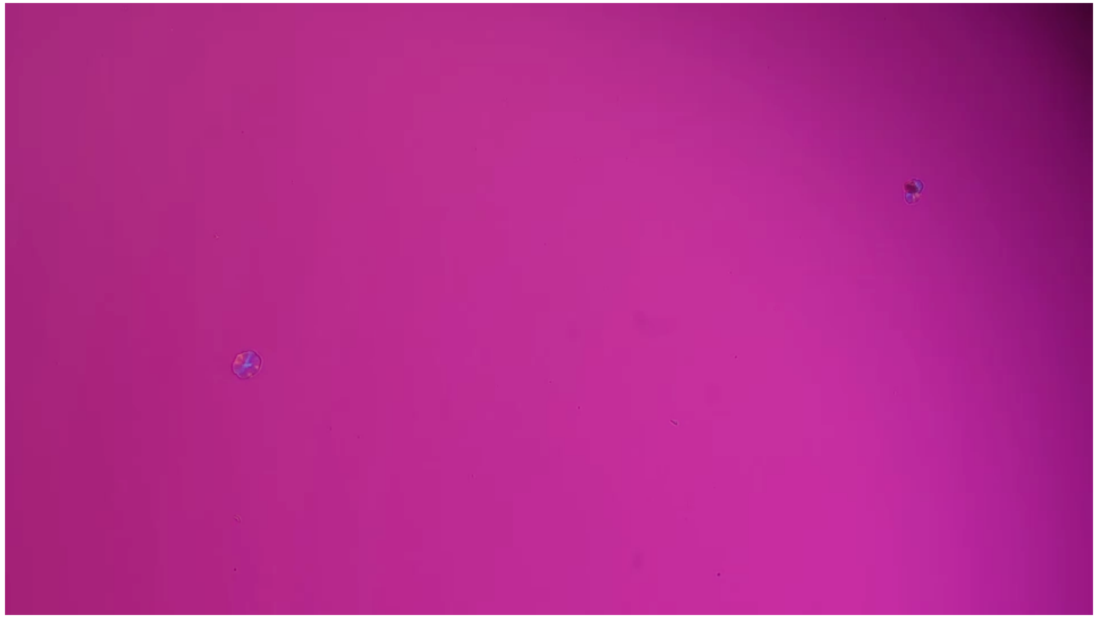
Glass transition temperature (T_g)
→ Temperature range where amorphous regions starts to move

Melting temperature (T_m)
→ Temperature range where crystalline regions starts to move

How do polymers crystallize?

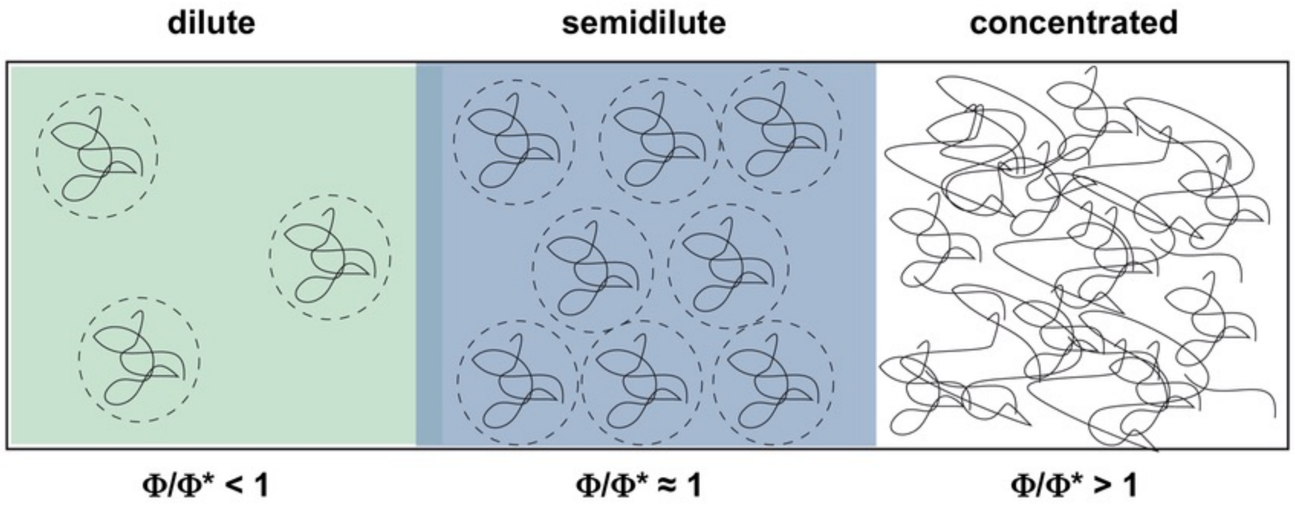
For crystallization to happen, the polymer chains need to be able to get themselves into the right configurations

Crystallization from the melt



Heat polymer beyond T_m to liquid state, cool slowly to below T_m but above T_g

Crystallization from solution



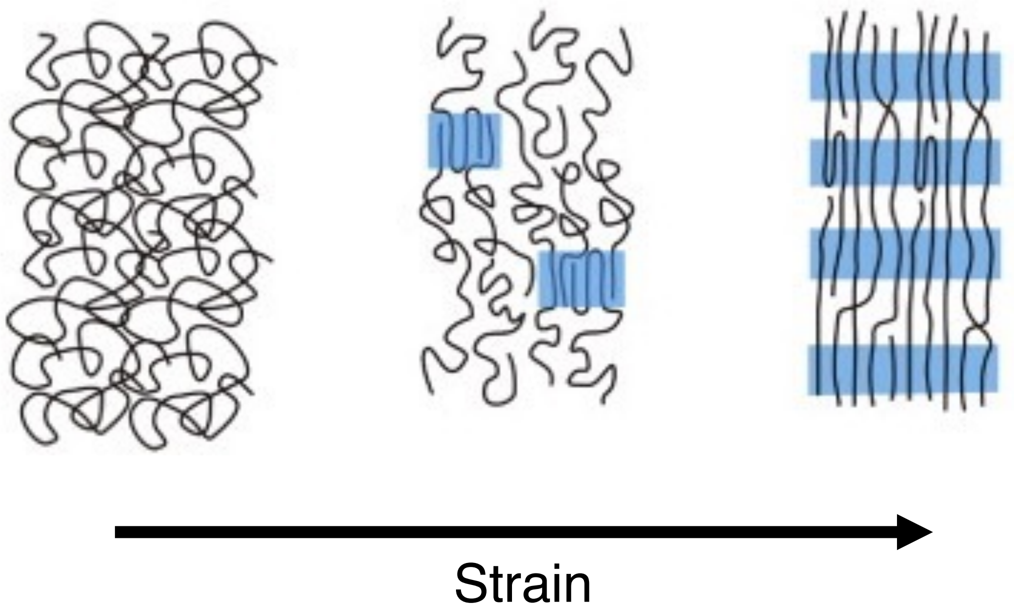
As solvent evaporates, polymer concentration increases → Chains interact → Crystallize

EPFL

How do polymers crystallize?

For crystallization to happen, the polymer chains need to be able to get themselves into the right configurations

Crystallization by stretching



<u>Crystallization is also kinetically controlled!</u>

Chains need time to arrange themselves into the right configuration

If a polymer can crystallize but does not have the time to do so, then it will become amorphous

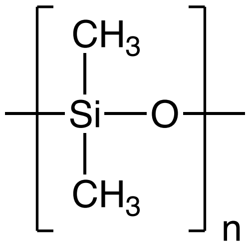
Example: Rapid cooling from the melt → Amorphous
Slow cooling from the melt → Semi-crystalline

What influences the T_g and T_m values of the polymer?

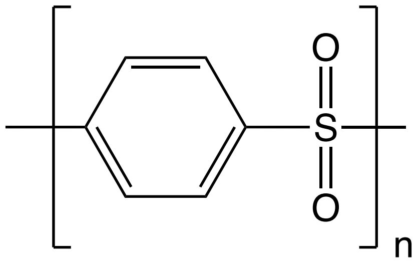
Can think of both transitions as the temperature range where the polymer chains (amorphous or crystalline) have the energy to move around

→ What will impact the ease of motion of the polymer chains?

1. Backbone flexibility / Chain rigidity



Polydimethylsiloxane (PDMS) has a really flexible backbone
T_g ~ –130˚C



Poly(phenylene sulfone) has a really stiff backbone
T_g can be >200˚C

Rigid backbone → More energy needed for movement → Higher T_g and T_m

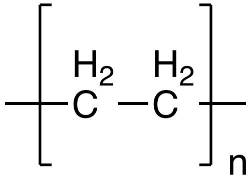
EPFL

What influences the T_g and T_m values of the polymer?

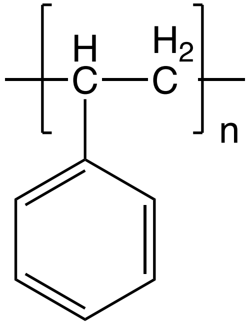
Can think of both transitions as the temperature <u>range</u> where the polymer chains (amorphous or crystalline) have the energy to move around

→ What will impact the ease of motion of the polymer chains?

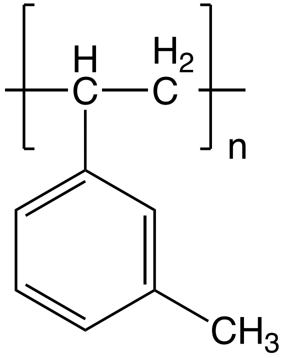
2. Size of side group



Polyethylene
$T_g \sim -110^\circ C$



Polystyrene
$T_g \sim 100^\circ C$



Methyl substituted polystyrene
$T_g \sim 170^\circ C$

Bulky side group can "catch" onto adjacent chains → More energy needed for movement → Higher T_g and T_m

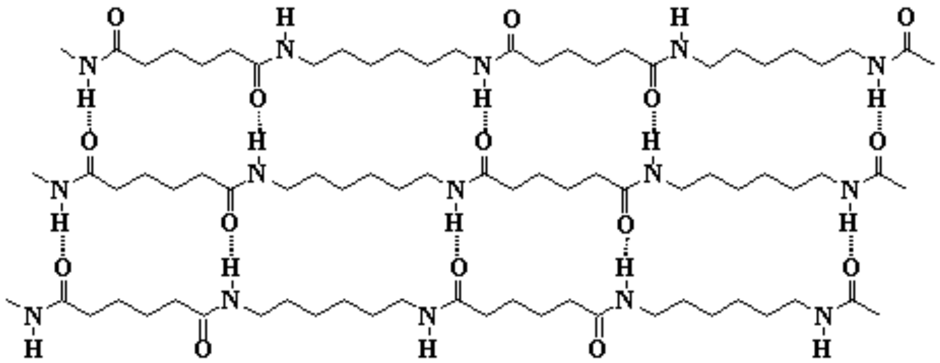
What influences the T_g and T_m values of the polymer?

Can think of both transitions as the temperature range where the polymer chains (amorphous or crystalline) have the energy to move around

→ What will impact the ease of motion of the polymer chains?

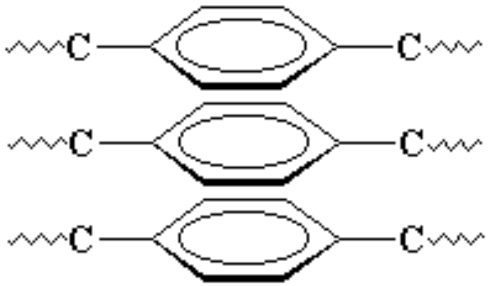
3. Intermolecular interactions

Hydrogen bonding in Nylon 6,6



T_g = ~50˚C
T_m = ~250˚C

Pi-stacking in PET



T_g = ~75˚C
T_m = ~250˚C

Stronger intermolecular interactions make it hard for the chains to move → Higher T_g and T_m

What influences the T_g and T_m values of the polymer?

Can think of both transitions as the temperature range where the polymer chains (amorphous or crystalline) have the energy to move around

→ What will impact the ease of motion of the polymer chains?

4. Processing conditions

Faster cooling rate from melt → Amorphous chains have less time to arrange into crystals

↗ Less crystals + more defects in crystals → Lower T_m on reheating

↘ Less time to equilibrate → "Freezes" at a higher temperature → Higher T_g

What influences the T_g and T_m values of the polymer?

Can think of both transitions as the temperature range where the polymer chains (amorphous or crystalline) have the energy to move around

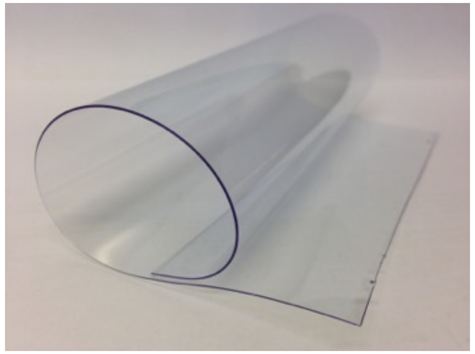
→ What will impact the ease of motion of the polymer chains?

5. Introduction of plasticizers

Small molecules that lower the T_g and T_m by spacing out the chains so that it is easier for the chains to move past one another

Rigid PVC
T_g ~85˚C

Plasticized PVC
T_g ~50˚C



→ Partially responsible for cracked dashboards

Plasticizer in polymer outgasses over time / degrade under UV → Polymer gets more brittle → Cracks!

EPFL

What influences the T_g and T_m values of the polymer?

Can think of both transitions as the temperature range where the polymer chains (amorphous or crystalline) have the energy to move around

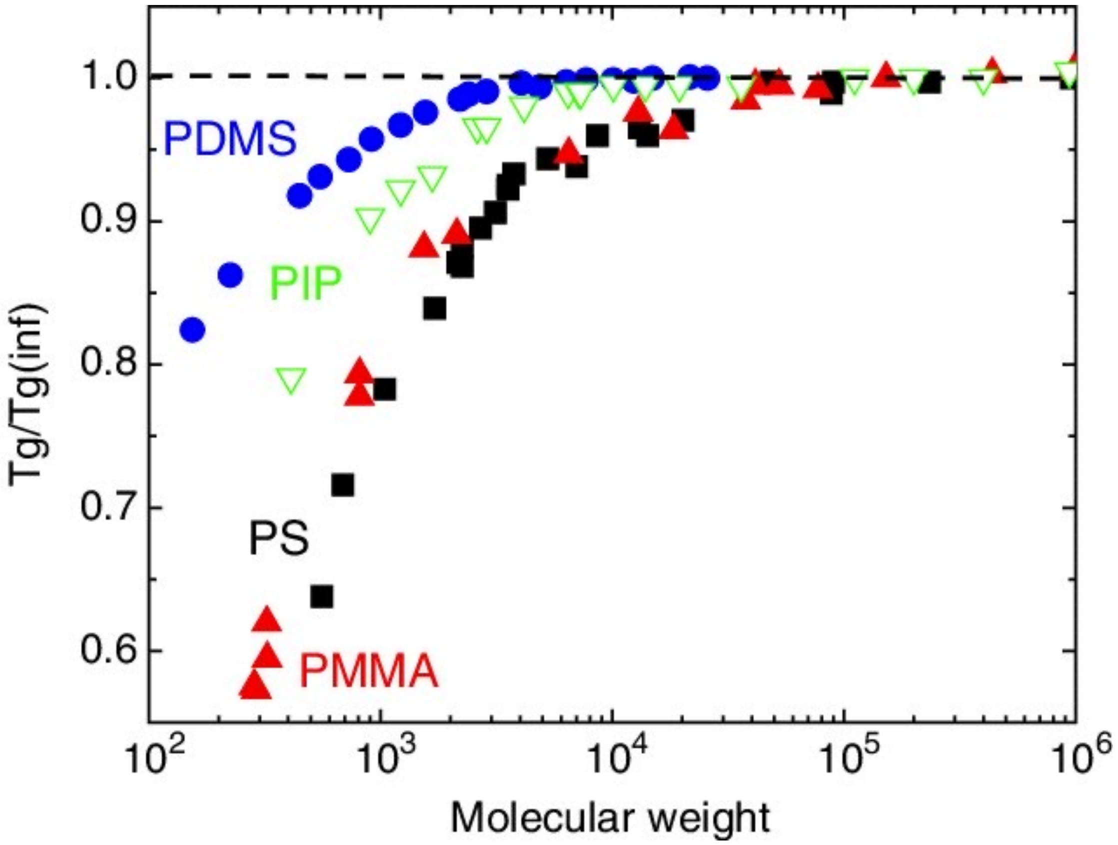
→ What will impact the ease of motion of the polymer chains?

6. Molecular weight*

$$T_g = T_{g,\infty} - \frac{K}{M_n}$$ (Fox-Flory equation)

T_g = Glass transition for polymer with M_n
$T_{g,\infty}$ = Glass transition for polymer with "infinite" molecular weight
K = Empirically determined parameter
M_n = Number average molecular weight

T_g increases with M_n and then tapers off to a steady value



*we won't go into the molecular reasons here

Sokolov, A. P., V. N. Novikov, and Y. Ding. *Journal of Physics: Condensed Matter* 19.20 (2007): 205116.

What influences the T_g and T_m of the polymer?

Some takeaways:

Polymers with high T_g usually have high T_m → Polymers that do not easily move and go past the glass transition would probably not melt easily

Molecular regularity, chain rigidity, and intermolecular forces don't always affect T_g and T_m in the same way → Eg. Polyethylene has low T_g because it has flexible chains but their simple structure means it can pack well and form crystals with high T_m.

T_m more dependent on regularity, T_g more dependent on secondary forces and chain flexibility.

Factors that decrease the crystallization tendency also lead to increased T_m → Polymers with rigid chains are difficult to crystallize, but the portions that do will be difficult to melt, i.e. high T_m

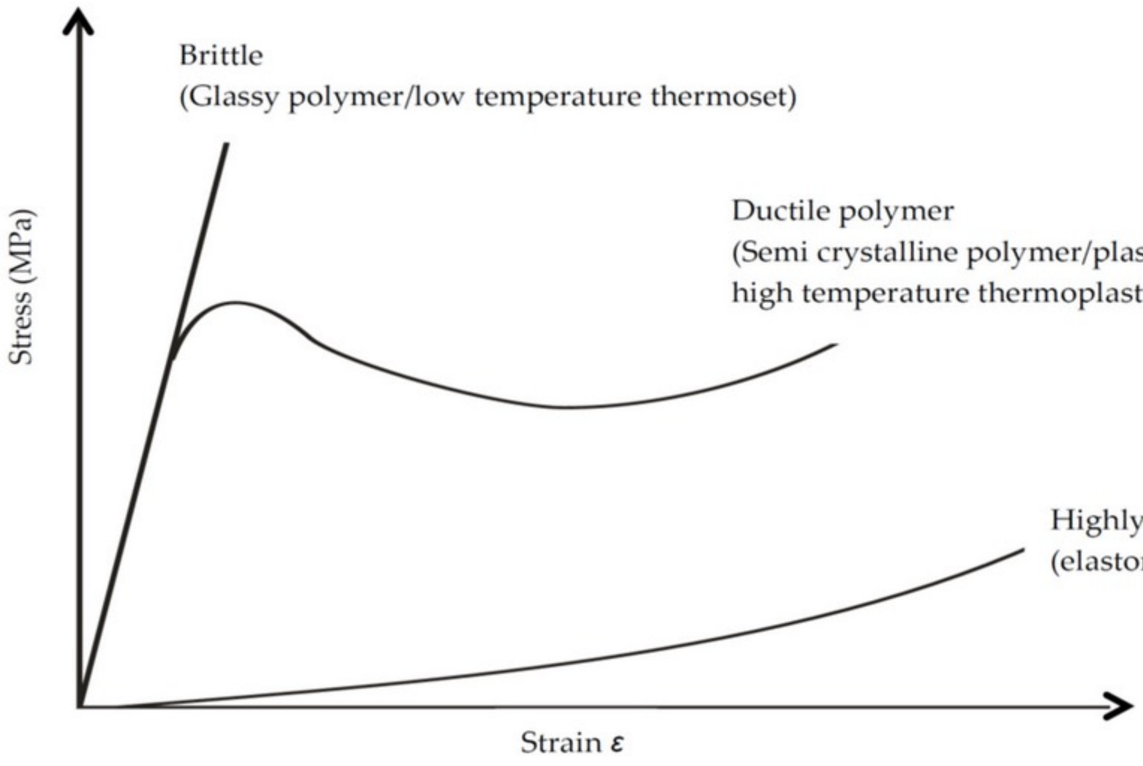
Crystallinity Impacts Properties and Behavior

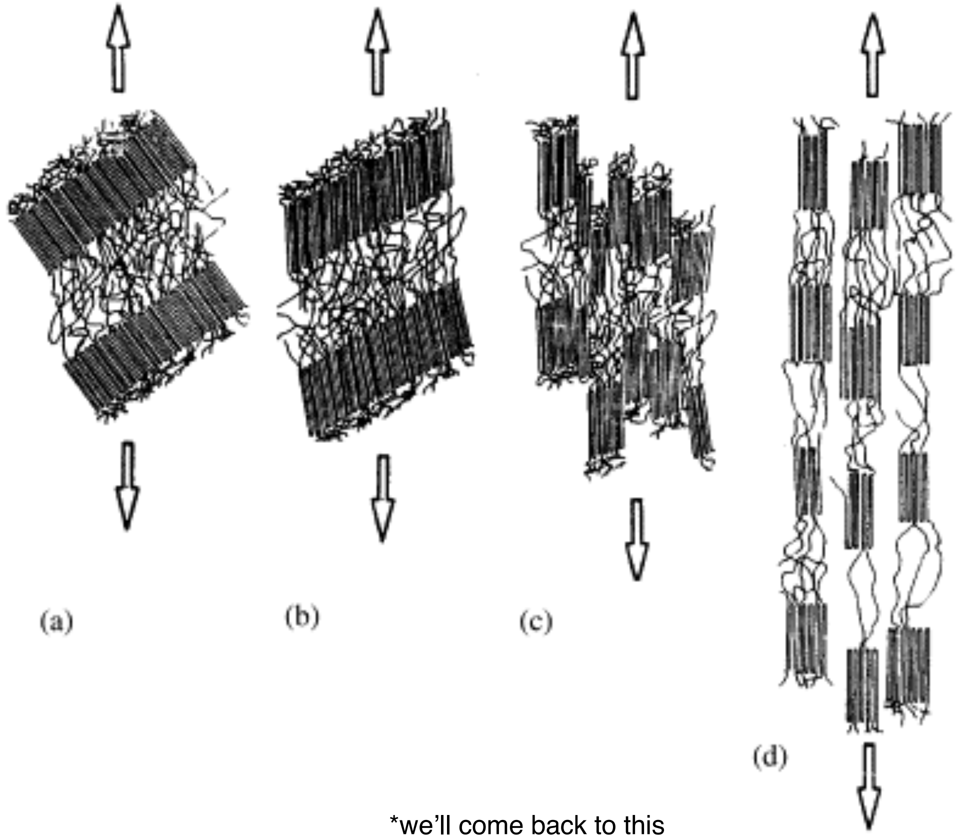
Mechanical Properties* (above T_g and below T_m)

Crystalline domains are hard but brittle

Amorphous regions are elastic and provide toughness

→ Relative ratio will dicate mechanical properties

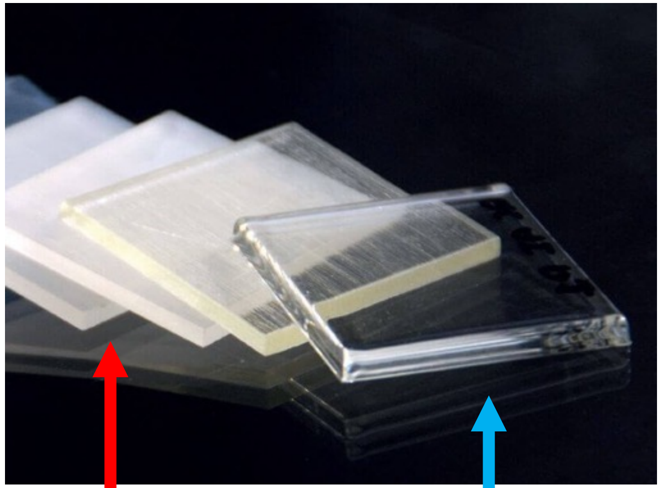




*we'll come back to this

Crystallinity Impacts Properties and Behavior

Optical Properties

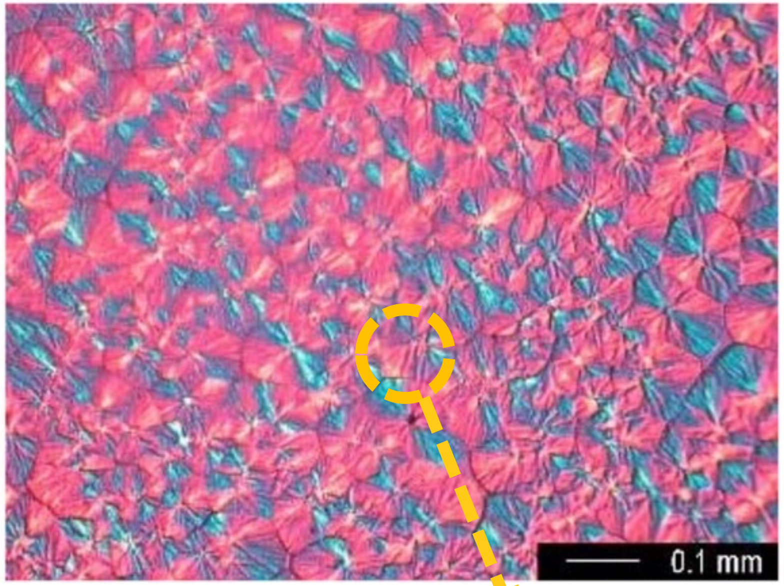


Semicrystalline

Amorphous

Degree of crystallinity is inversely proportionate to light transmission

Semicrystalline polymer viewed under polarized light



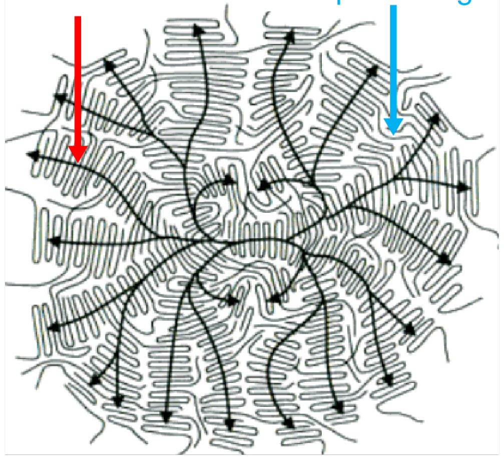
Spherulites

Polycrystalline structure

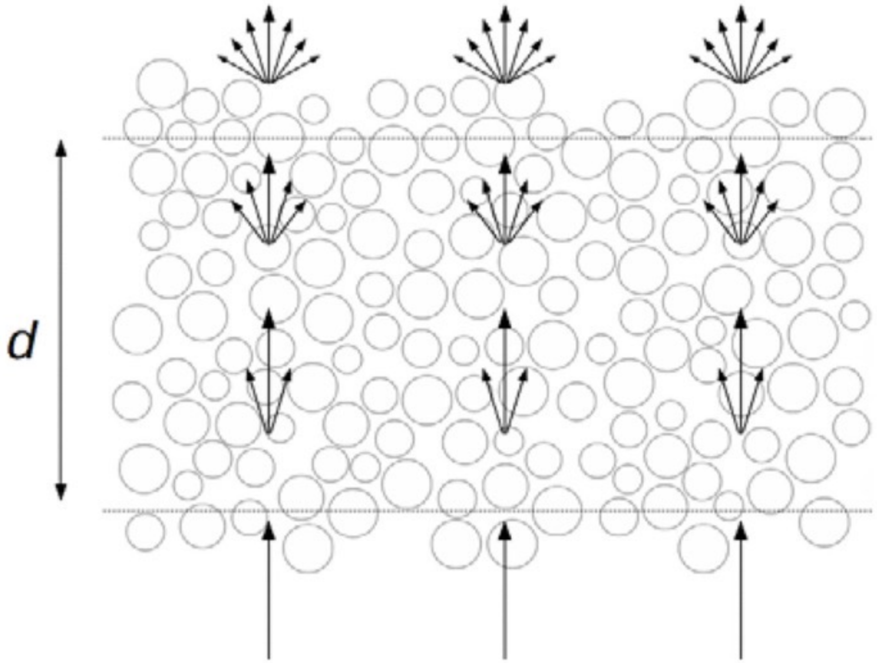
Optically active

Crystalline region

Amorphous region



Light scattering off crystallites



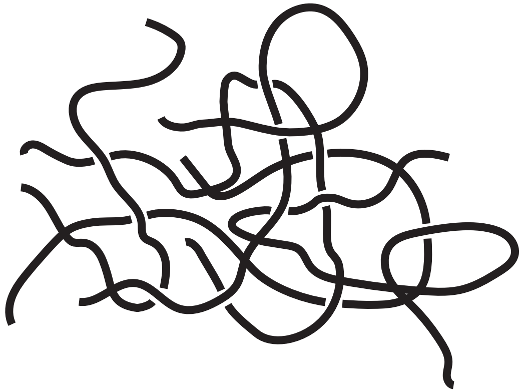
Light propagation direction

Molnár, János, et al. *Journal of Polymer Science* 58.13 (2020): 1787-1795.

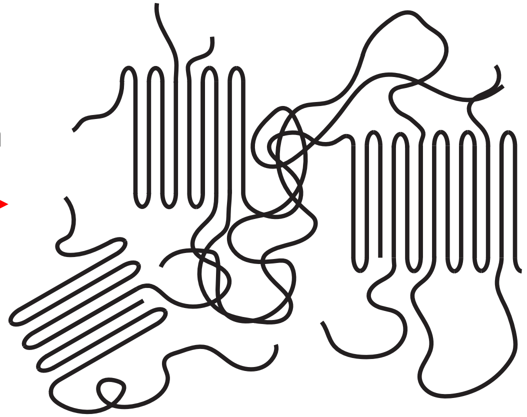
Crystallinity Impacts Properties and Behavior

Thermal Behavior

Cold crystallization



Heat at
$T_g < T < T_m$



Polymer that wants to crystallize but was cooled so quickly that it stayed amorphous

Polymer chains have energy to rearrange themselves into crystals

Annealing of amorphous PET

Cold crystallization can lead to undesired mechanical properties

Crystallinity Impacts Properties and Behavior

Thermal Behavior

The polymer chemistry → Thermal transitions → Processability

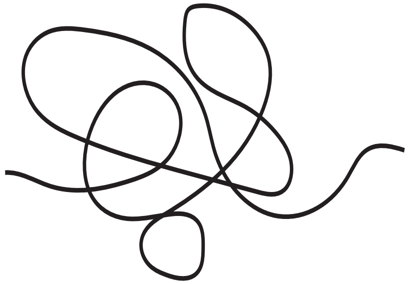
Easier to reshape above T_m but want properties from crystalline domains

Fast crystallization speed means less processing time

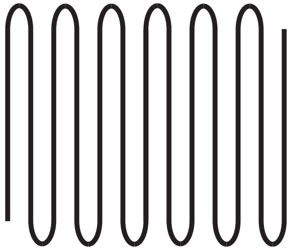
Crystallinity Impacts Properties

Density

Amorphous



Crystalline



More mass in same volume!

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

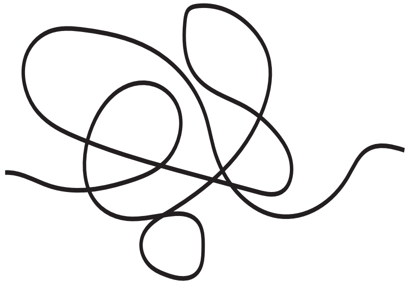
Crystallization leads to shrinkage on solidification from the melt → Dimensional inaccuracies

*we will derive this in the exercise

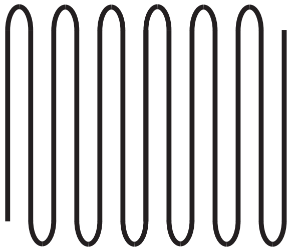
Crystallinity Impacts Properties and Behavior

Solvent/chemical resistance

<u>Amorphous</u>



<u>Crystalline</u>

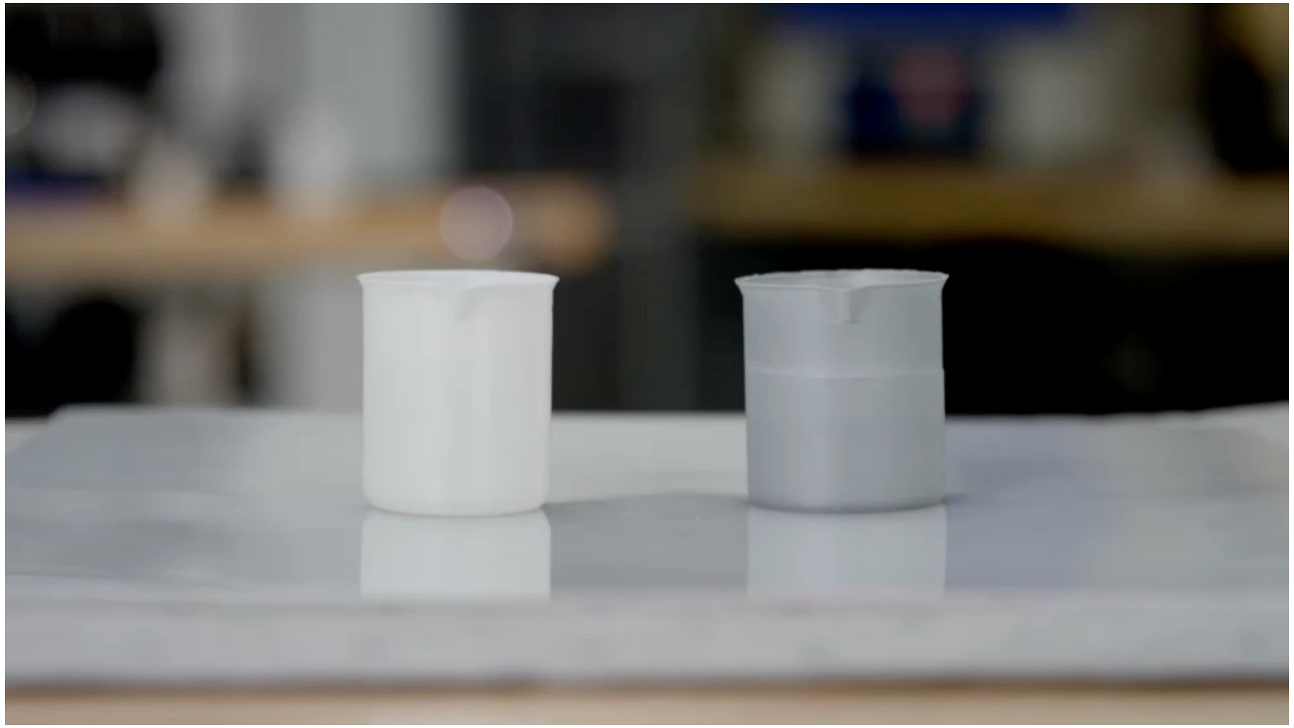


Solvents/chemicals cannot easily penetrate the crystalline domains.

Need to overcome the strong interactions between chains to disrupt them.

Crystallinity imparts chemical and solvent resistance

Acetone (solvent) inside these cups



Acetone dissolves the amorphous polymer

Crystallinity Impacts Properties and Behavior

Whether to use an amorphous or semicrystalline polymer will depend on your application

Requirement	**Type of polymer**
High strength, little strain expected	High crystallinity polymer
Low strength, high strains expected	Amorphous polymer
Strong and tough	Semicrystalline
Flexible in Norway in the winter	Amorphous and low T_g
Load-bearing inside an oven	Semicrystalline with high T_m
Transparent and rigid	Amorphous with high T_g
Transparent and flexible	Amorphous with low T_g
Extrusion 3D printing	Low T_g and/or low T_m
Chemical storage	High crystallinity polymer

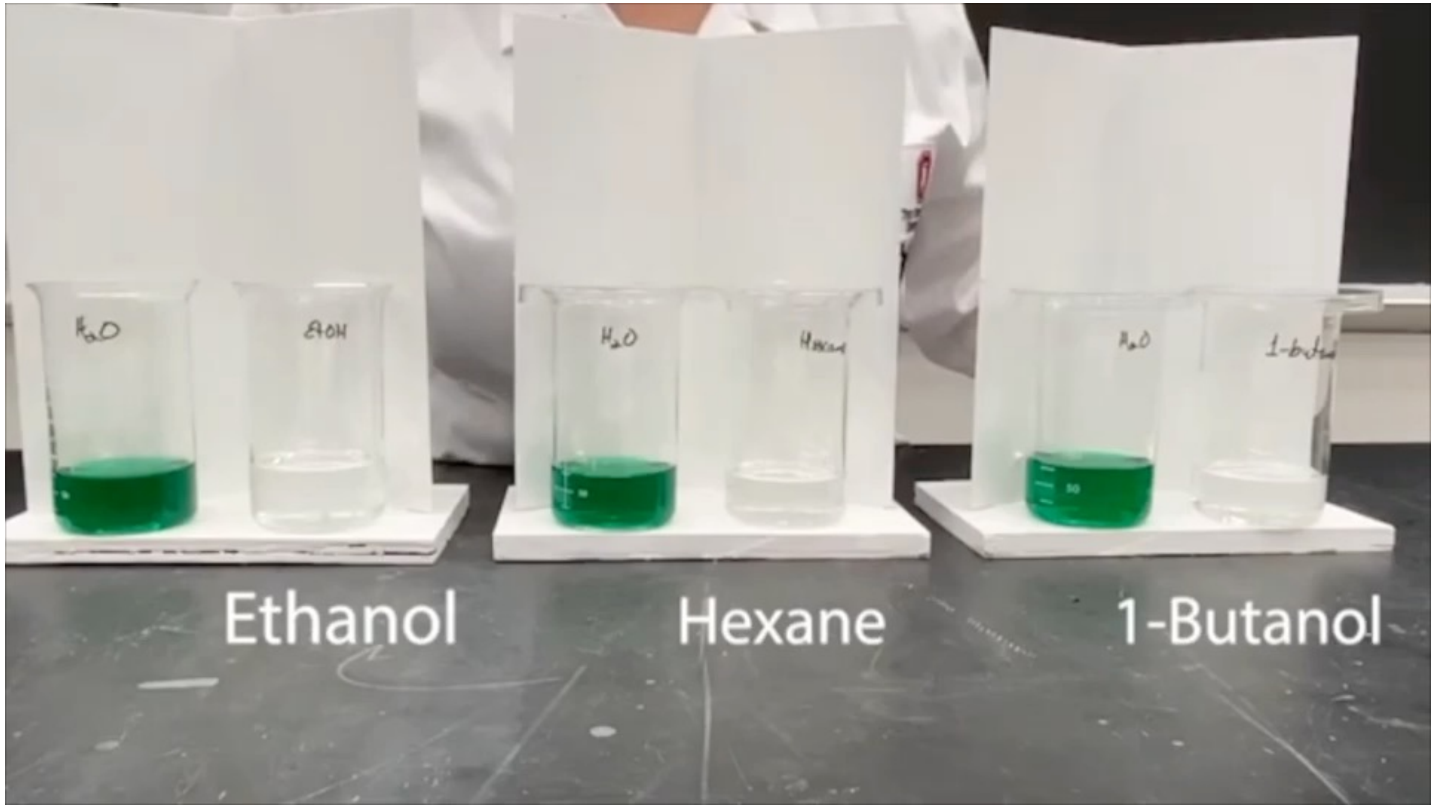
Key takeaway:

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

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

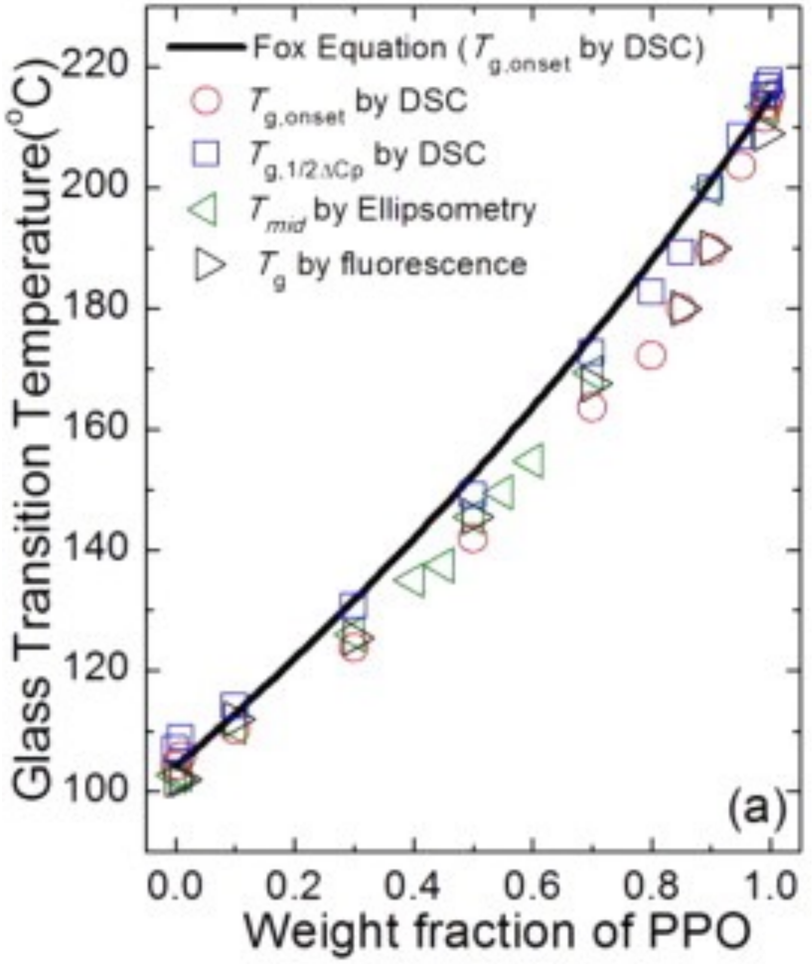
$$\frac{1}{T_g} = \frac{M_1}{T_{g,1}} + \frac{M_2}{T_{g,2}}$$ (Fox equation)

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

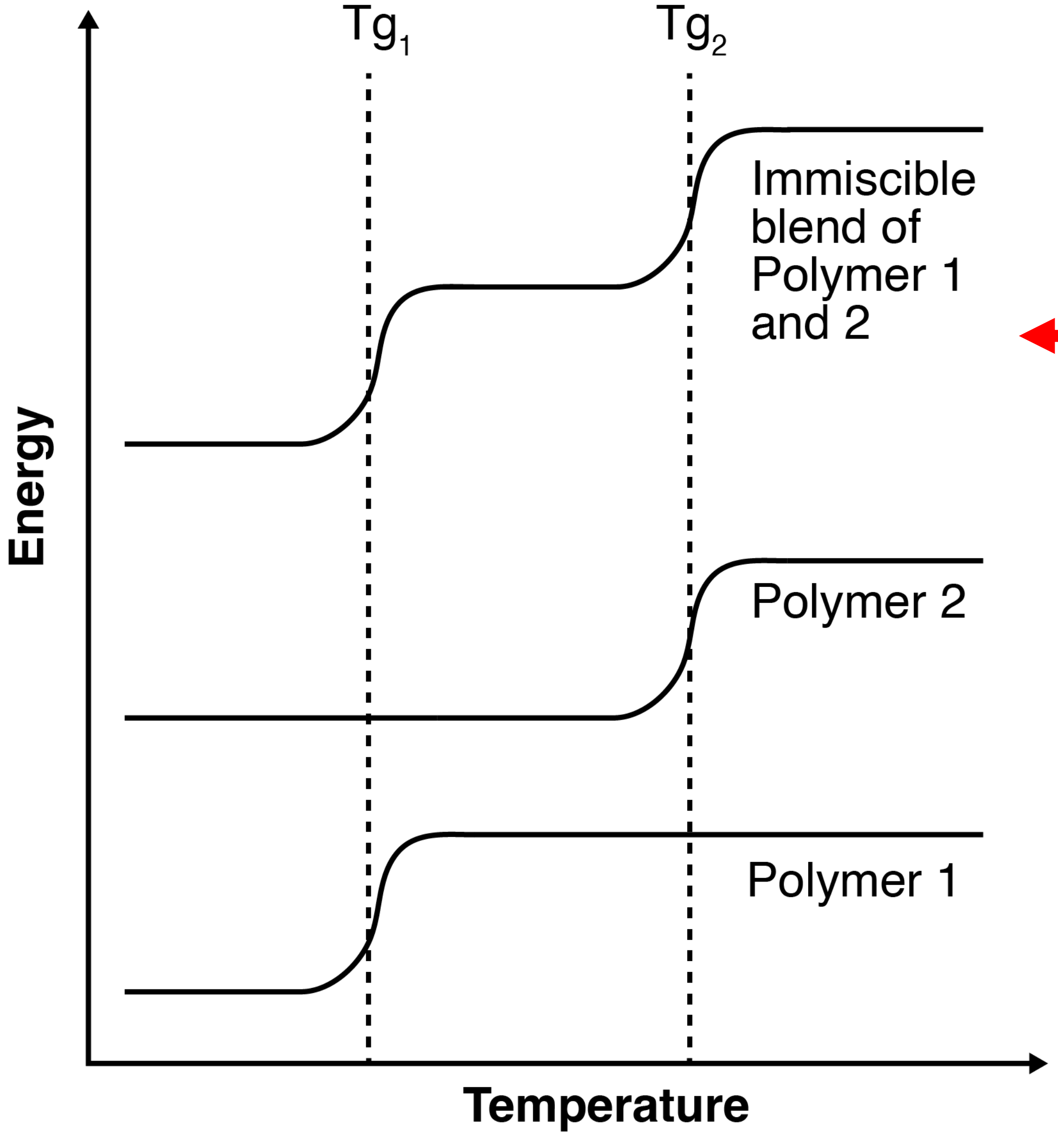
Immiscible blends

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

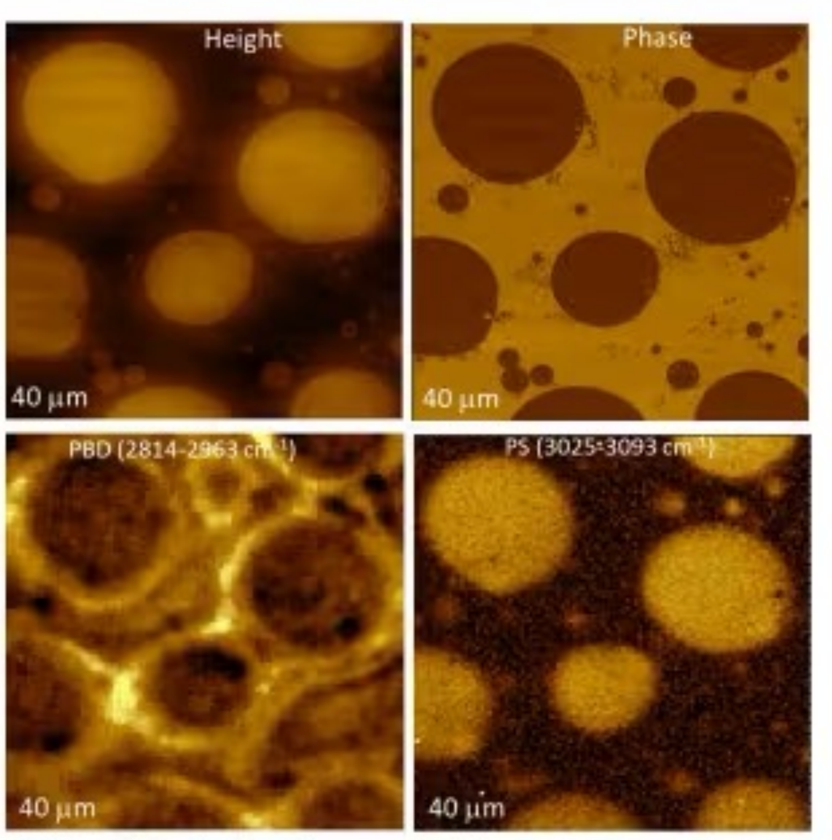
Why use immiscible blends?

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

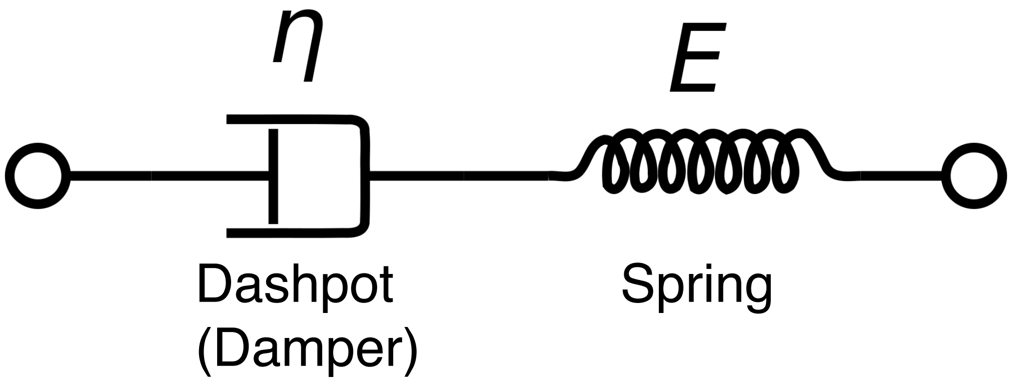
Polymers can deform in two ways:

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

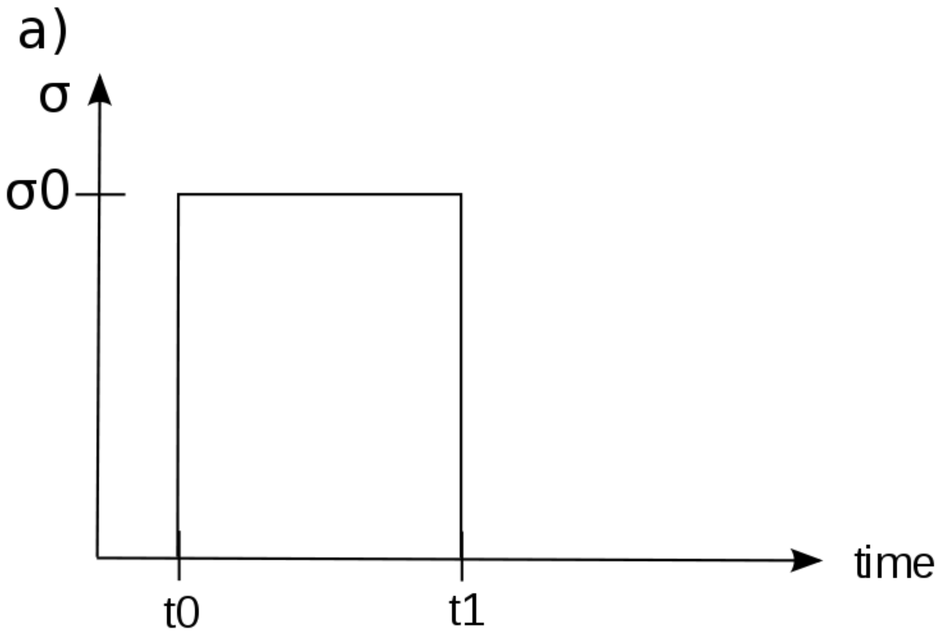


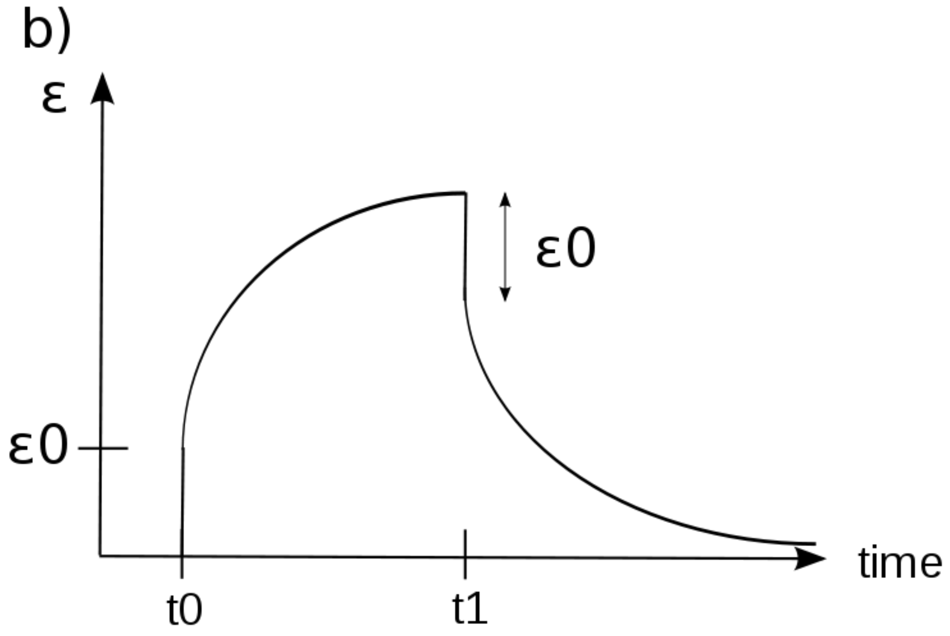
*viscoelasticity can be an entire course in itself!

Mechanical Properties of Polymers

Applied stress as a function of time

Induced strain as a function of time





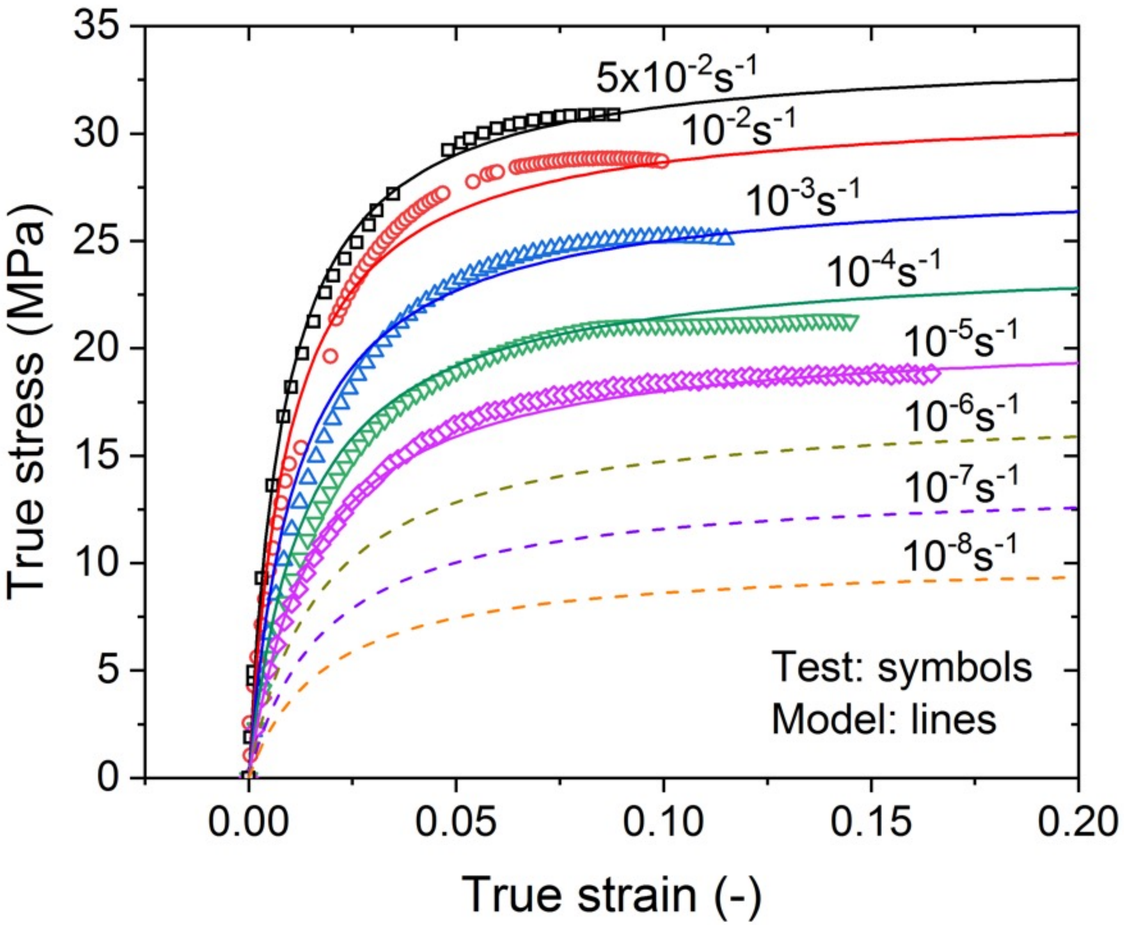
Elastic response

$$E = \frac{\sigma 0}{\varepsilon 0}$$

Strain evolves over time when force is applied and when force is removed

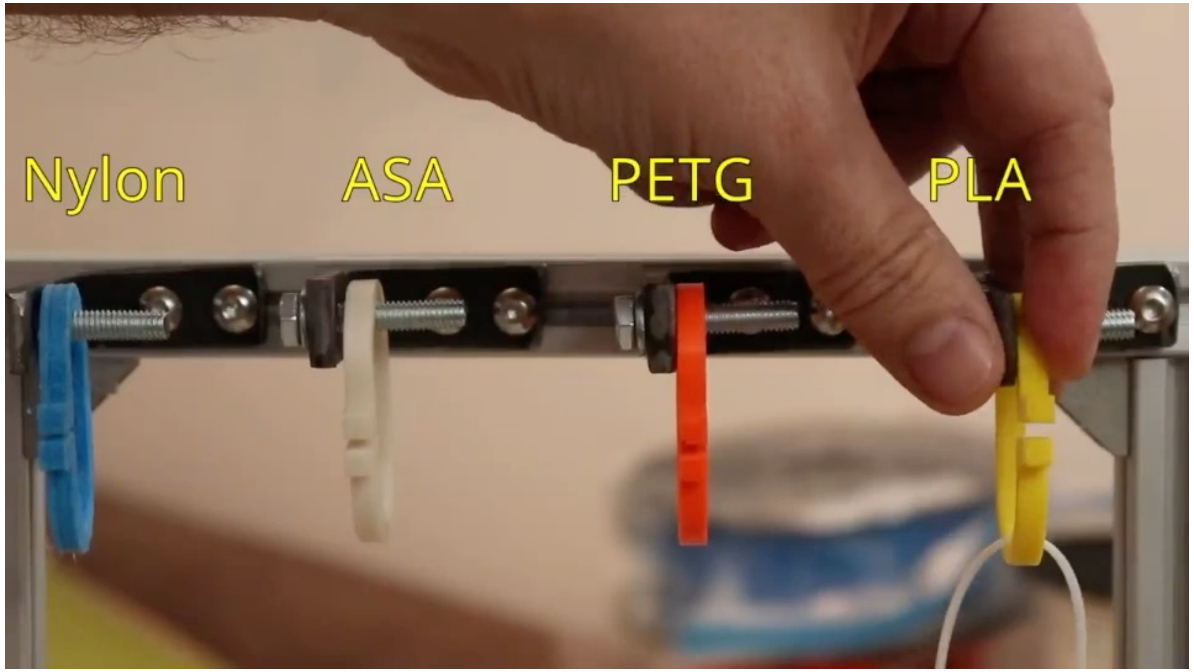
Mechanical Properties of Polymers

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



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

Creep can occur: slow deformation over time with a constant load



Need to take viscoelasticity of polymers into consideration when using them

Week 4 Learning Objectives

- Understand the difference between amorphous, semi-crystalline, and crystalline polymers
- Understand the factors that favors polymer crystallization
- Understand what the glass transition temperature is and how it differs from the melting temperature
- Understand the factors that impact the T_g and T_m temperature
- Understand the impact that T_g and T_m has on material properties and behavior