Lecture 12: Properties and Applications of Polymers

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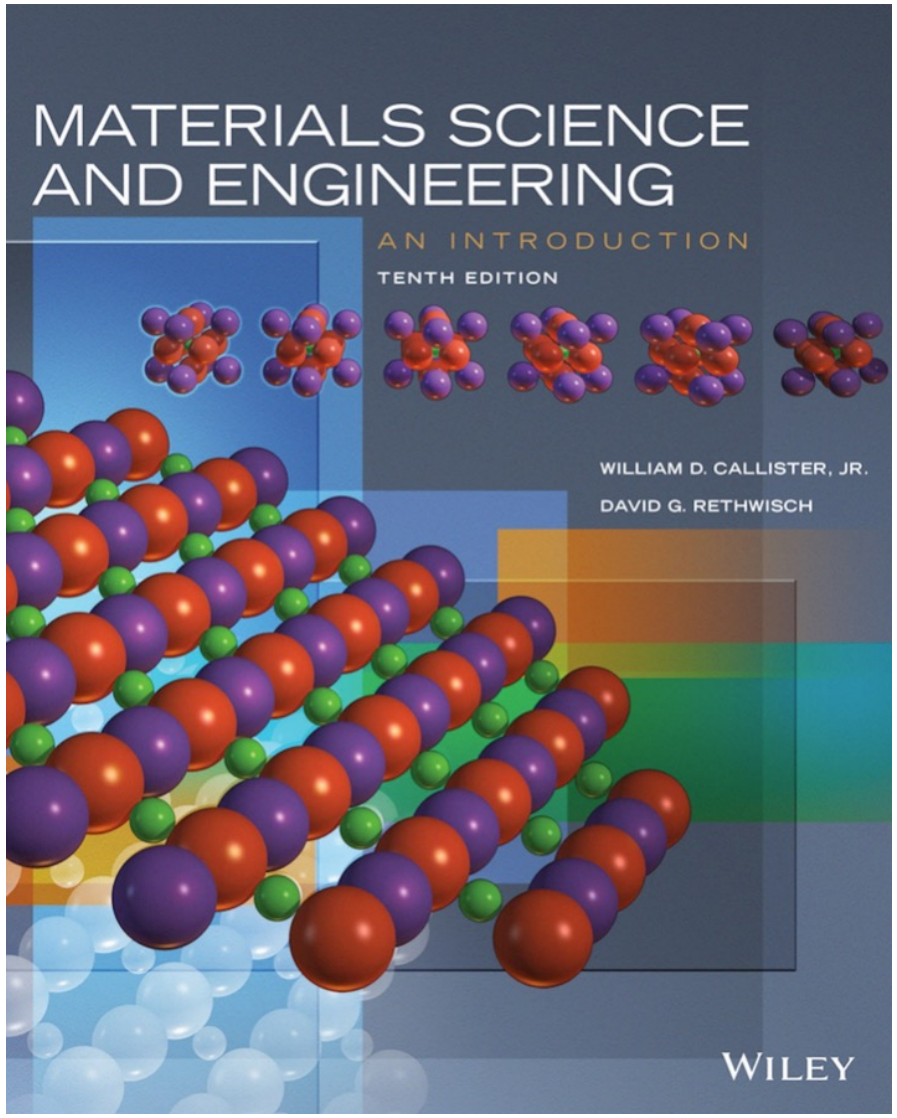
Reading for this subject



Chapter 15 Characteristics, Applications, and Processing of Polymers

This discussion will closely follow **Chapter 15** of Callister, **pages 512-560** of the 10th edition.

Polymers are often used for their unique and wide-ranging mechanical properties



Rubber bands: very **elastic**!



Kevlar: **Absorbs impact energy** very well

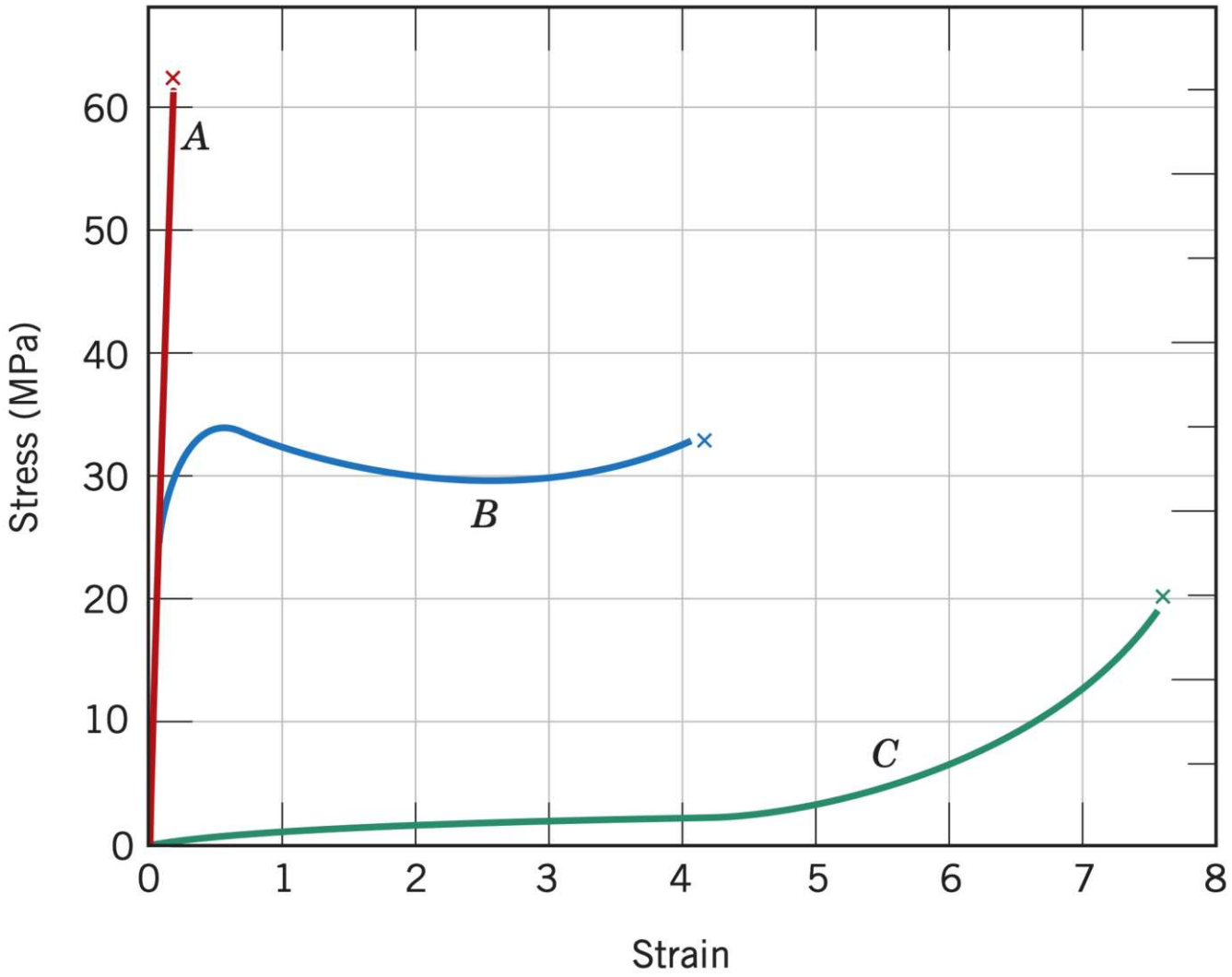
Silly putty: Lots of **plastic** deformation



Fiberglass (in epoxy): Provides structural support and is **resistant to fracture**



Polymers are often used for their unique and wide-ranging mechanical properties

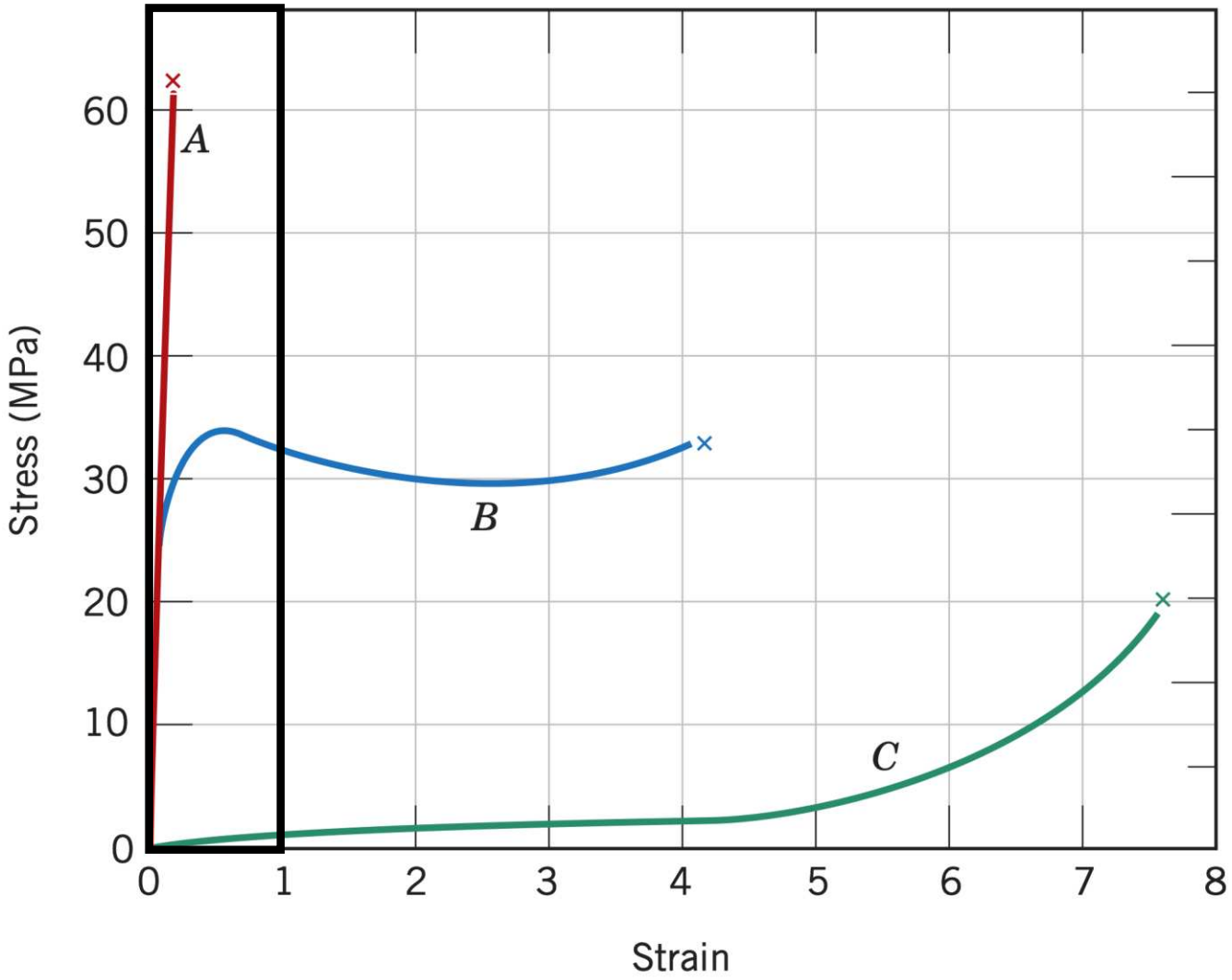


A) Brittle polymers

B) Plastic polymers

C) Elastomers

Polymers are often used for their unique and wide-ranging mechanical properties



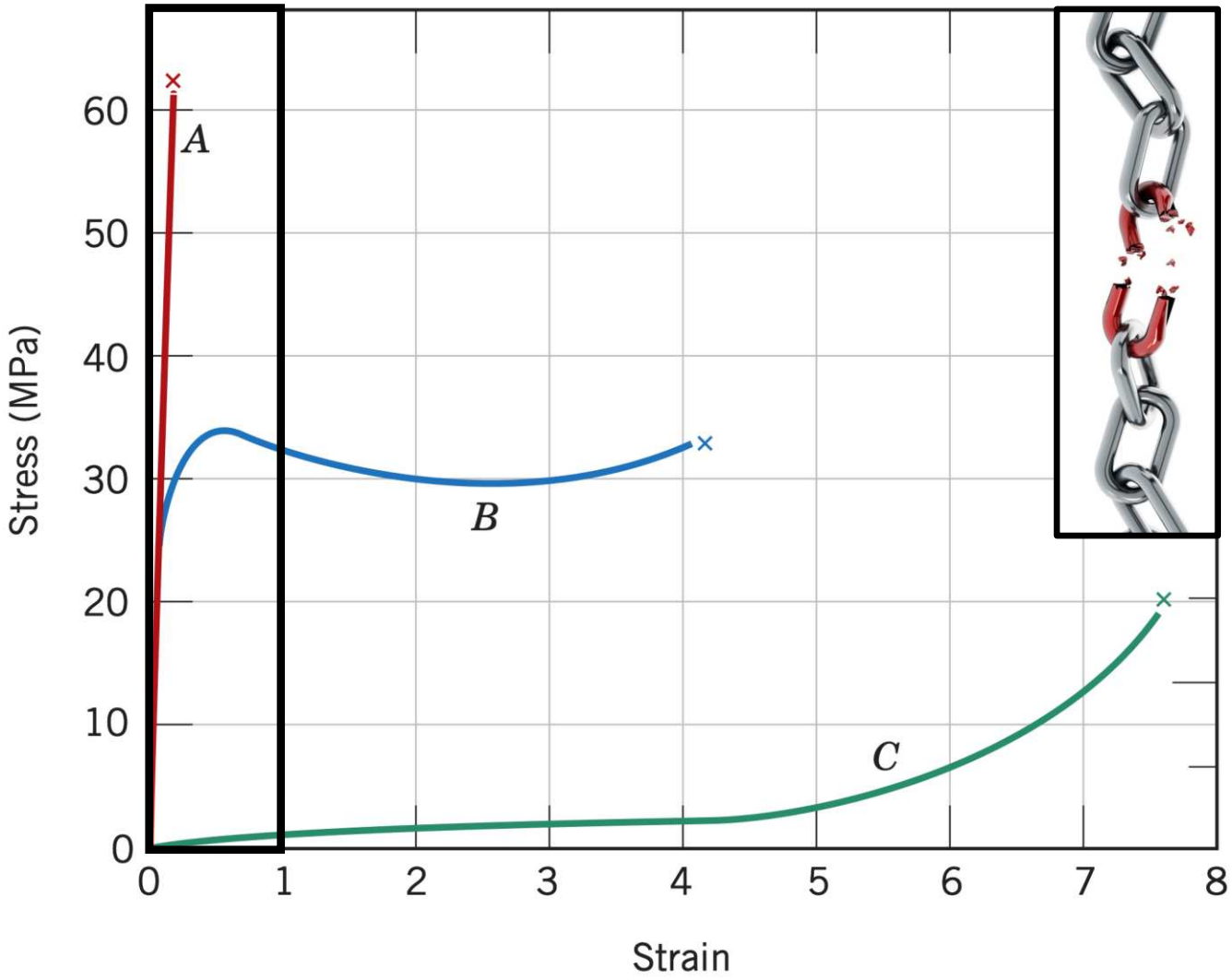
A) Brittle polymers

→ similar to ceramics

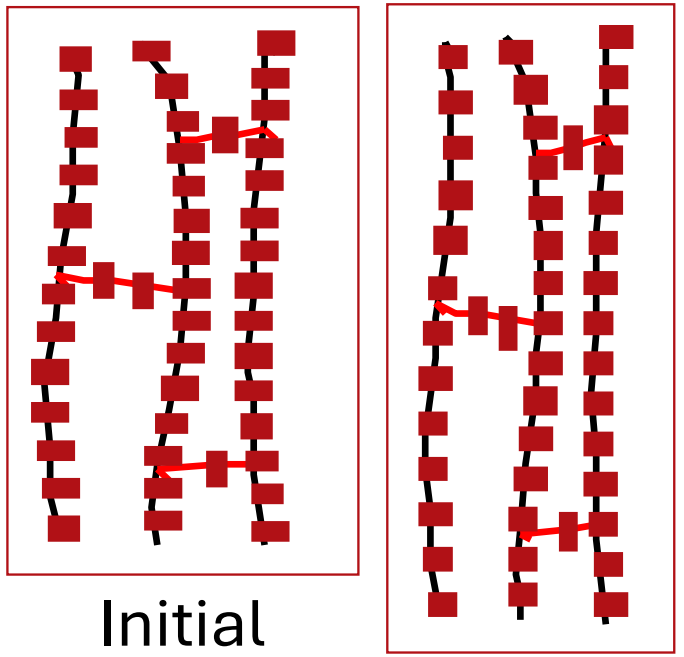


Stiff (high E) and fracture easily

Polymers are often used for their unique and wide-ranging mechanical properties



Aligned, crosslinked polymer



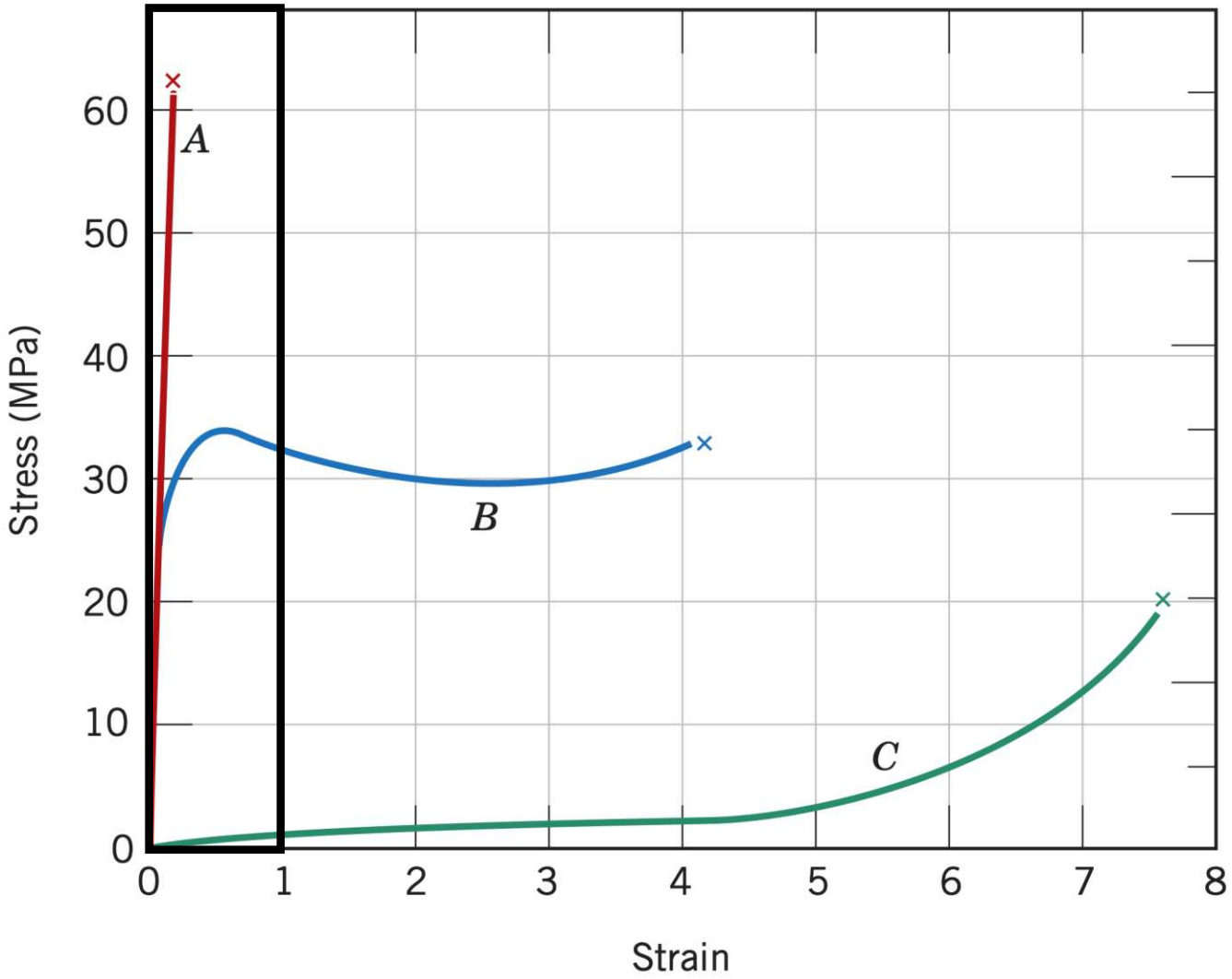
Initial

Final

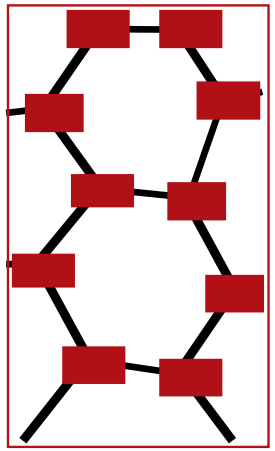
At some point, a link in the chain will break

As we pull, bonds are stretched

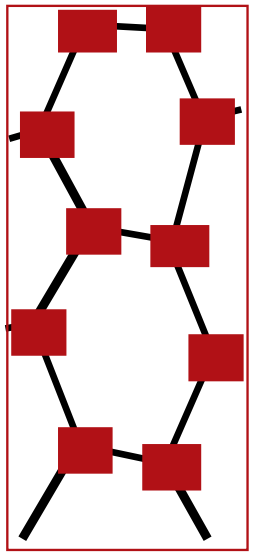
Polymers are often used for their unique and wide-ranging mechanical properties



Network polymer



Initial

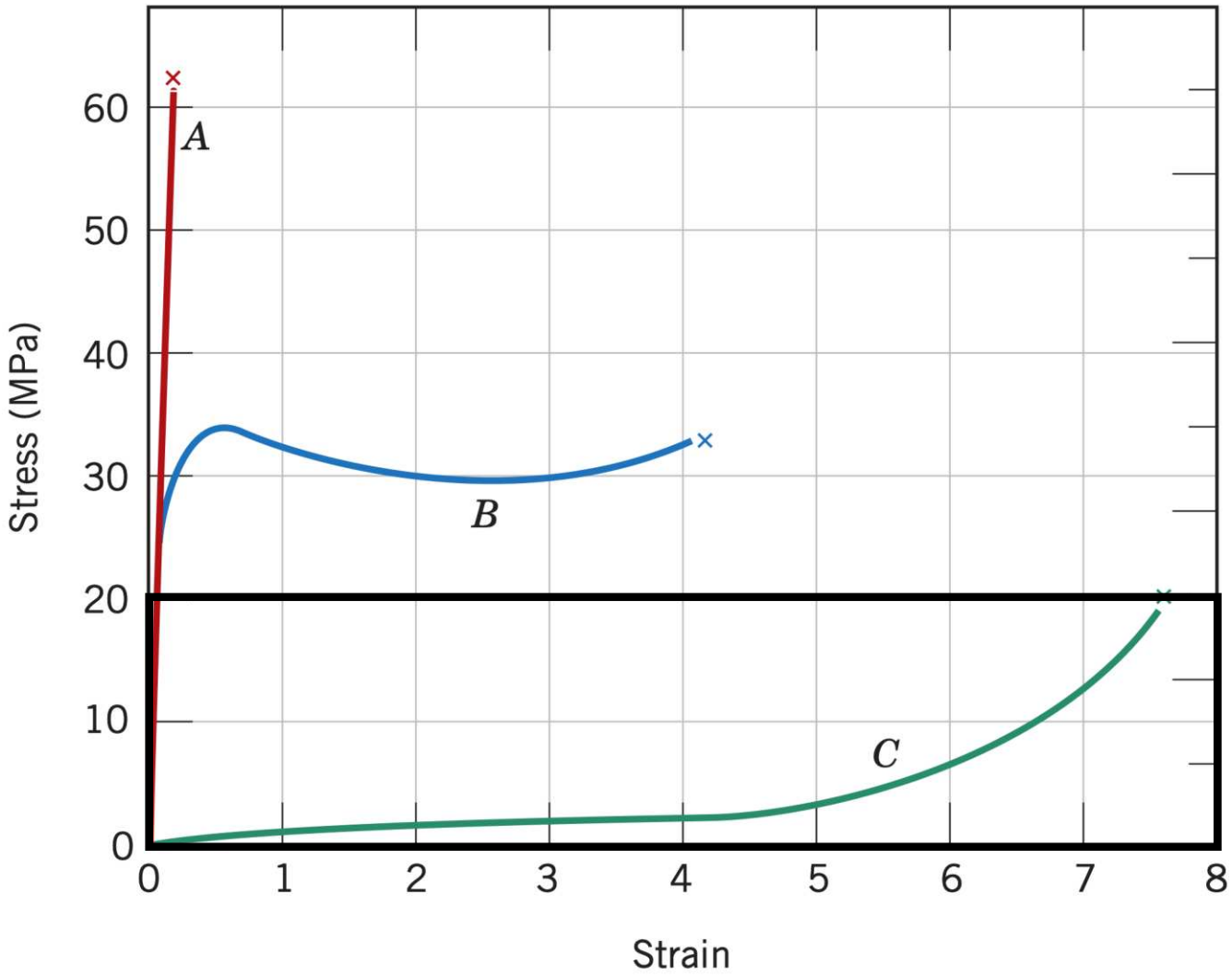


Final

In this case, higher stresses are usually needed to cause fracture.

Same idea, except these distribute forces evenly across the network

Polymers are often used for their unique and wide-ranging mechanical properties

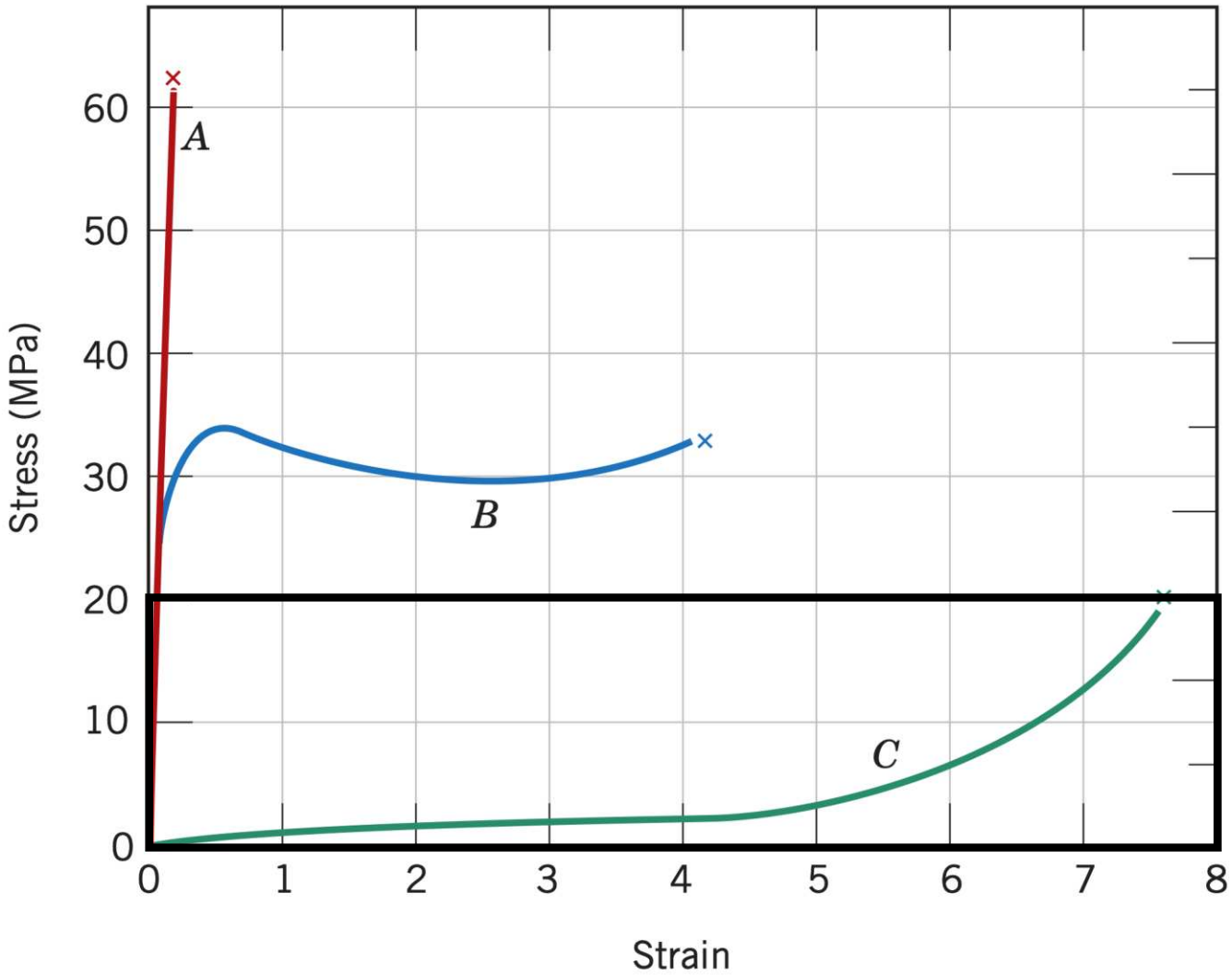


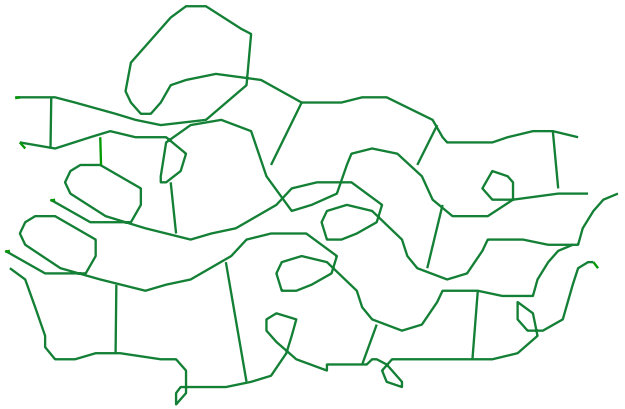


C) Elastomers

→ Unique! They can sustain **huge deformation** with full (elastic) recovery

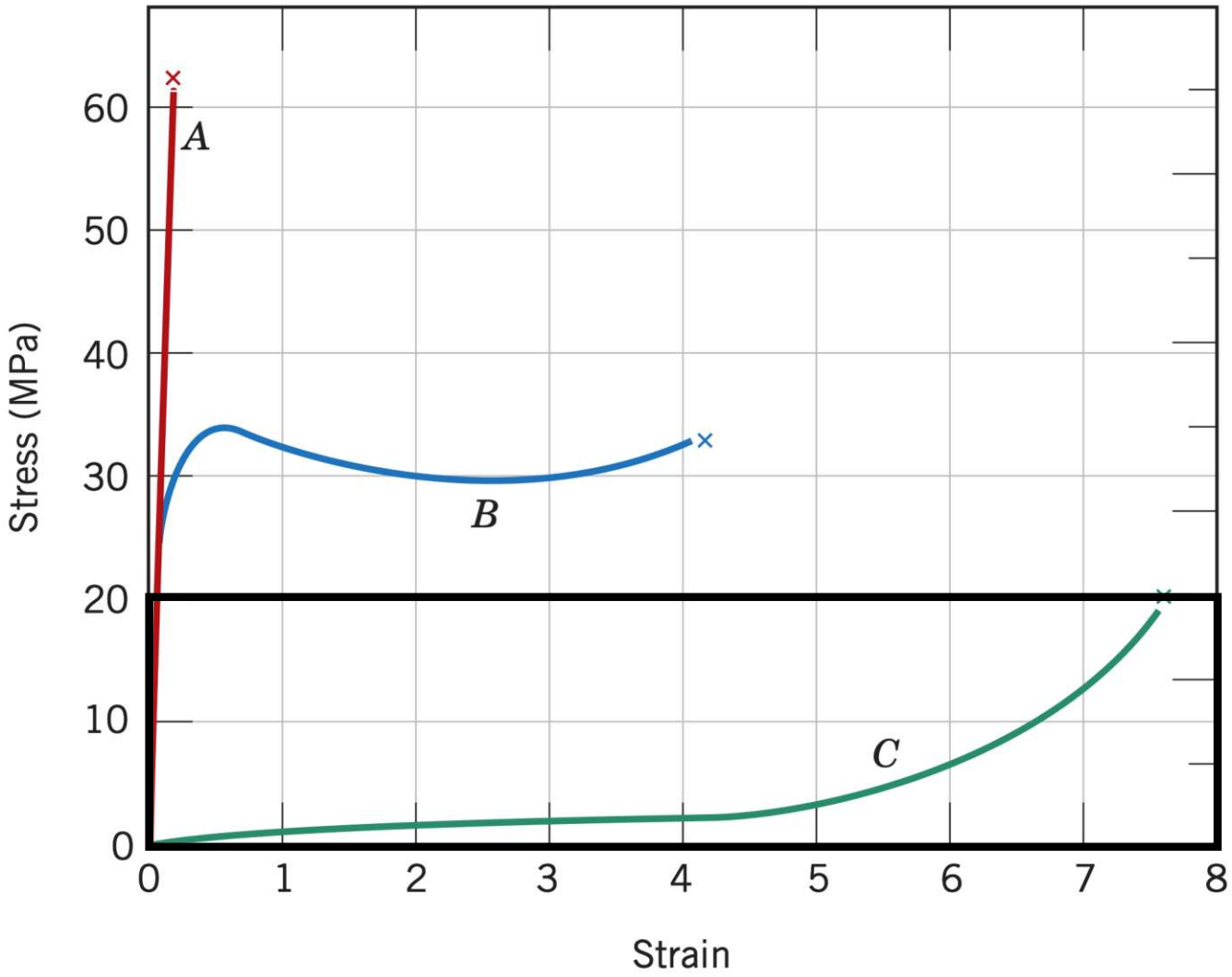
Polymers are often used for their unique and wide-ranging mechanical properties

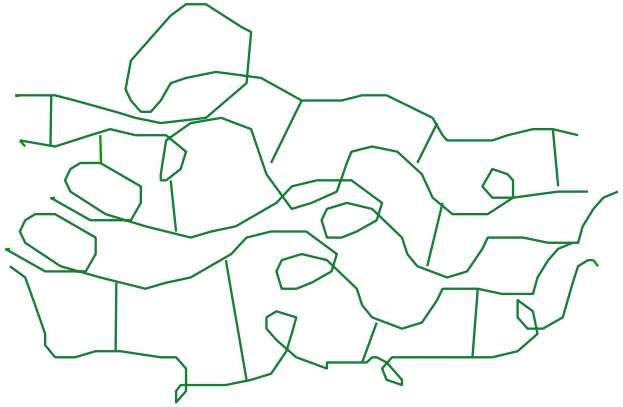




Initial state: highly amorphous, “spaghetti-like” chains with some crosslinking between them

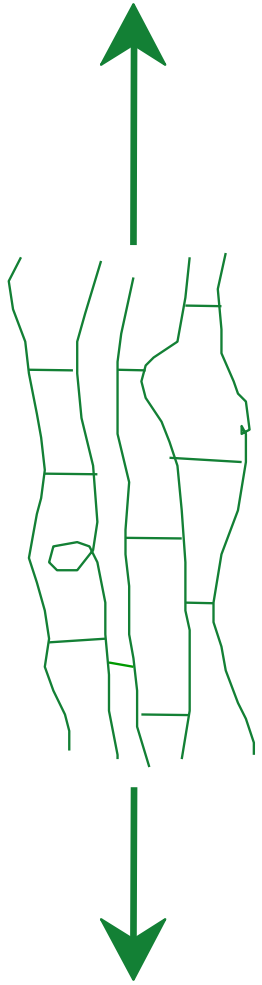
Polymers are often used for their unique and wide-ranging mechanical properties



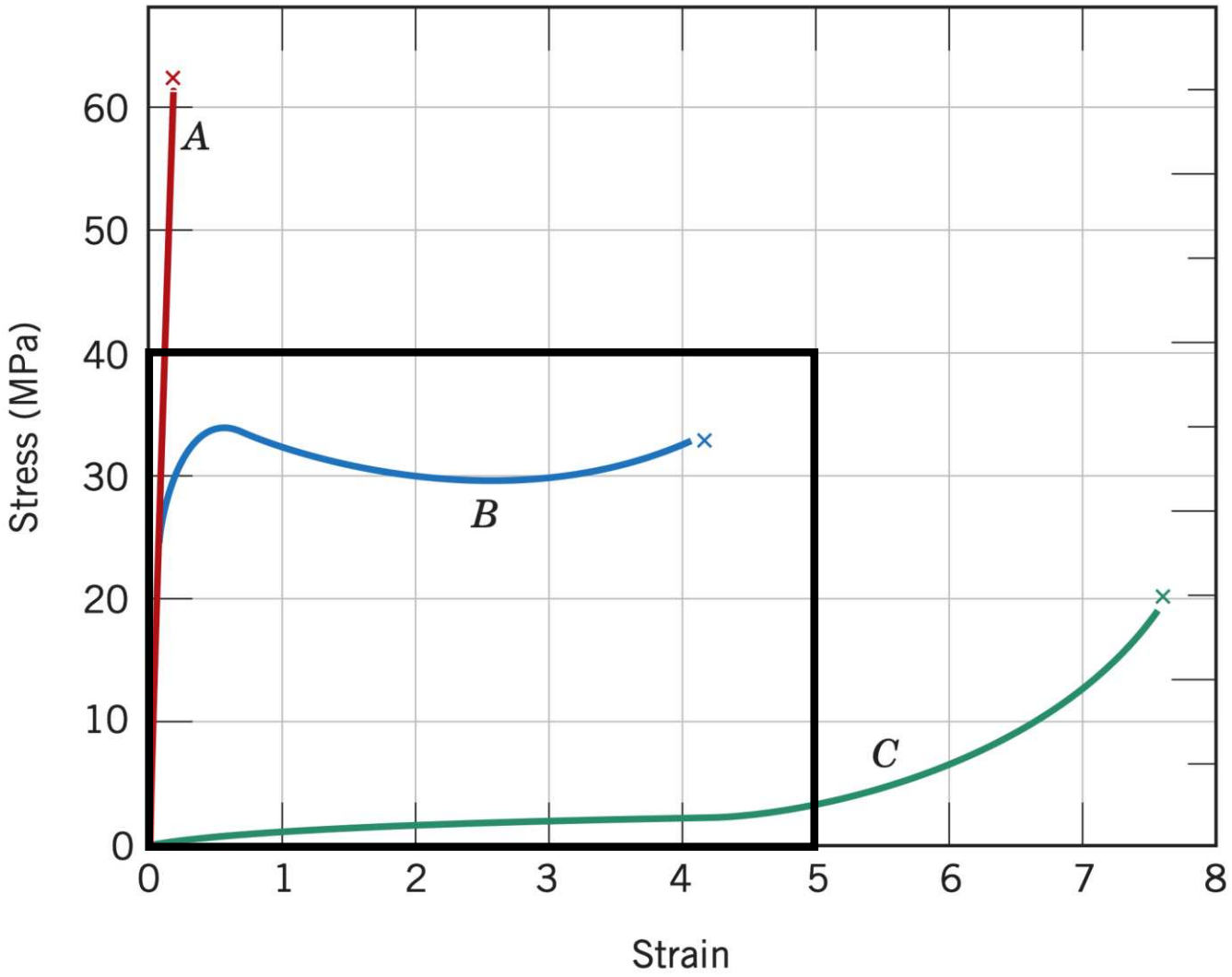


Final state: chains are straightened out and well aligned, still crosslinked…

Lower entropy



Polymers are often used for their unique and wide-ranging mechanical properties

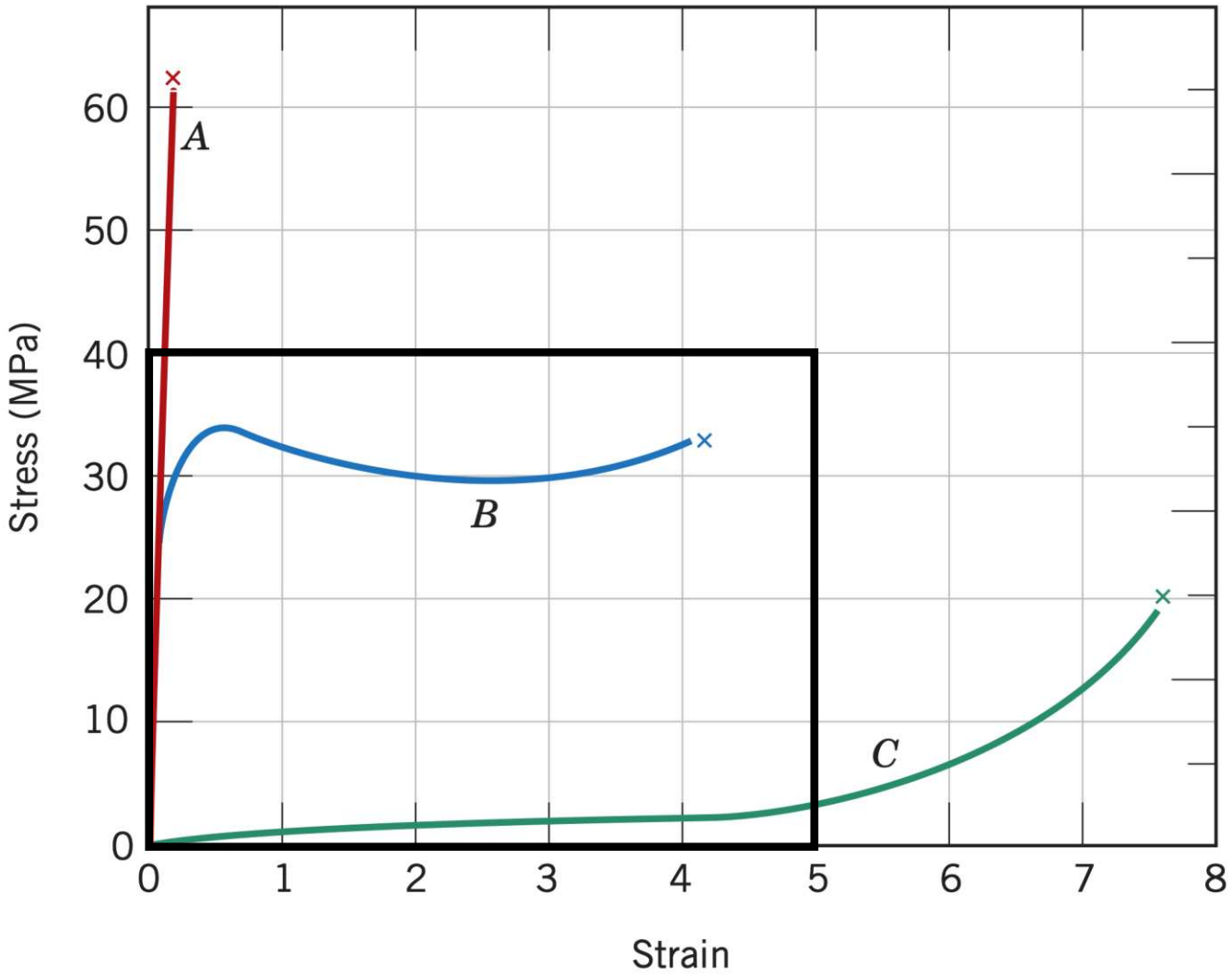




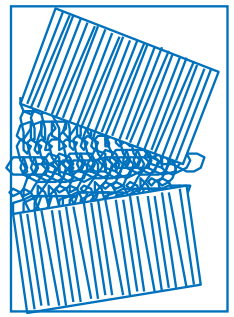
B) Plastic polymers

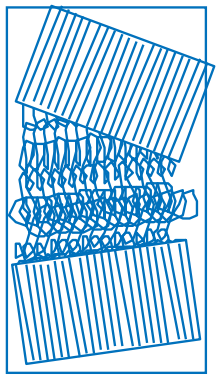
→ similar to ductile metals, except these polymers can often sustain much higher levels of strain (~5%)

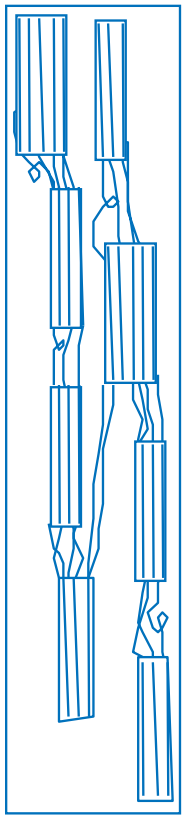
Polymers are often used for their unique and wide-ranging mechanical properties



Plastic behavior is often observed for **semicrystalline polymers**



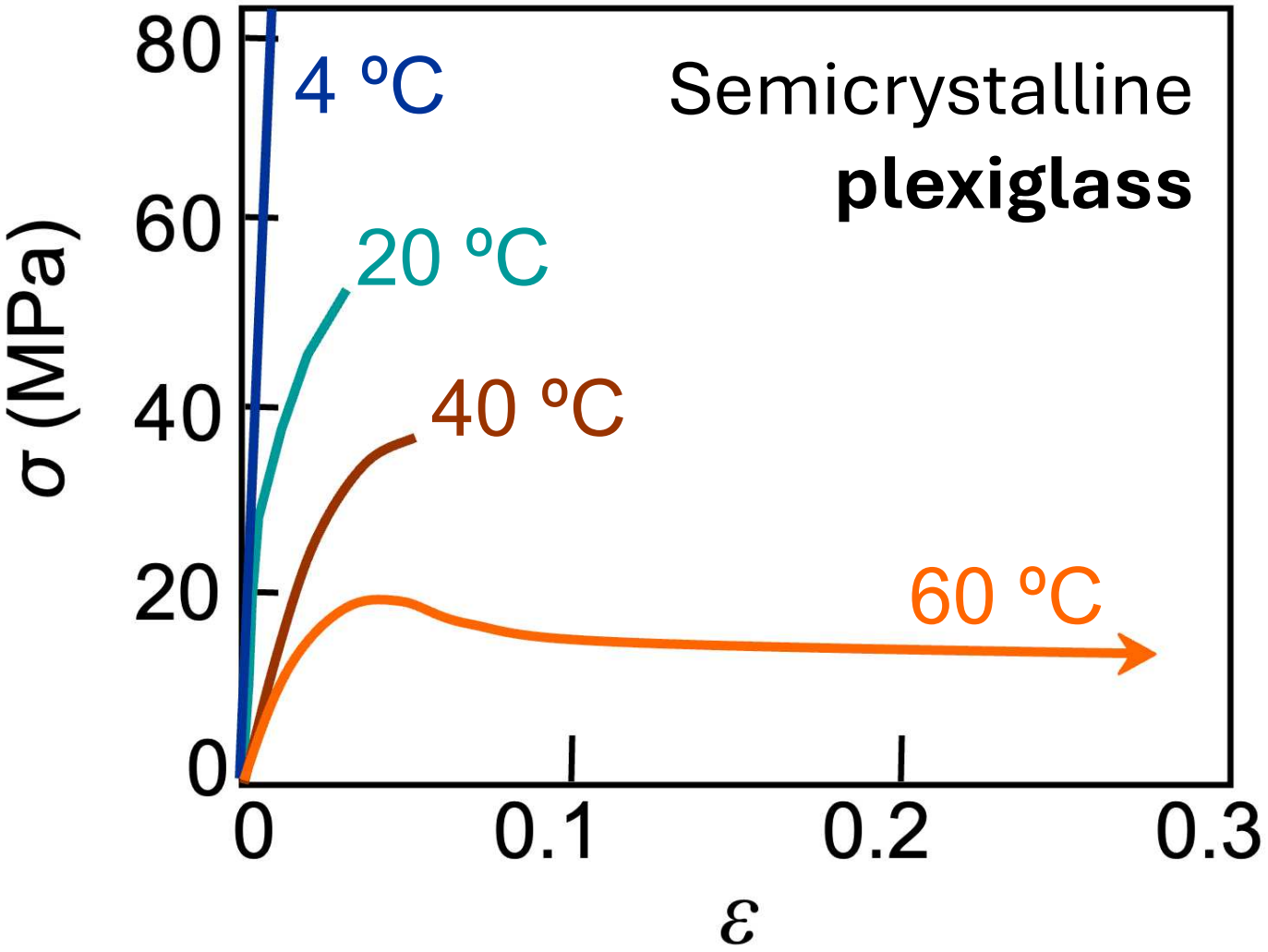




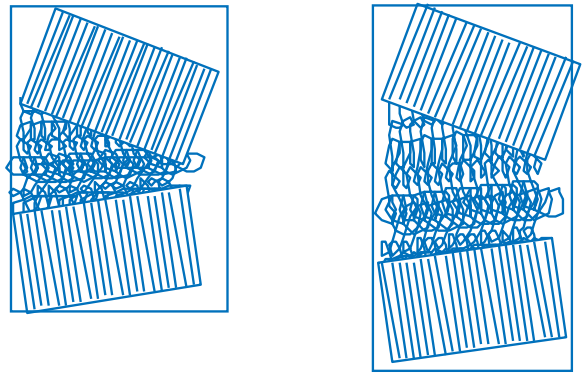
After aligning, a link in the chain may break

Some (but not 100%) recovery is possible

Polymers are often *very* temperature sensitive

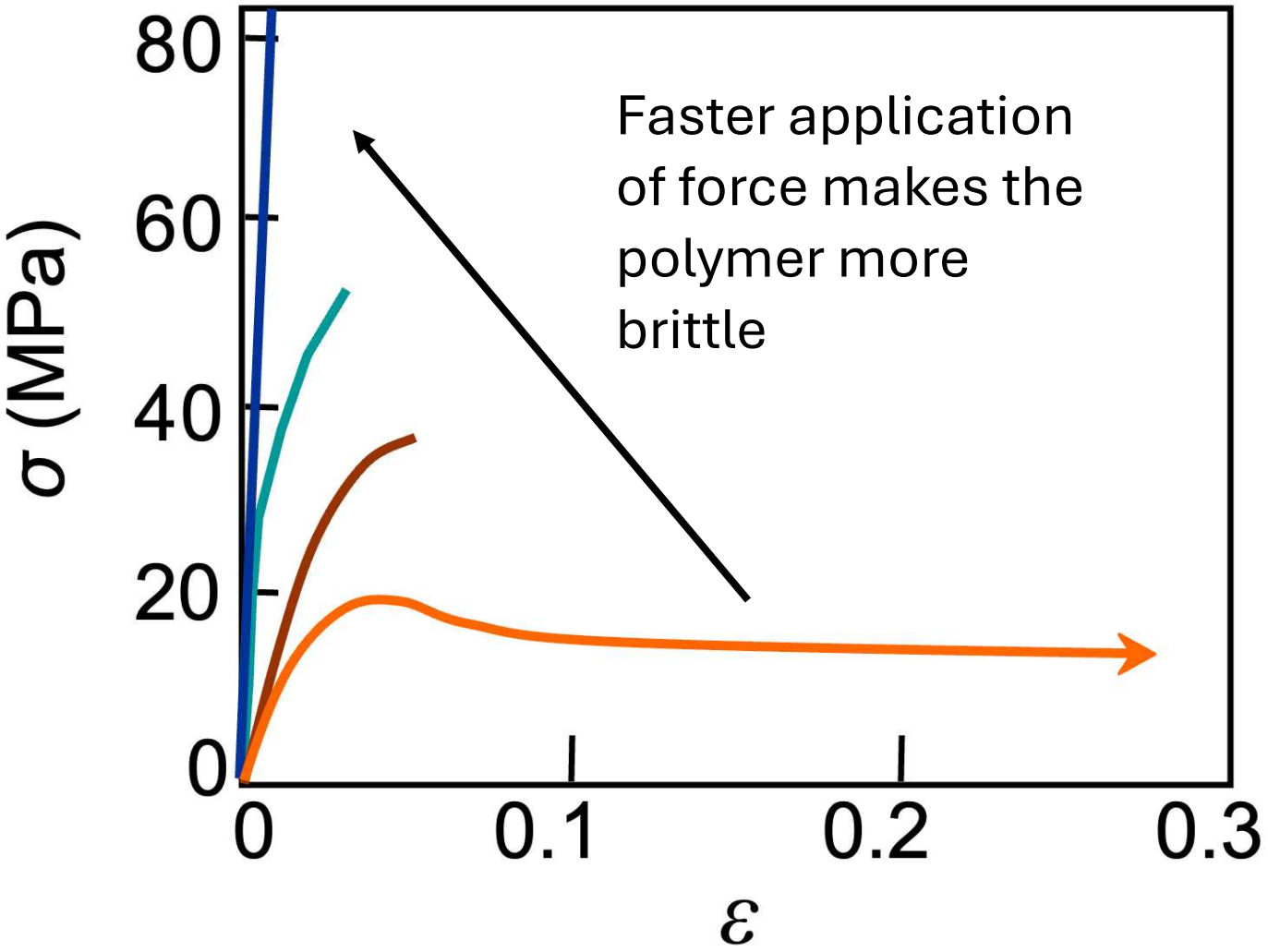


Higher temperature
→ easier deformation



Thermal energy helps these chains to slide past one another

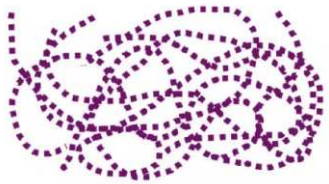
Polymers are often *very* temperature sensitive



A similar trend is observed if we change the **strain rate** – *i.e.*, how fast we deform the material

Fast strain rates have a similar effect as lower temperature **(fast strain = stiff response)**

This is because polymers tend to be ***viscous*, having a delayed response to stress**

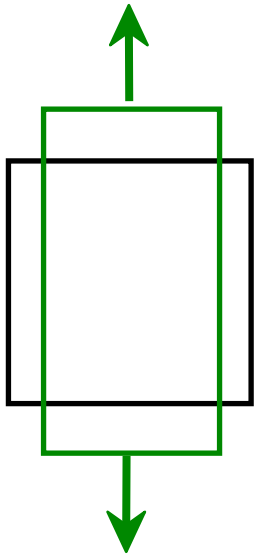


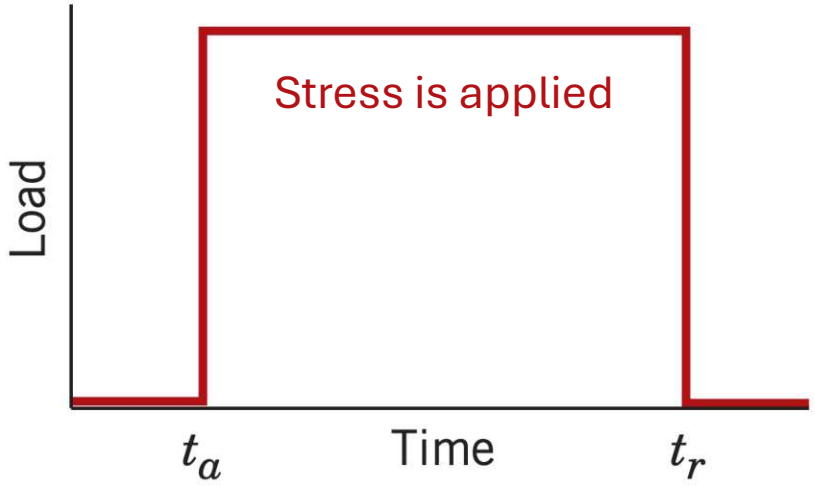
Takes time for the spaghetti to unravel

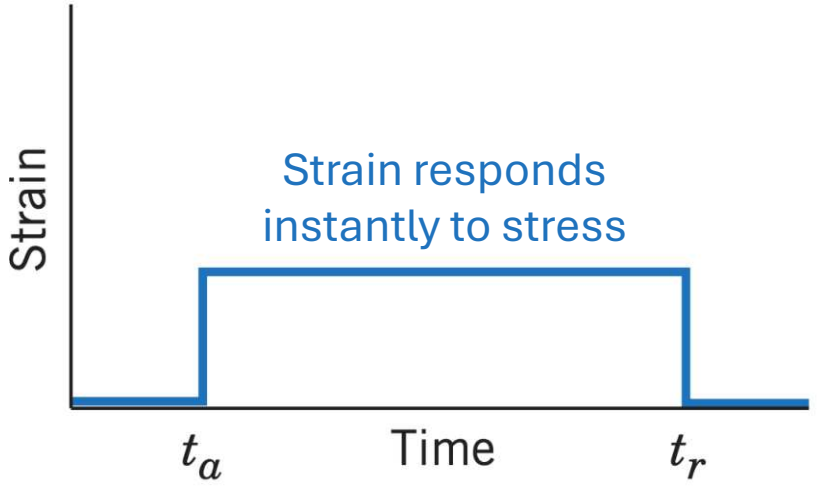
Viscoelasticity: time-dependent deformation



Viscoelasticity: time-dependent deformation

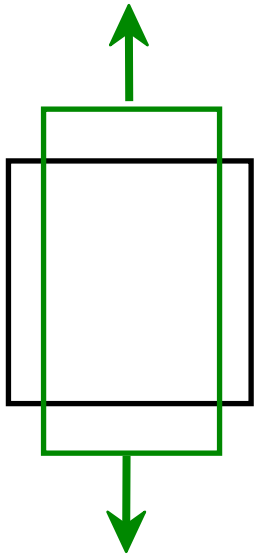


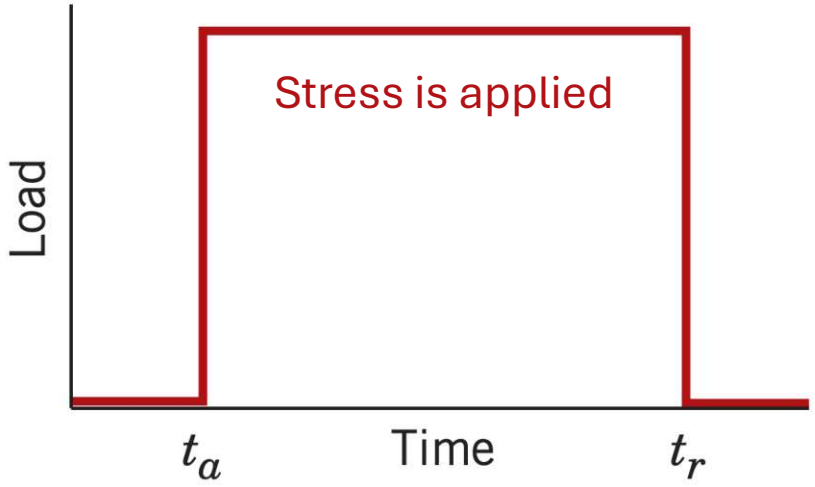


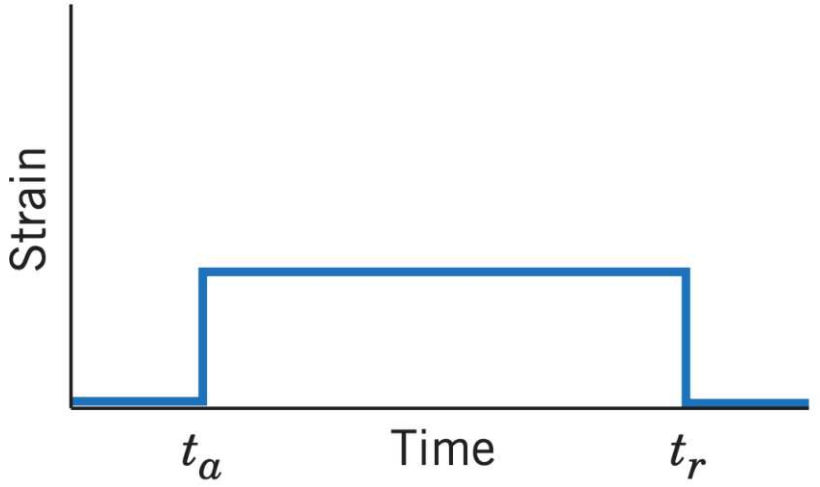


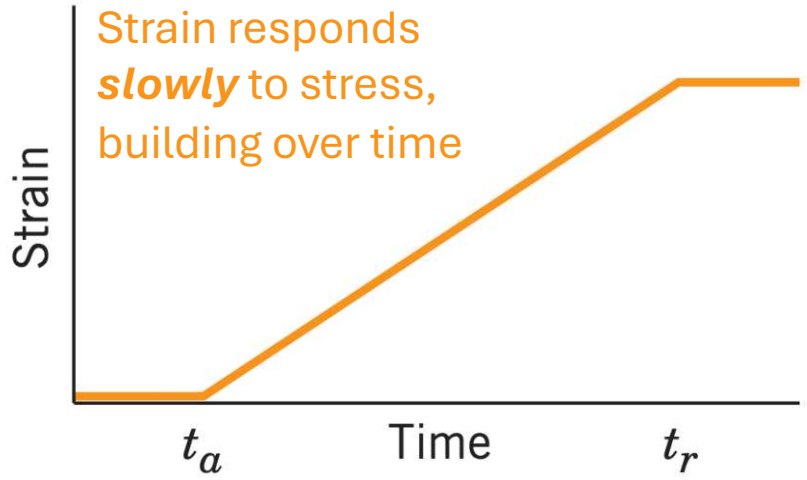
In the elastic deformation of metals and ceramics, strain is effectively instantaneous and fully recovered on de-loading

Viscoelasticity: time-dependent deformation





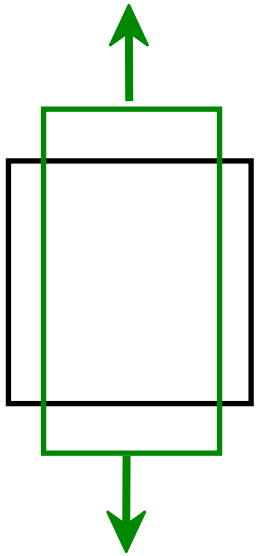


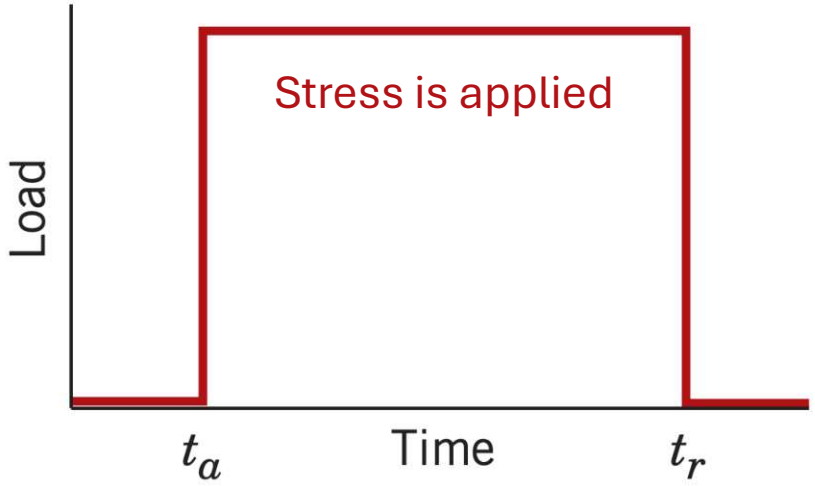


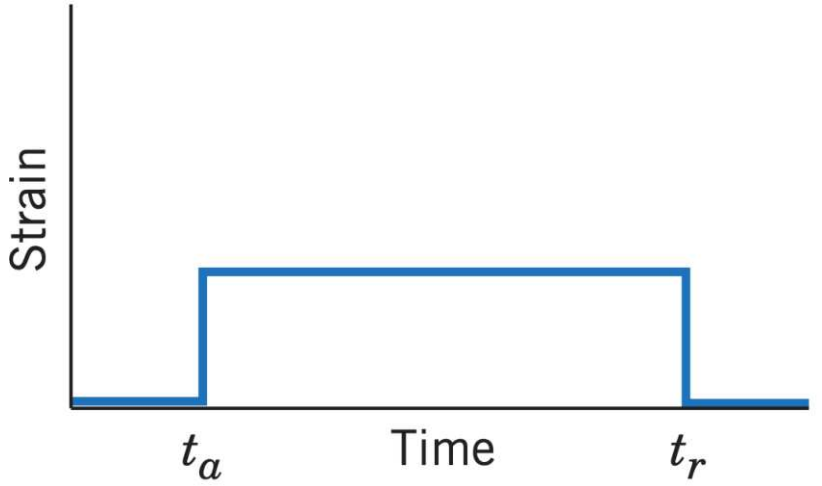


Viscous behavior:
Time-delayed response and strain is *not* recovered on de-loading

Viscoelasticity: time-dependent deformation



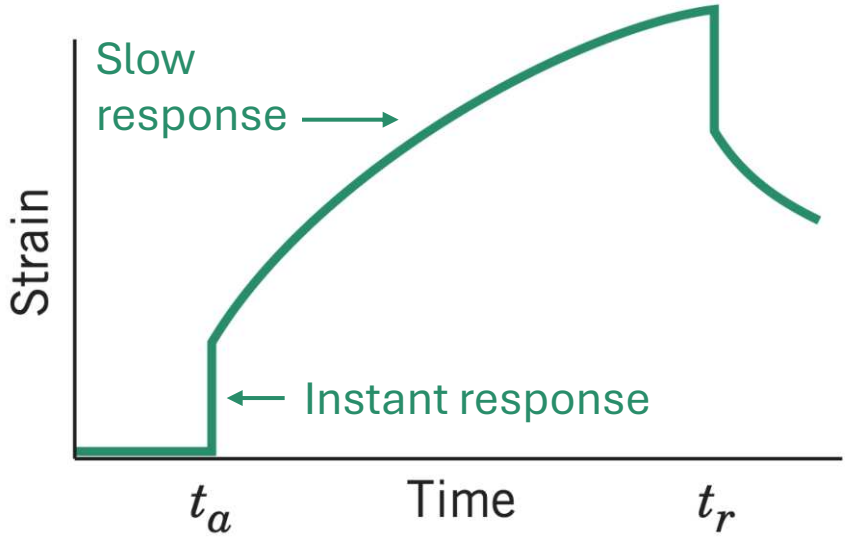






Viscoelasticity:

- Some instant response
- Some delayed response
- Strain *partially* recovered on de-loading



Viscoelasticity: time-dependent deformation



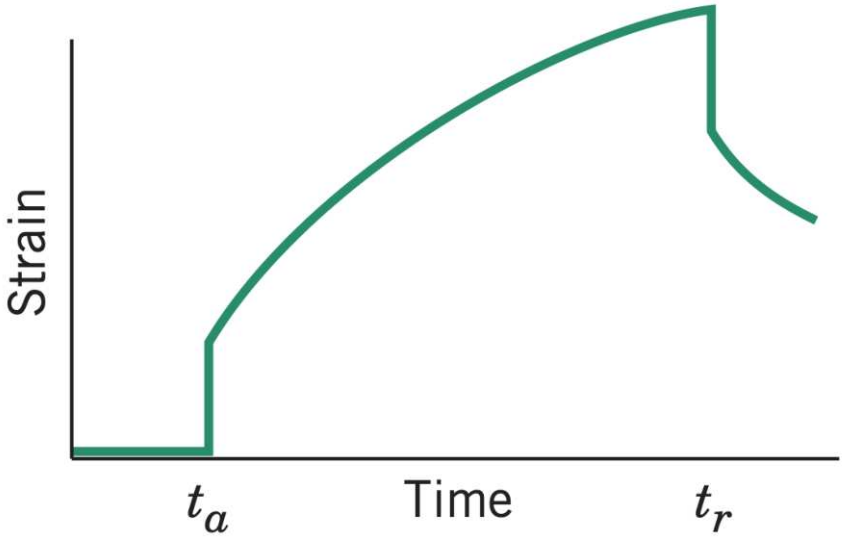
If you slowly stretch it, the putty will deform easily

Yet it bounces quite well, caused by elastic response when stress is applied fast



Viscoelasticity:

- Some instant response
- Some delayed response
- Strain *partially* recovered on de-loading



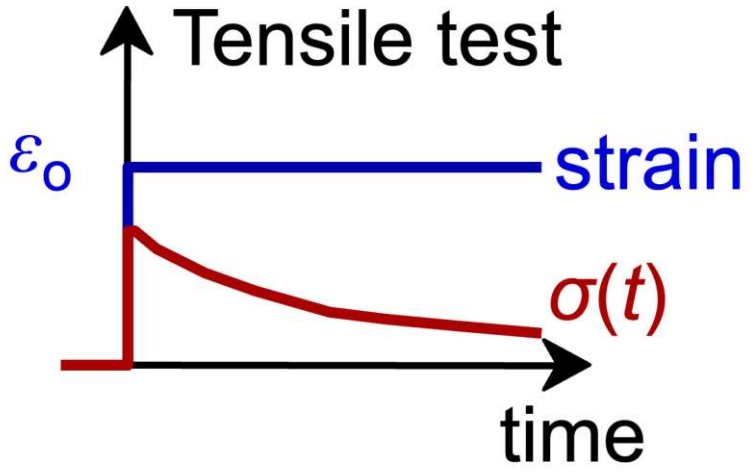
Viscoelasticity: time-dependent deformation

We can measure this property by very quickly applying a **constant strain** and then monitoring the **time-dependent stress.**

Relaxation modulus: $E_r(t) = \sigma(t)/\varepsilon_0$

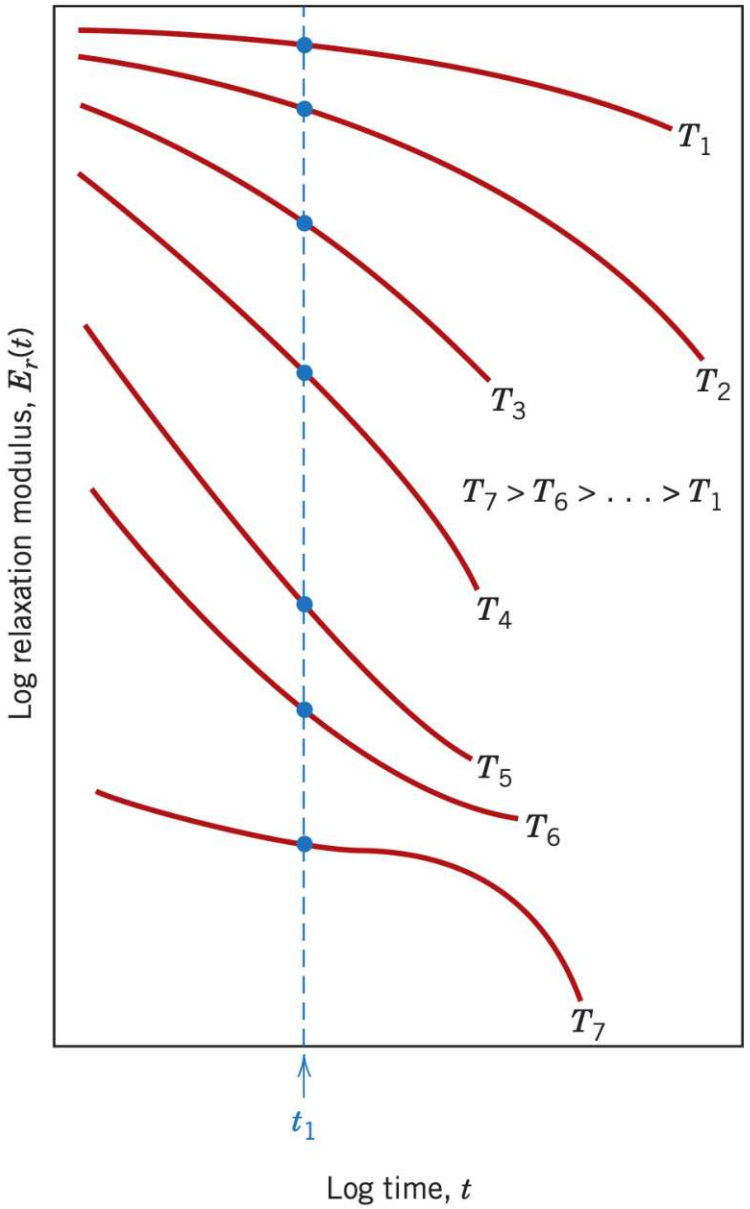
This is basically a time-dependent version of the elastic modulus.

Basically: how much force do I need to maintain a fixed deformation?



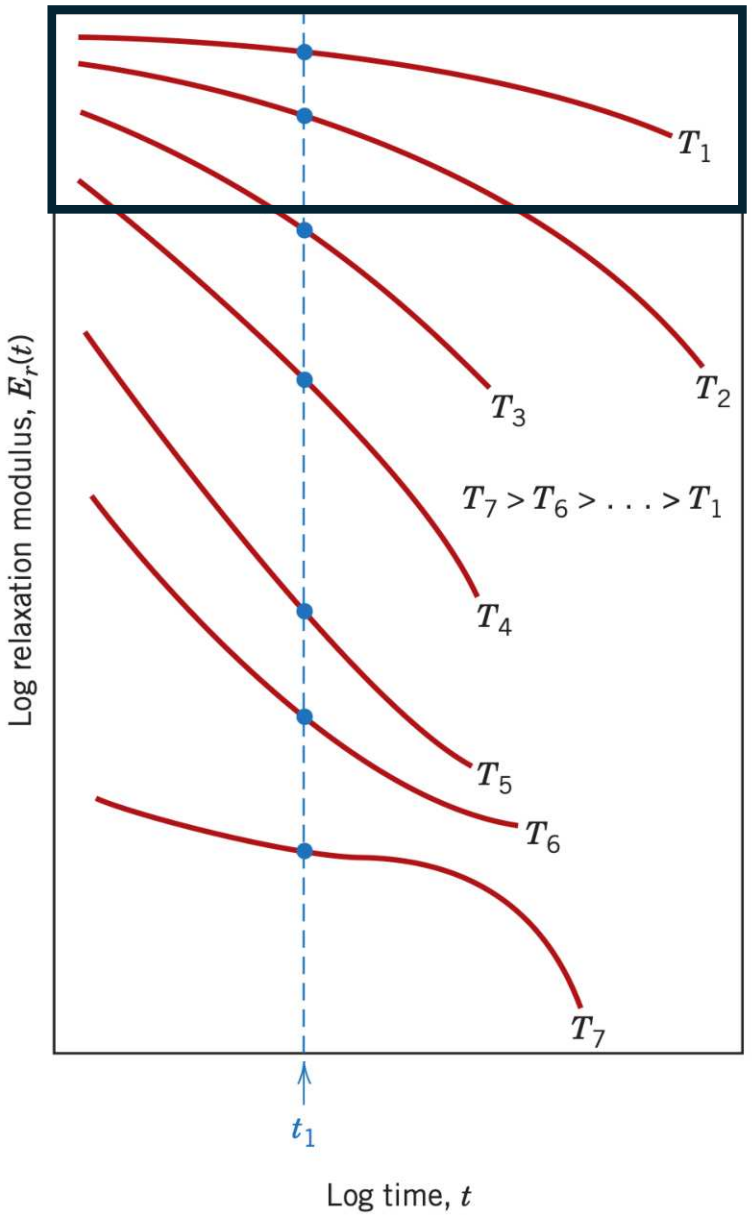
Less force will be needed over time as the materials gives way

Viscoelasticity: time-dependent deformation



This plot (log-scale) shows how some relaxation modulus curves might look for a polymer

Viscoelasticity: time-dependent deformation

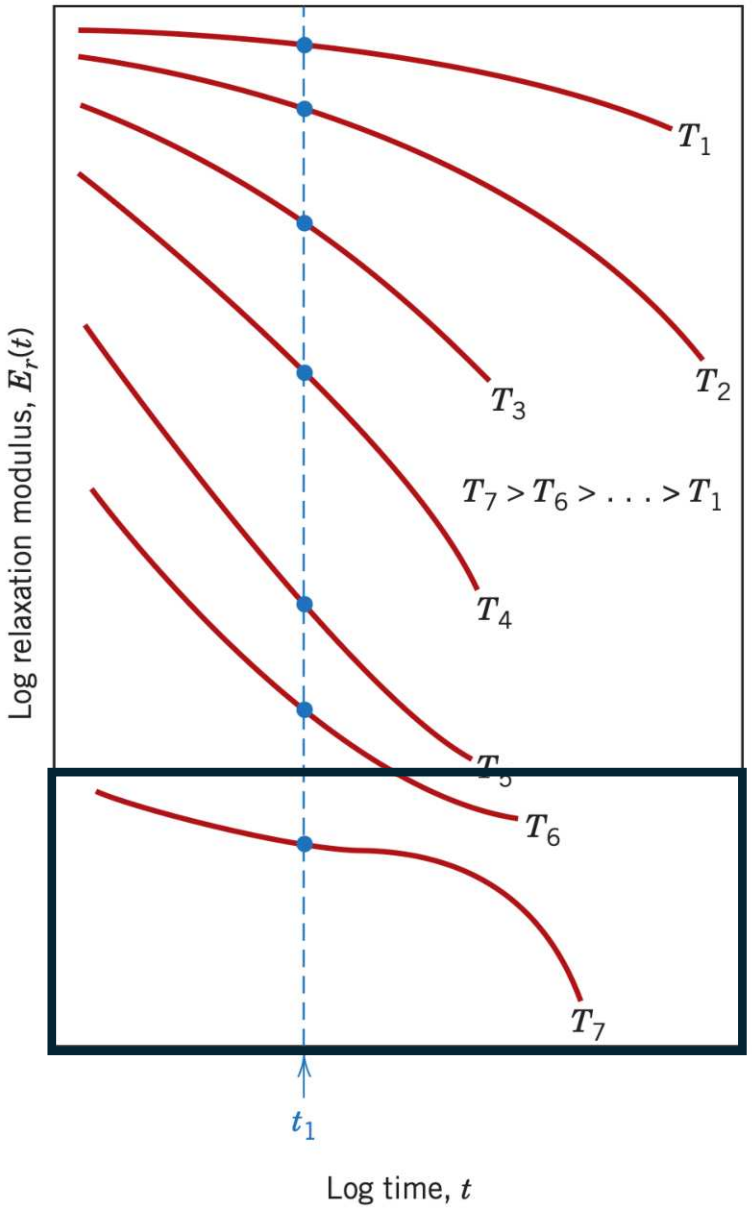


This plot (log-scale) shows how some relaxation modulus curves might look for a polymer

At **lower temperature** (*e.g.*, T_1) there is a large stress response (**stiffer material**) that decays rather slowly with time (**low viscosity**)



Viscoelasticity: time-dependent deformation



This plot (log-scale) shows how some relaxation modulus curves might look for a polymer

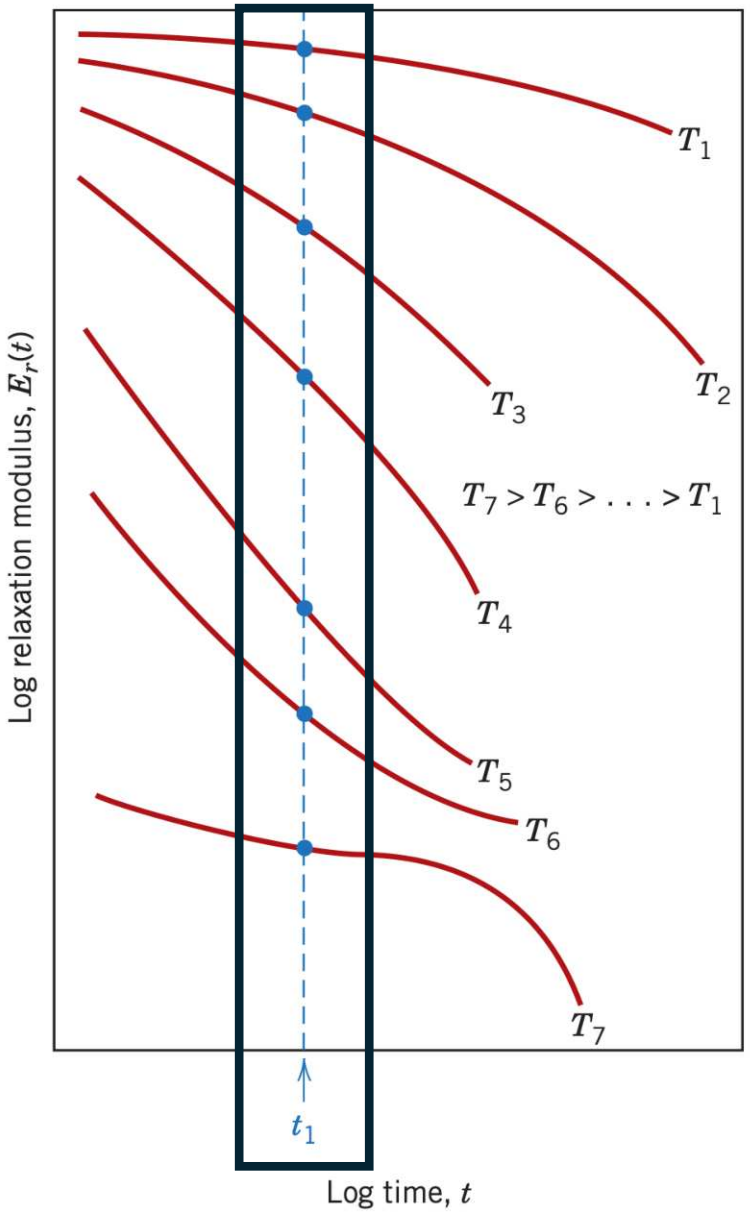
At **lower temperature** (*e.g.*, T_1) there is a large stress response (**stiffer material**) that decays rather slowly with time

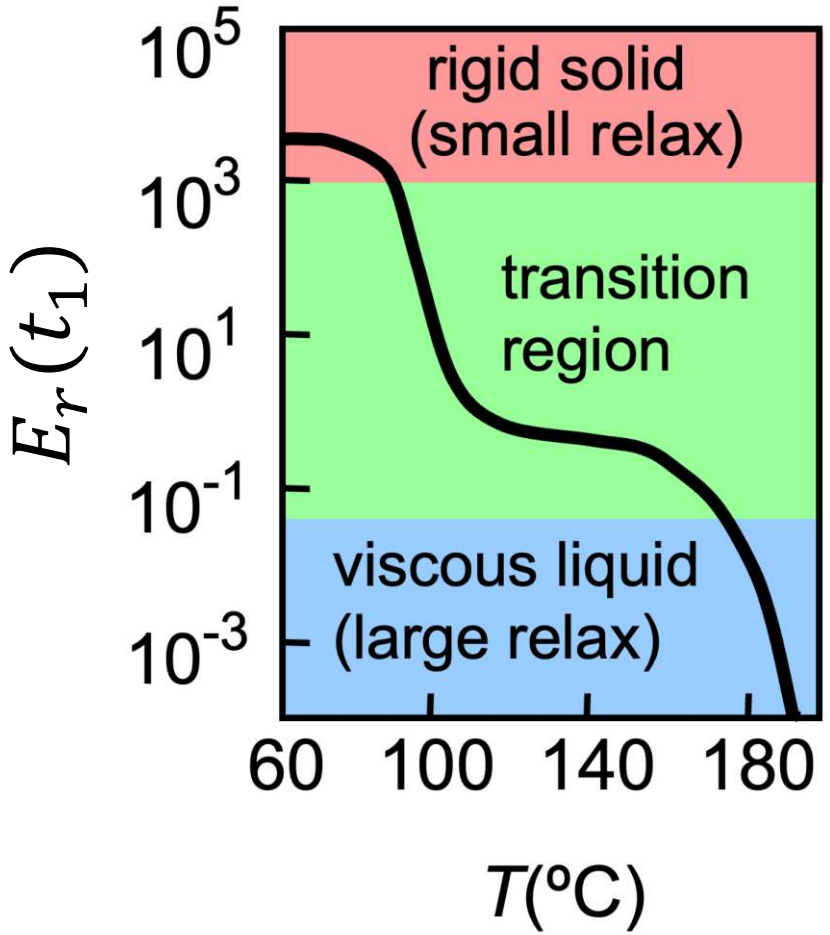
At **higher temperature** (*e.g.*, T_7) there is a much smaller stress response (**softer material**) that decays quickly with time (**high viscosity**)





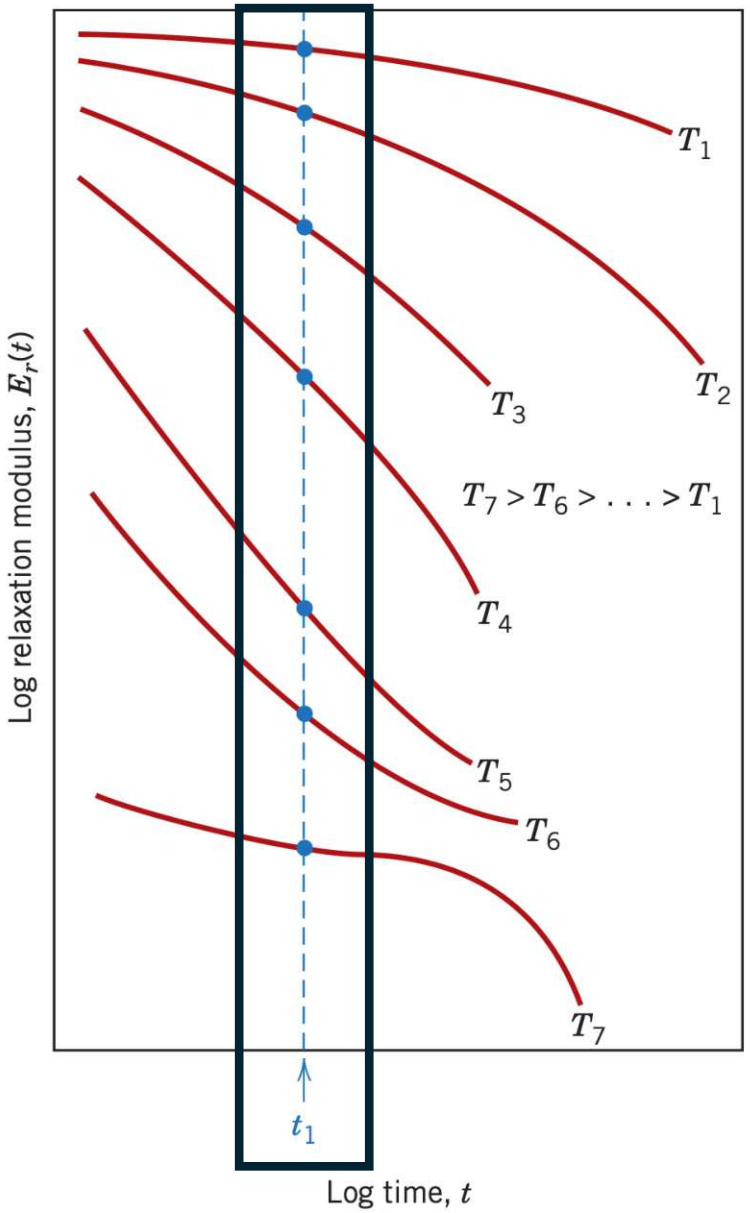
Viscoelasticity: time-dependent deformation

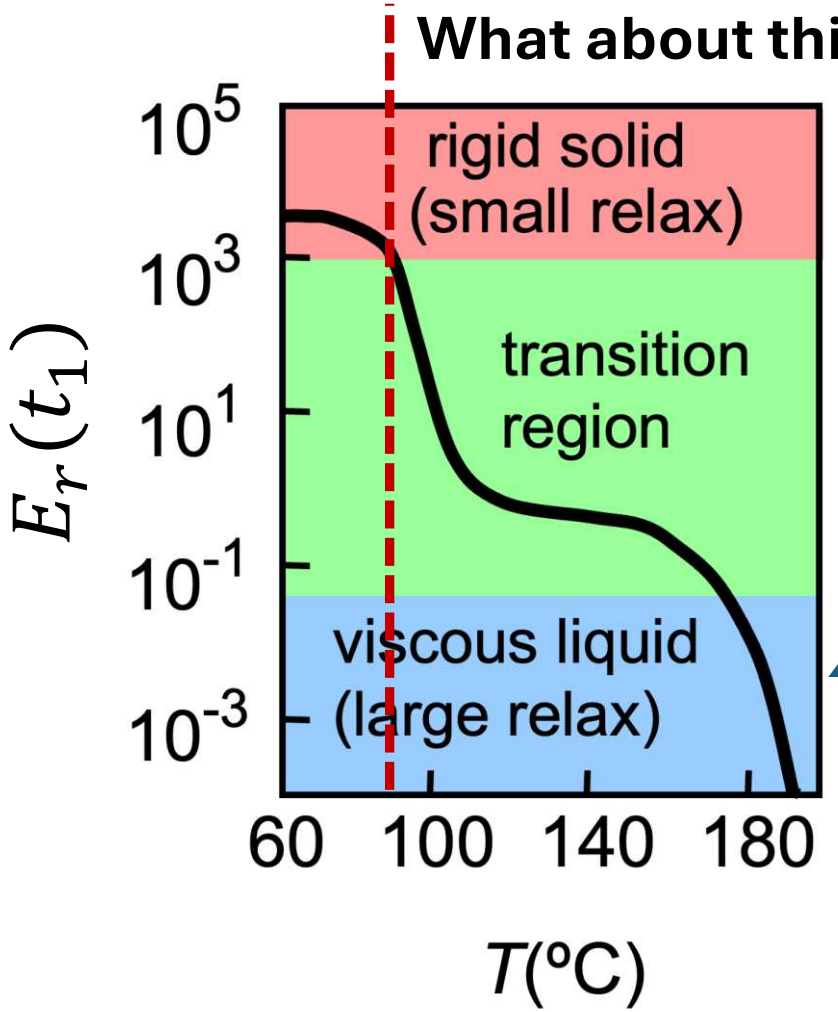




This plot is constructed by measuring the relaxation $E_r(t)$ modulus at a fixed time but **different temperatures**

Viscoelasticity: time-dependent deformation

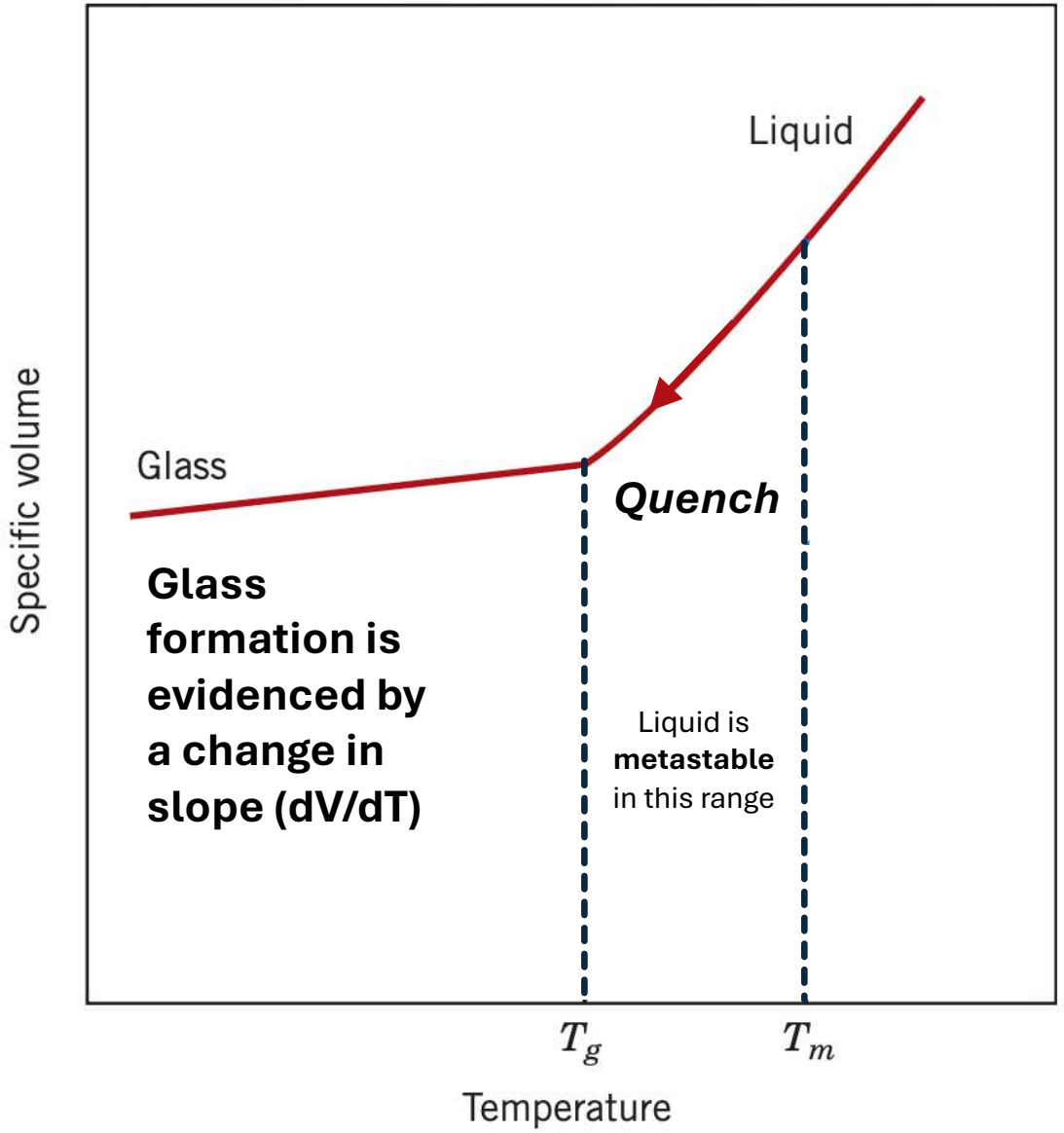




This dip occurs as we approach the melting point and form a viscous liquid

The glass transition temperature

- As we cool a polymer below its melting point, there is some driving force to crystallize into a solid
- But recall that nucleation typically requires some undercooling
- If we cool fast enough, to below the **glass transition temperature**, the melted polymer "freezes" in place → **forming an amorphous solid**

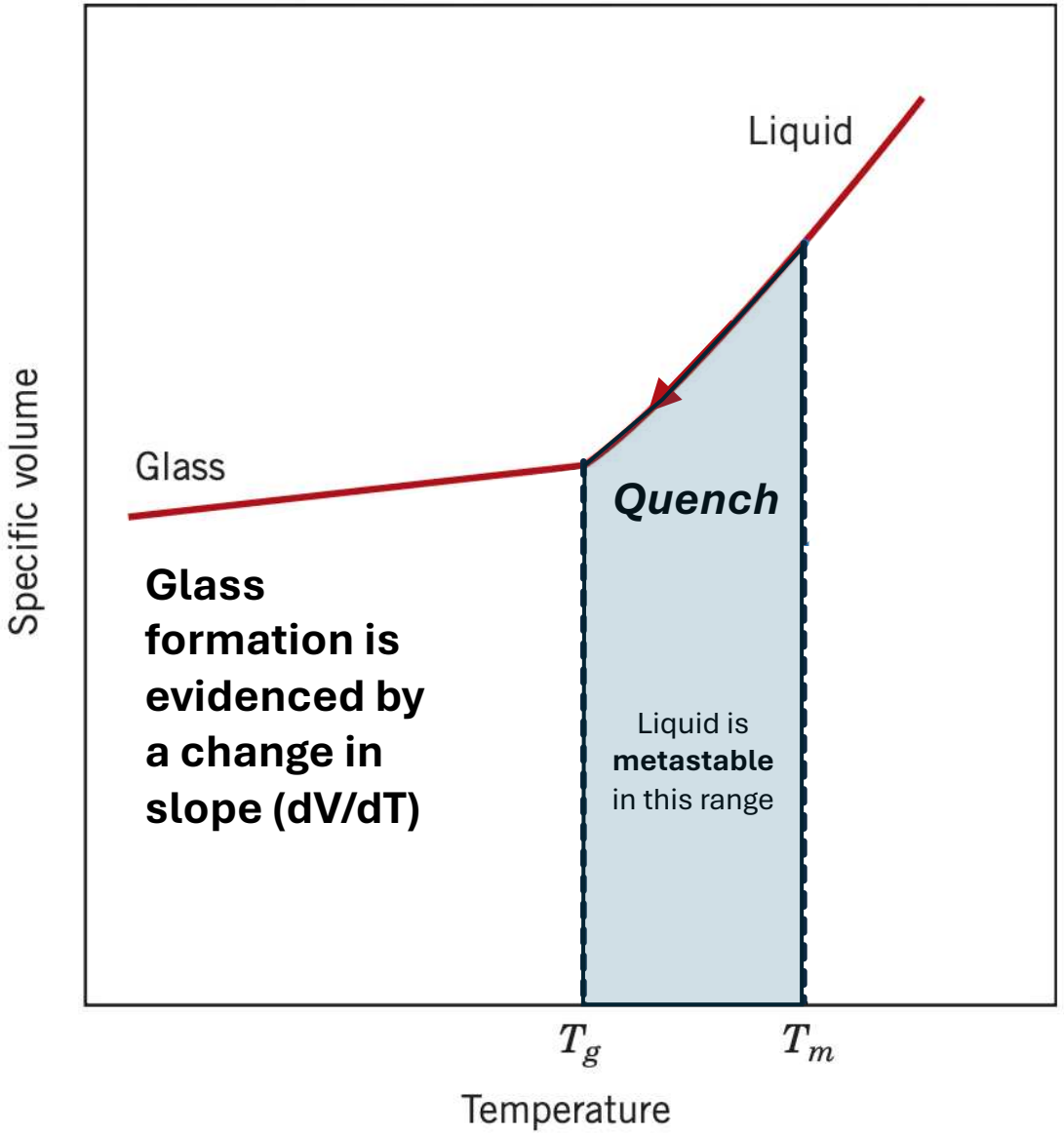


The glass transition temperature

T_g is the temperature above which there is enough thermal energy for polymer **chains to slide past one another**, but not so much energy that the solid melts



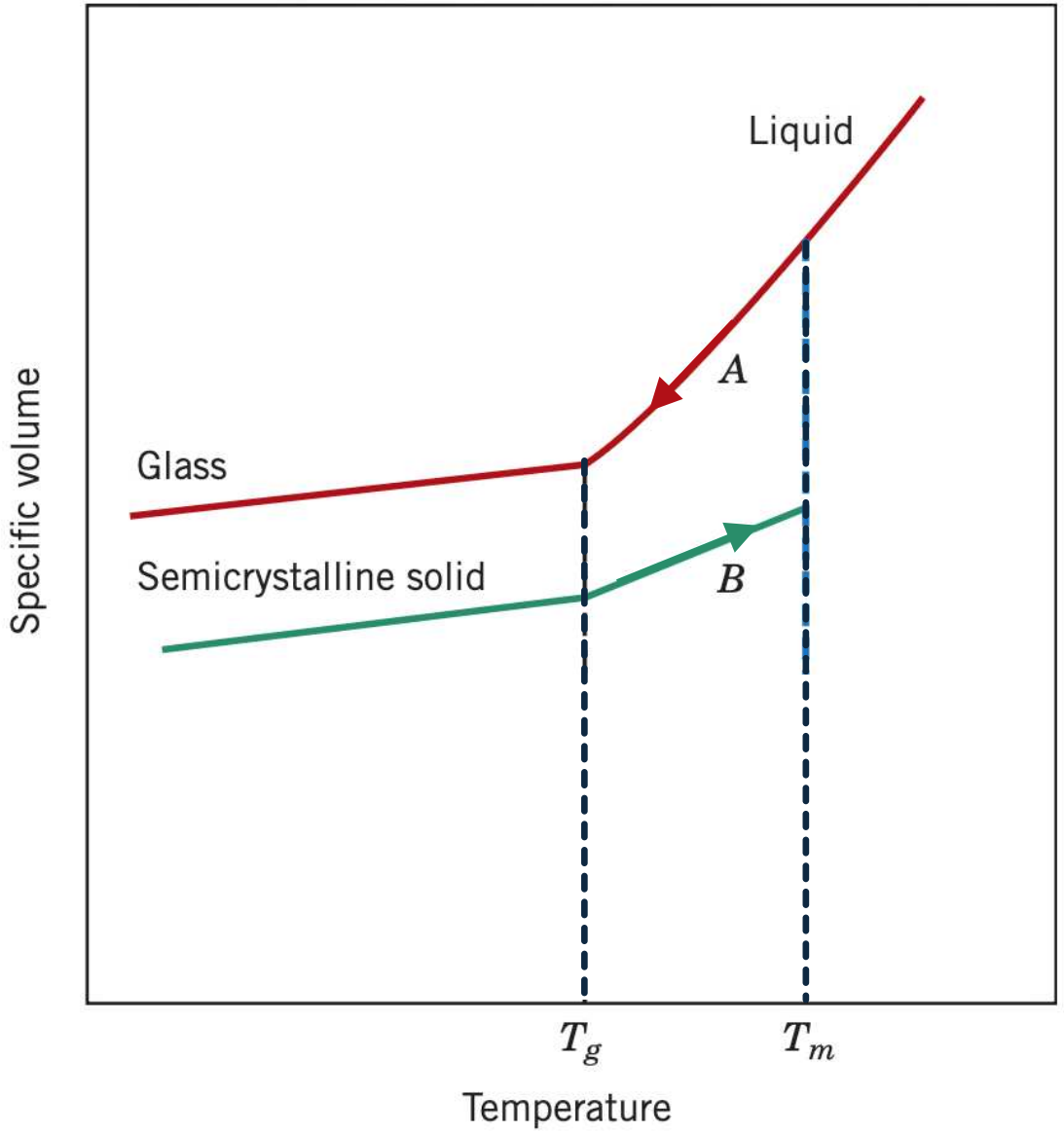
At temperatures $T_g < T < T_m$ the polymer is in a **"rubbery"** state, where it is relatively **soft and easily deformed** (but it is not a liquid)



The glass transition temperature

This transition happens in both directions (heating and cooling), assuming the polymer is amorphous to some degree (may be semicrystalline)

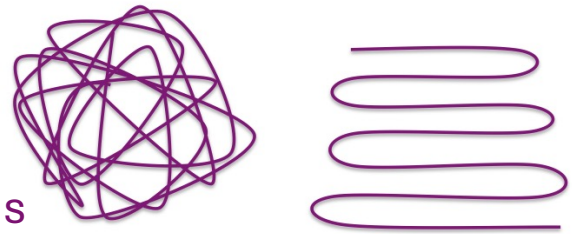
In other words:
The **material softens as we heat it**, much more so after $T > T_g$



The glass transition temperature

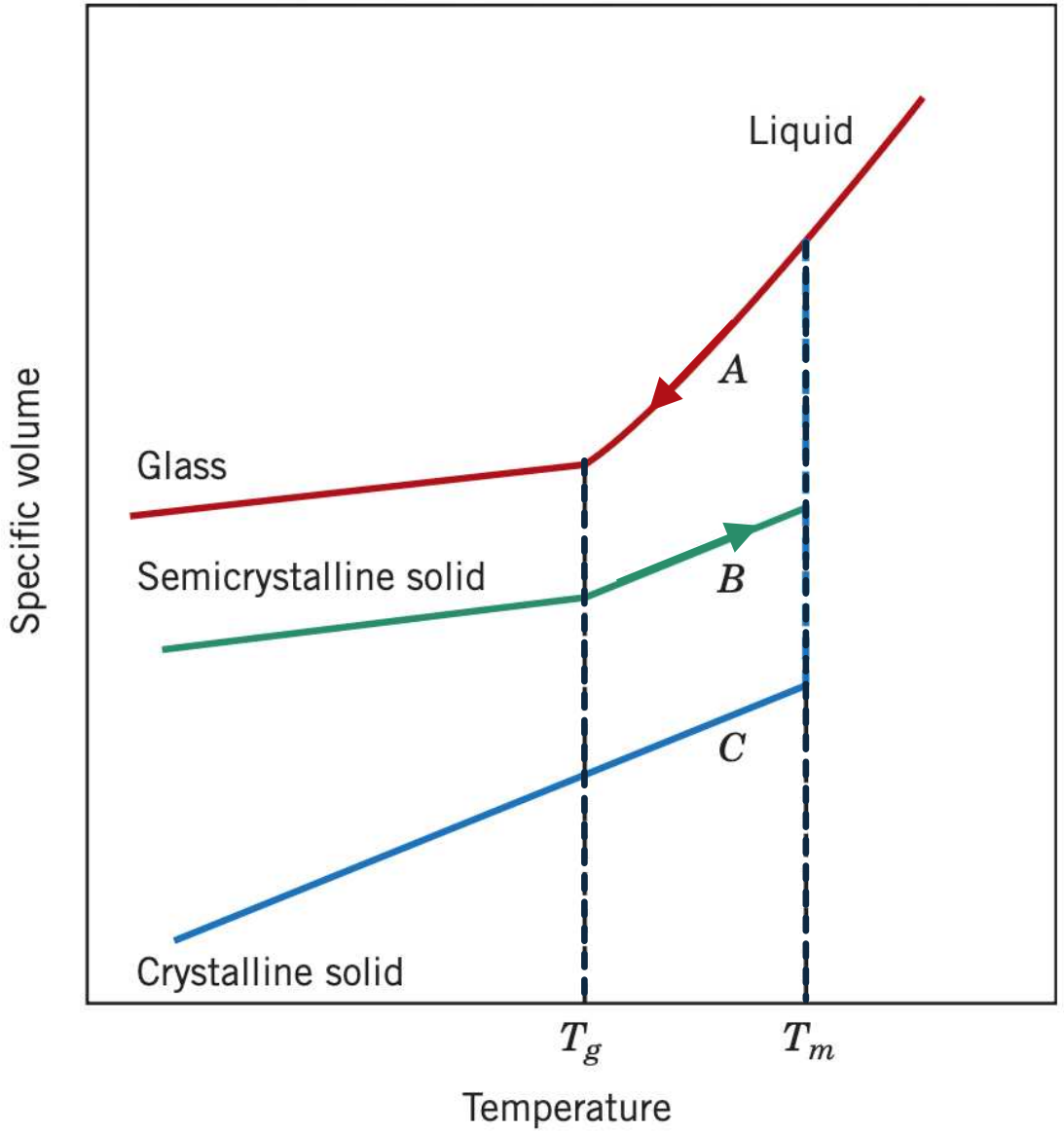
This transition happens in both directions (heating and cooling), assuming the polymer is amorphous to some degree (may be semicrystalline)

But *not* for 100% crystalline solids.
There is no amorphous mobility left to "unfreeze" – chains are completely ordered and will not easily move past one another until $T > T_{\mathrm{m}}$



Amorphous

Crystalline

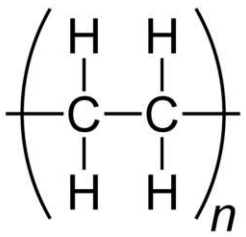


The glass transition temperature

Material	*Glass Transition Temperature [°C (°F)]*	*Melting Temperature [°C (°F)]*
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Poly(ethylene terephthalate) (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

Glass transition temperatures are closely correlated with melting points ($T_g \sim 0.6\, T_m$)

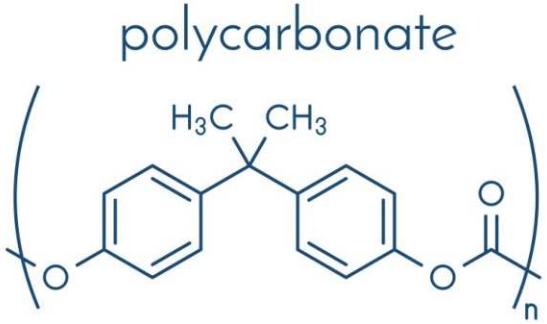
polyethylene



Low T_g , T_m

High glass transition and melting temps:

- Larger molecular weight (long chains)
- Bulky and/or polar side groups
- Strong inter-chain bonding (cross-linking)



High T_g , T_m





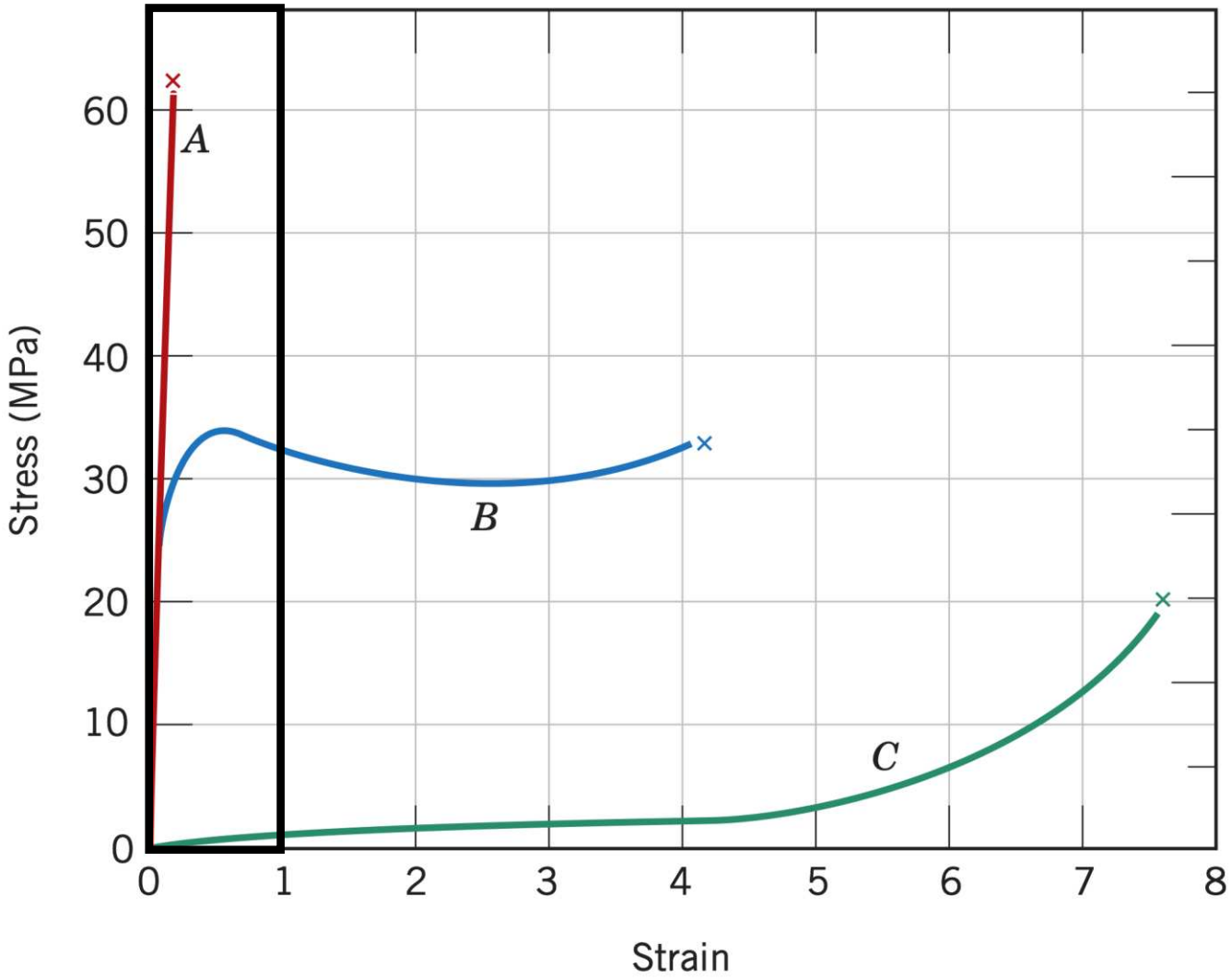
Not the new one...





Questions on the glass transition?

Fracture of polymers



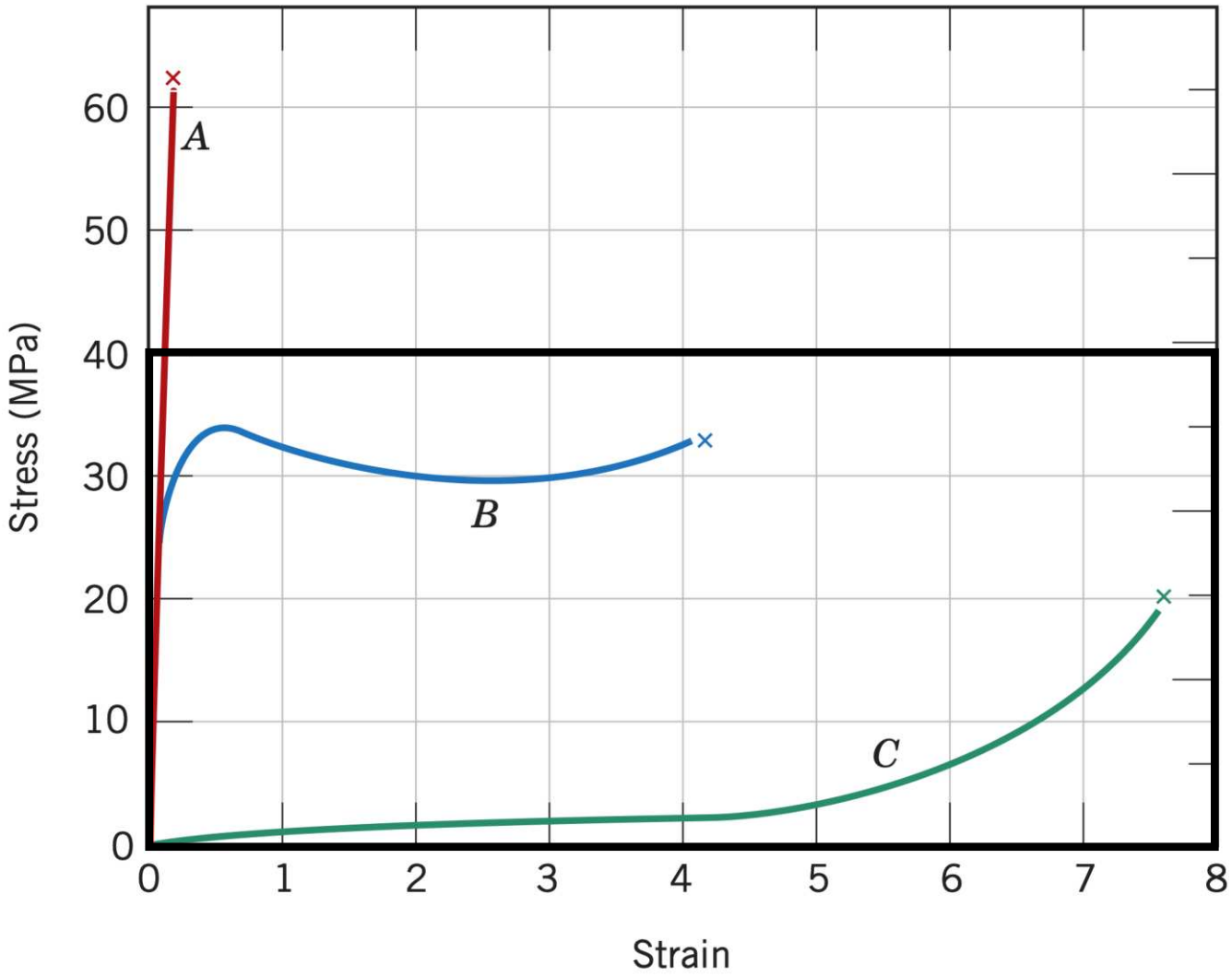
Brittle fracture is similar between polymers and metals/ceramics

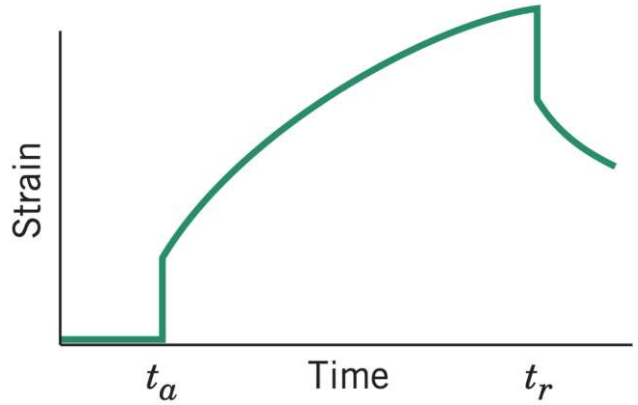


Rapid crack propagation



Fracture of polymers

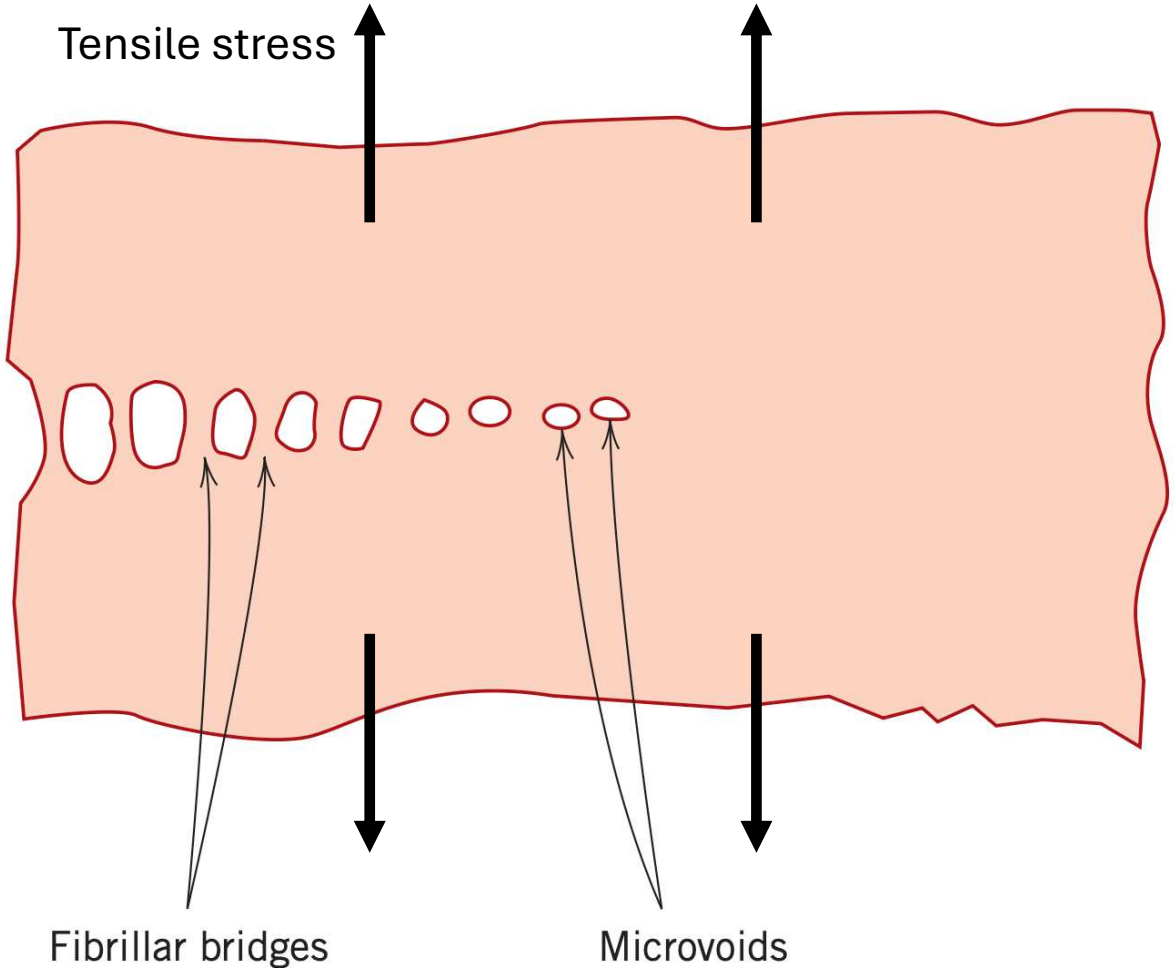




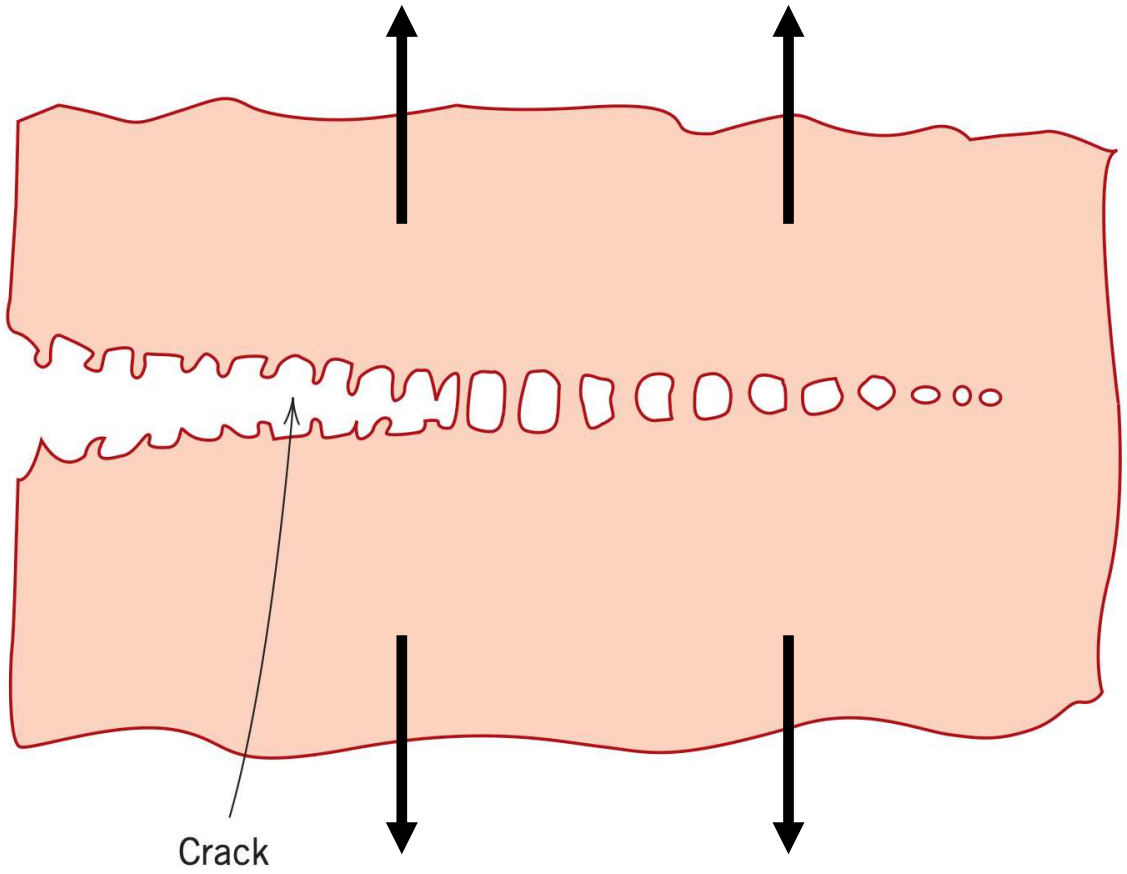
Ductile fracture is quite different for polymers owing to their highly plastic and sometimes viscoelastic behavior…

There is much more **“stretch”** prior to fracture

Fracture of polymers: crazing

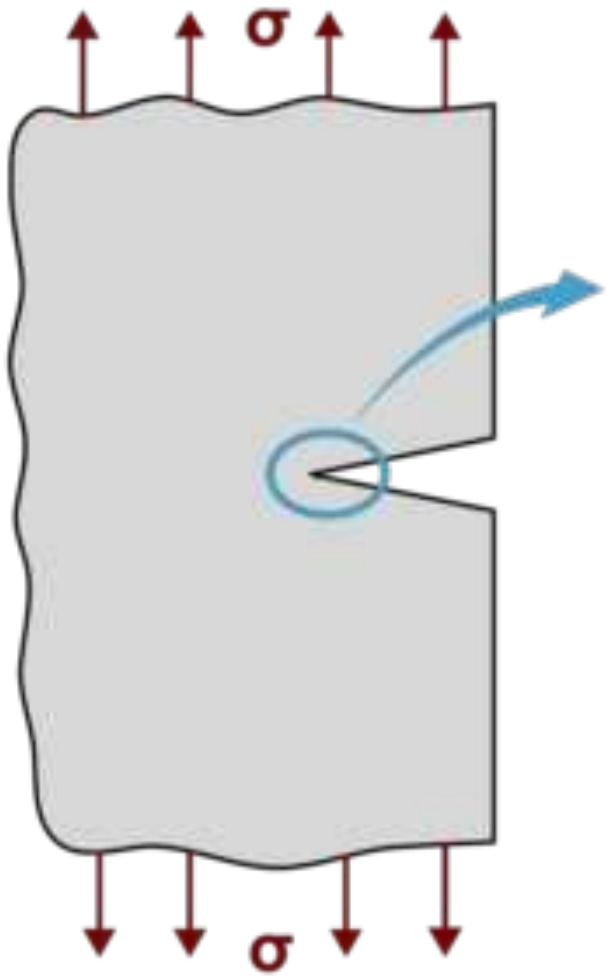


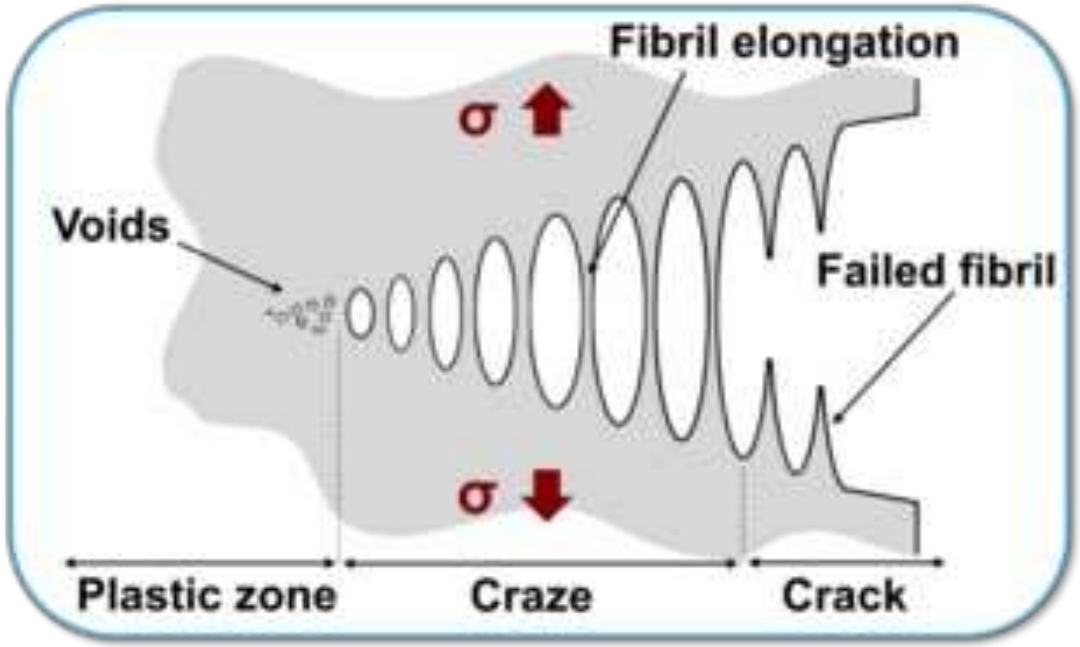
Stress is concentrated at flaws, producing not one but many voids



A crack grows as these voids connect with one another

Fracture of polymers: crazing

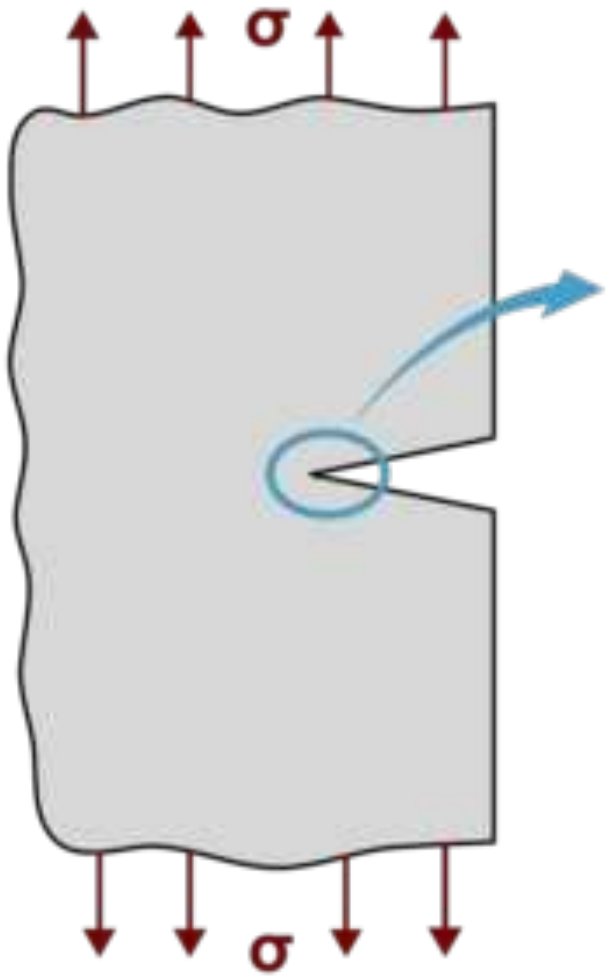


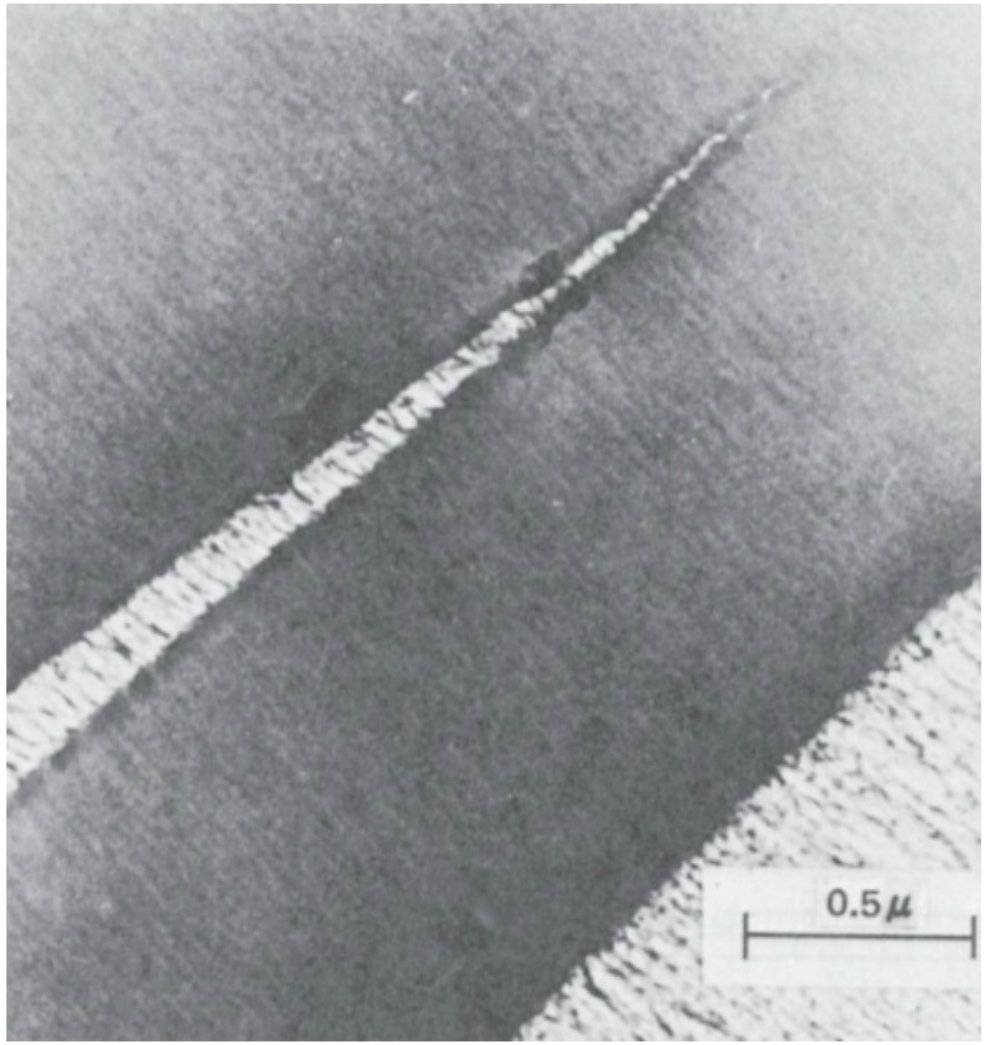


A craze is different from a crack because it can **still support a load *via* elongated fibrils**



Fracture of polymers: crazing





Easy to see in a microscope!

Types of polymers and their applications

Fibers





Polyester



Nylon

Filament

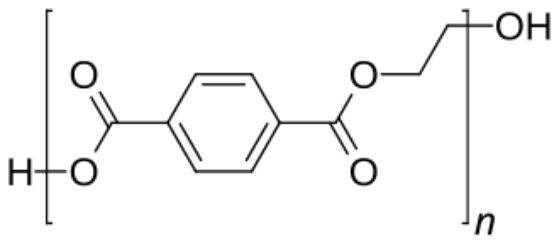


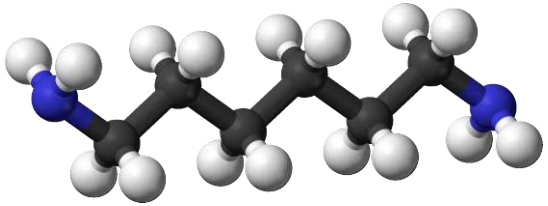
These are polymers capable of being draw into long filaments having at least a 100:1 length-to-diameter ratio

Examples:

- Ropes/cords/lines
- Clothing (textile industry)

These tend to require polymers with relatively **high molecular weights – strong enough to endure *drawing***



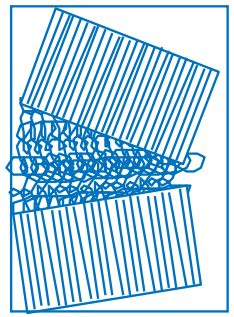


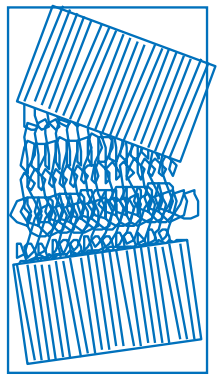
Strengthening polymers through drawing

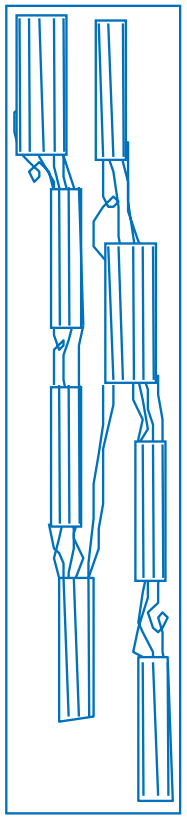
Recall that plastic deformation often occurs by aligning polymer chains that are initially randomly oriented



Drawing takes advantage of this by aligning the chains in the manufacturing process





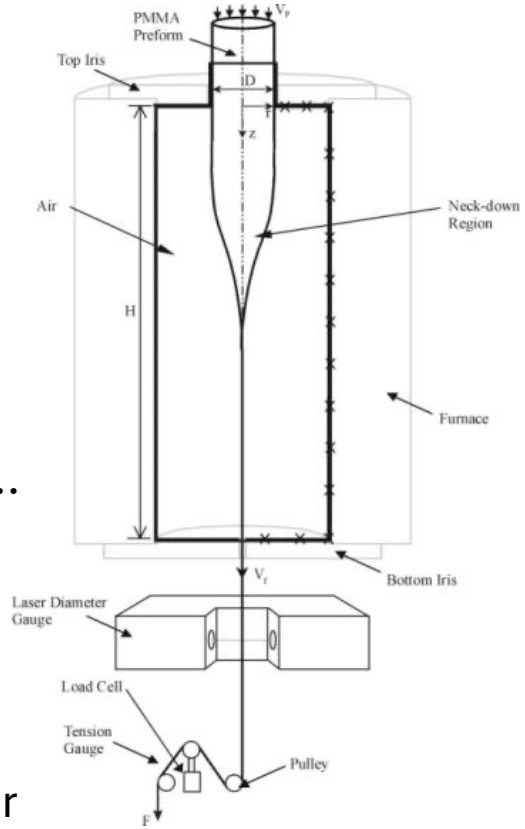


These initial steps of deformation are relatively easy

But deforming this aligned chain is much harder!



Puuuuuuu....



We'll watch a video later

Types of polymers and their applications

Fibers

Plastics





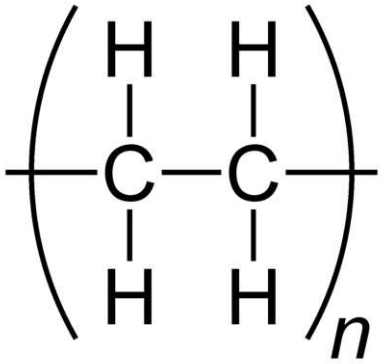




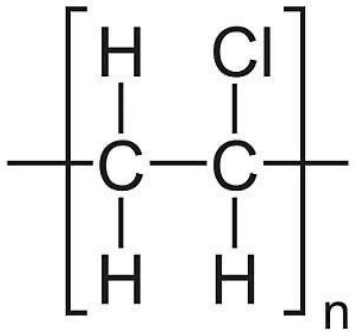
A very broad class of polymers used to provide **structural integrity** or protective coating while being reasonably **lightweight**

Their necessary properties will vary depending on the specific application

PE

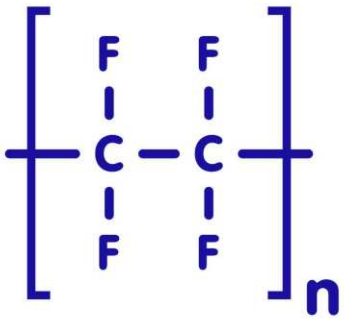


PVC





PTFE



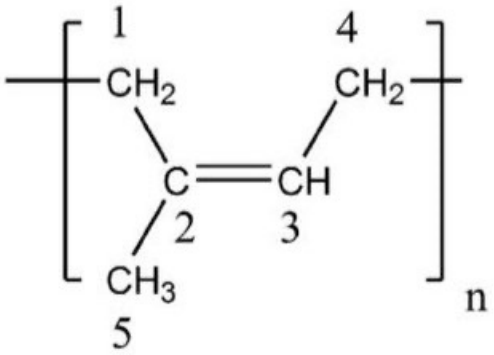
Types of polymers and their applications

Fibers

Plastics

Elastomers

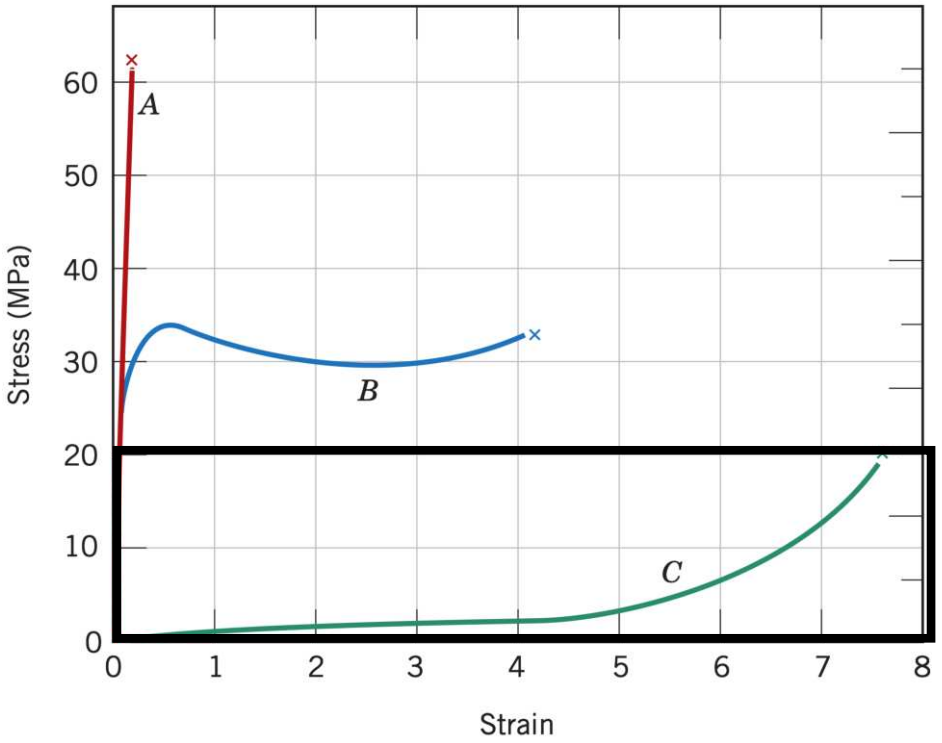
Natural rubber



cis-1,4-polyisoprene







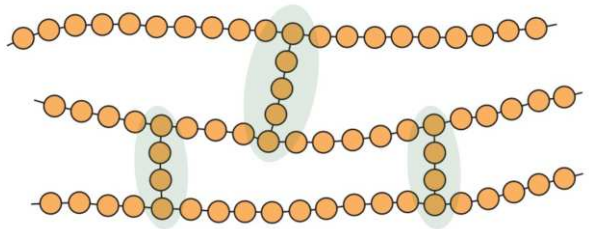
Used anywhere you need a **large and reversible deformation**

Types of polymers and their applications

Fibers

Plastics

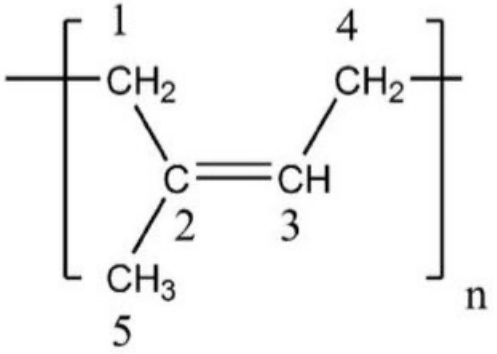
Elastomers



Crosslinked



Natural rubber

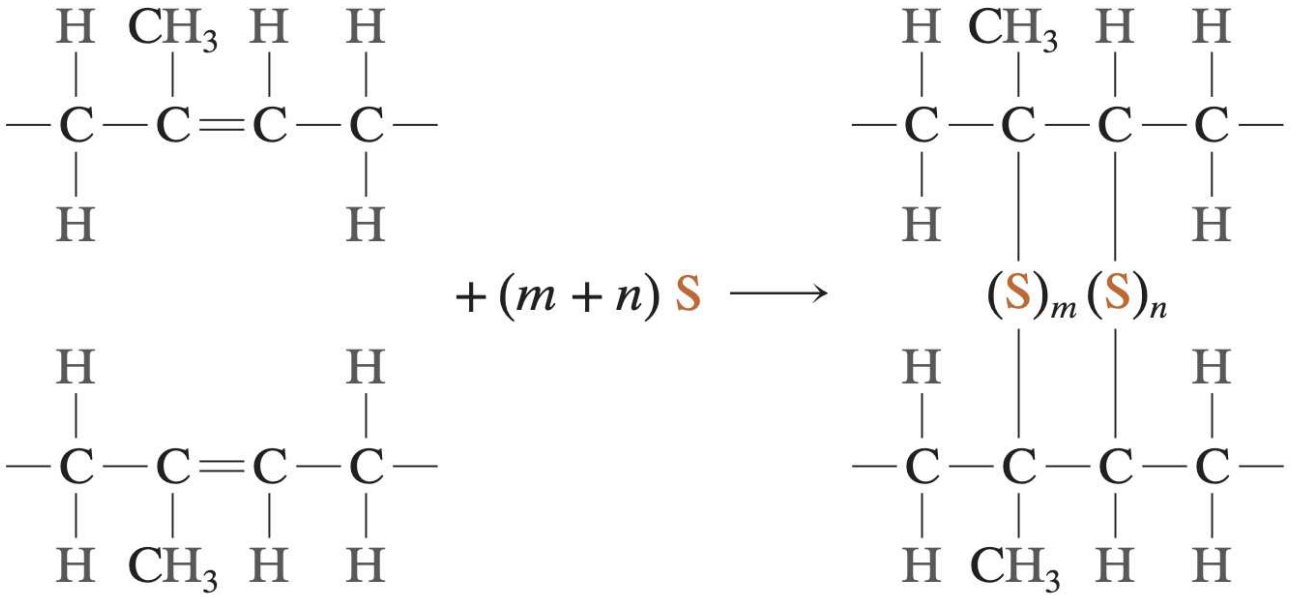


cis-1,4-polyisoprene



Vulcanization makes natural rubber much tougher

Addition of sulfur and heat to form cross-links





Types of polymers and their applications

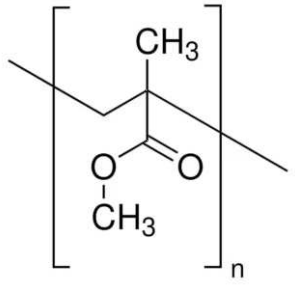
Fibers

Plastics

Elastomers

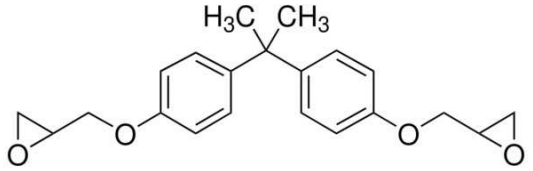
Coatings

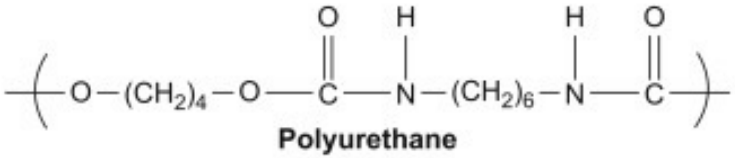












Used to provide a protective barrier or electrical insulation

EX: Acrylics, epoxies, and polyurethanes

The hardening (setting) process is often related to cross-linking

Types of polymers and their applications

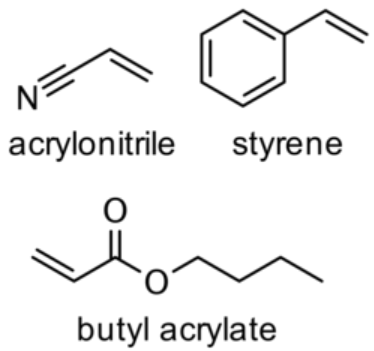
Fibers

Plastics

Elastomers

Coatings

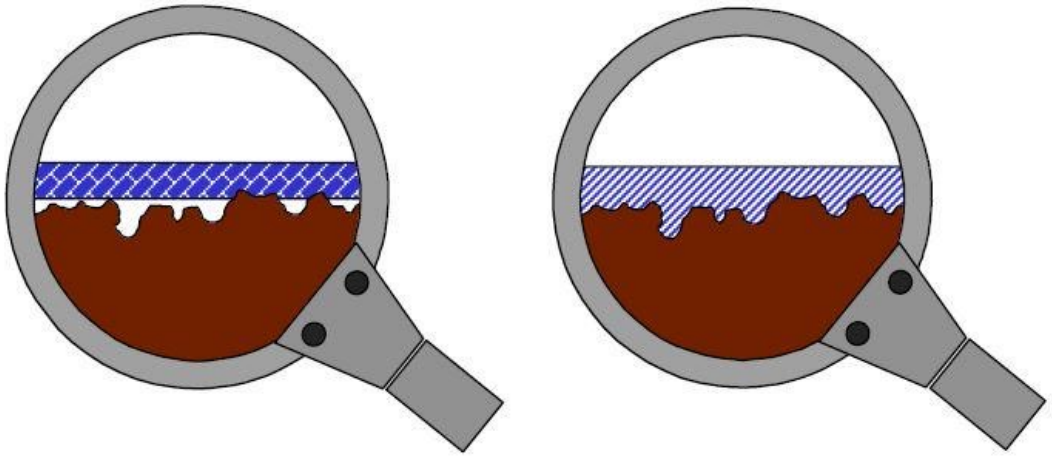
Adhesives





Scotch tape uses a mixture of viscoelastic acrylics

As we apply pressure to the tape, these polymers deform to fill gaps in the materials, adhering to them through van der Waals bonding



Used to bond together the surfaces of two materials

Types of polymers and their applications

Fibers

Biomaterials

Plastics

Liquid crystals

Elastomers

Coatings

Adhesives

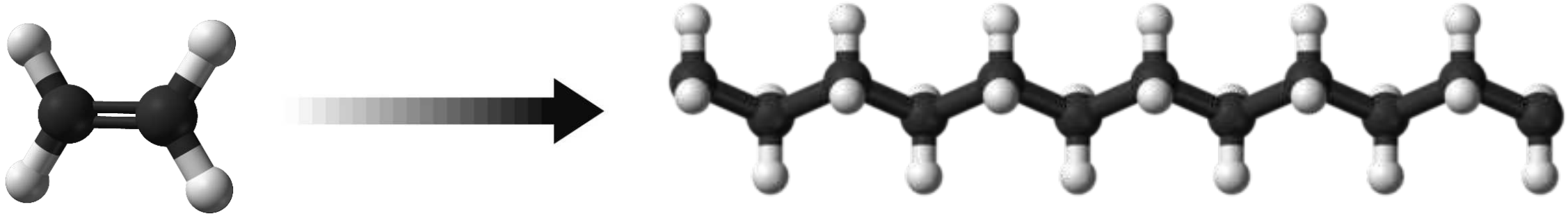
See the Callister textbook for more classes and applications

Note these are not distinct – many overlap

Questions on applications of polymers?

Polymer synthesis

The process of **linking monomers together** to form large molecular chains is called ***polymerization***



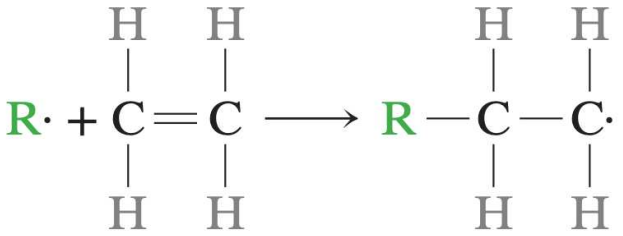
Type 1: Addition Polymerization

Type 2: Condensation Polymerization

Polymer synthesis: Addition polymerization

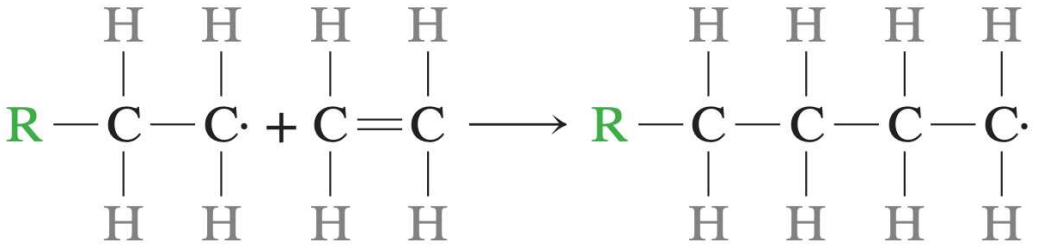
In addition polymerization, monomers are **chained together one-by-one**

Step 1: Initiation



Formation of an active center

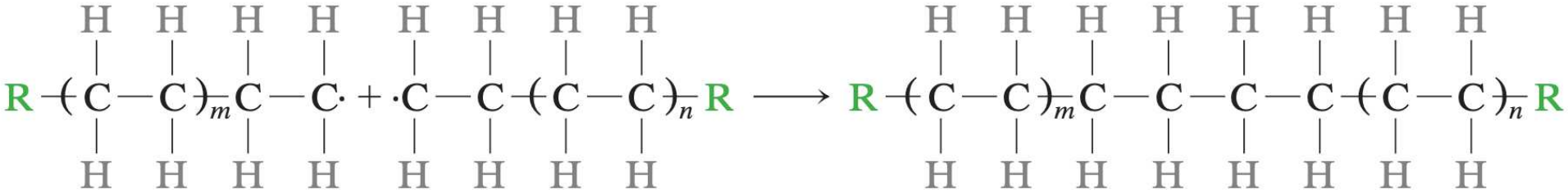
Step 2: Propagation



Sequential addition of monomers

Two polymer chains connect, passivating the active centers

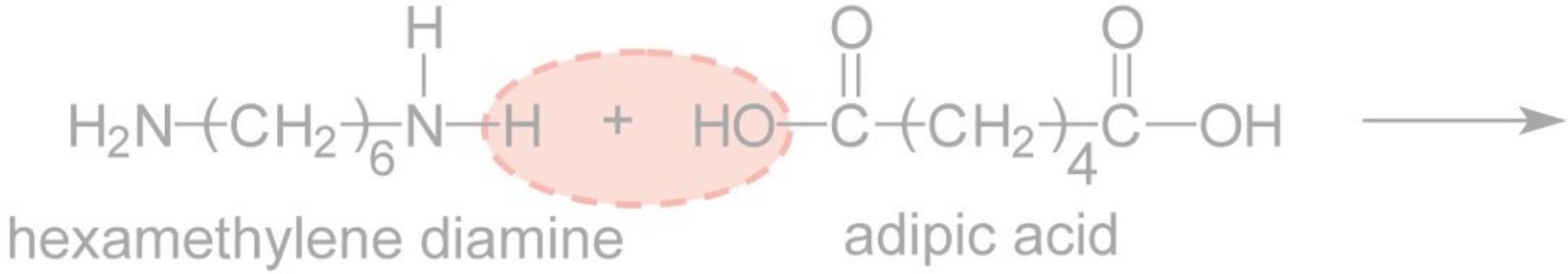
Step 3: Termination



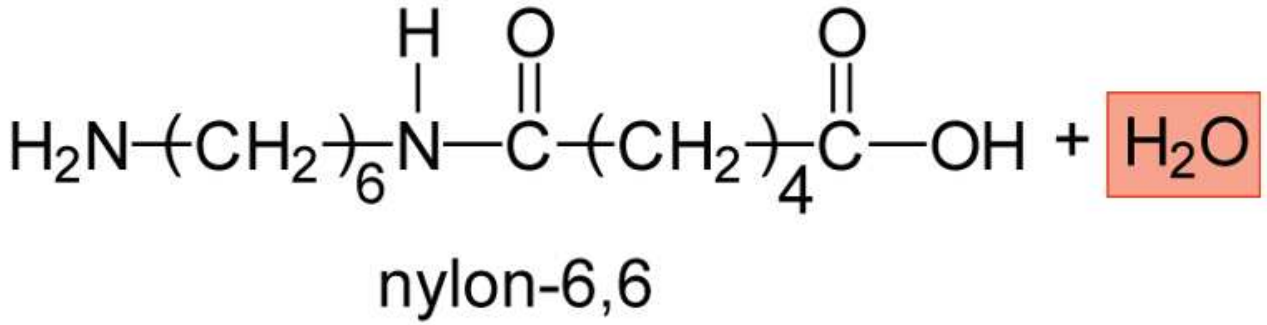
Polymer synthesis: Condensation polymerization

Condensation polymerization involves **chemical reactions** and atomic rearrangements, possibly between more than one monomer

(no reactant has same formula as the repeat unit)



Often forms byproducts, and tends to be much **slower than addition polymerization**



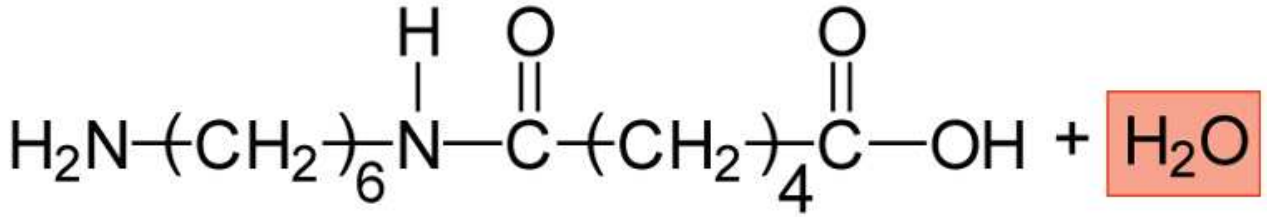
Polymer synthesis: Condensation polymerization



This process is less common than addition polymerization (used to make most plastics) but is still important



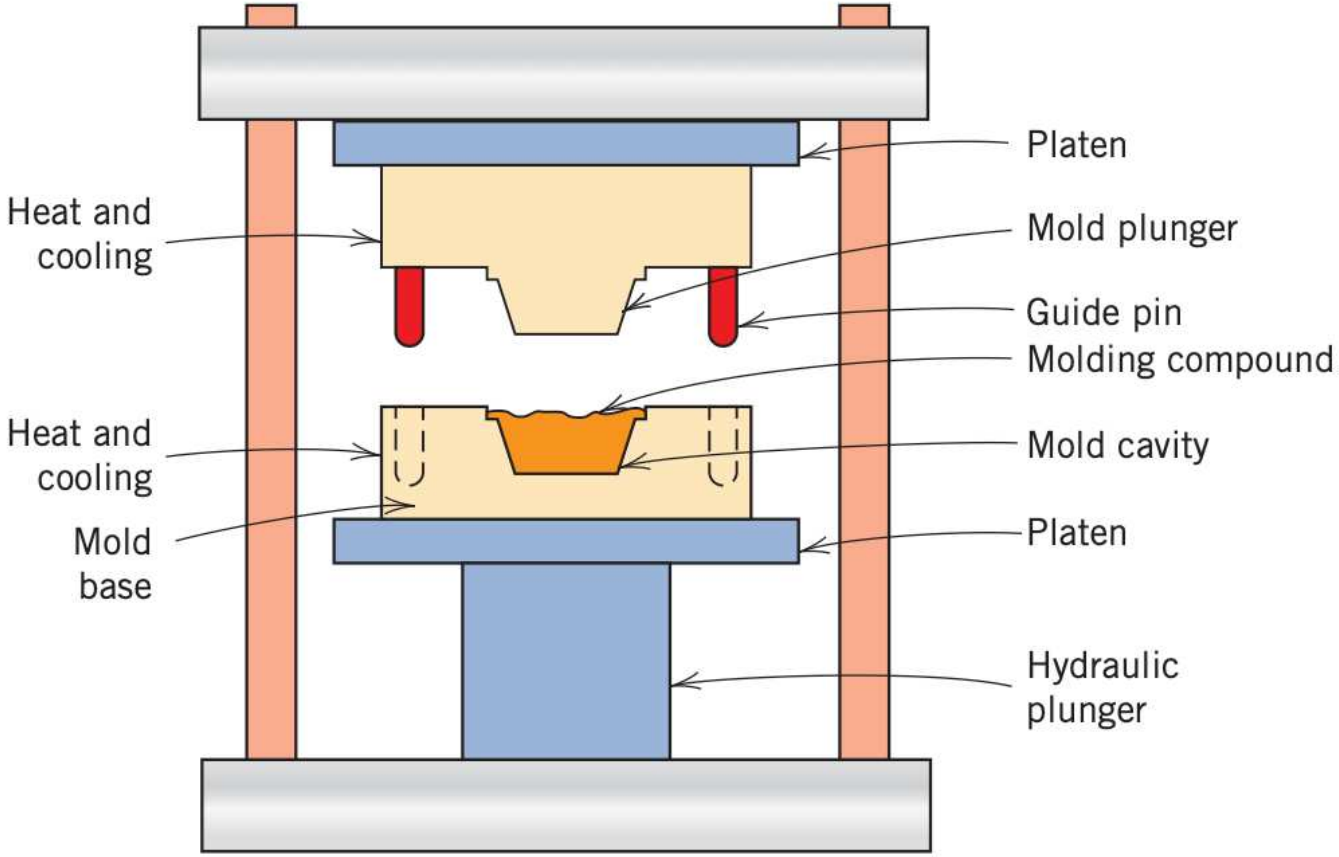
Often forms byproducts, and tends to be much **slower than addition polymerization**



nylon-6,6

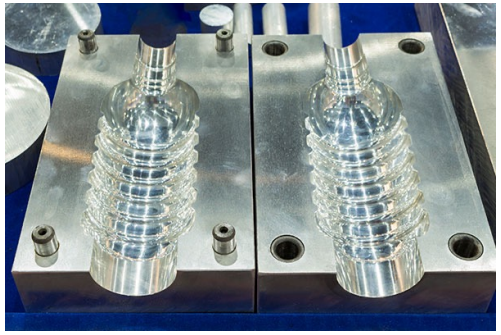
Polymer processing

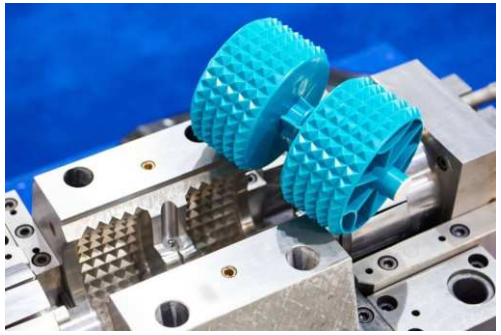
After synthesizing a polymer, how to form it into a desired shape?



Compression molding:

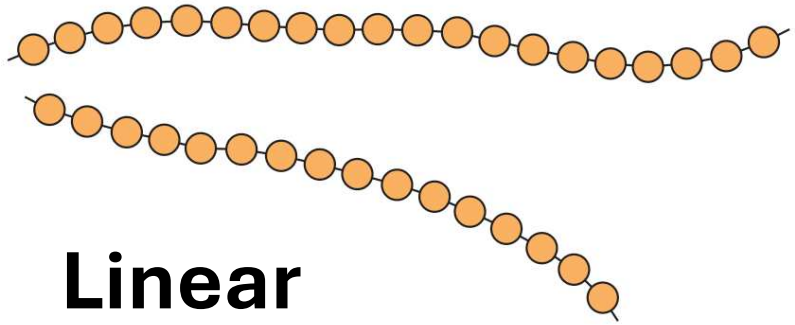
- Heat polymer above its glass transition or melting temp, so it is easily deformed to fit the mold
- Compress the material and let it cool to solidify





Recall from last time

Polymer processing



Linear

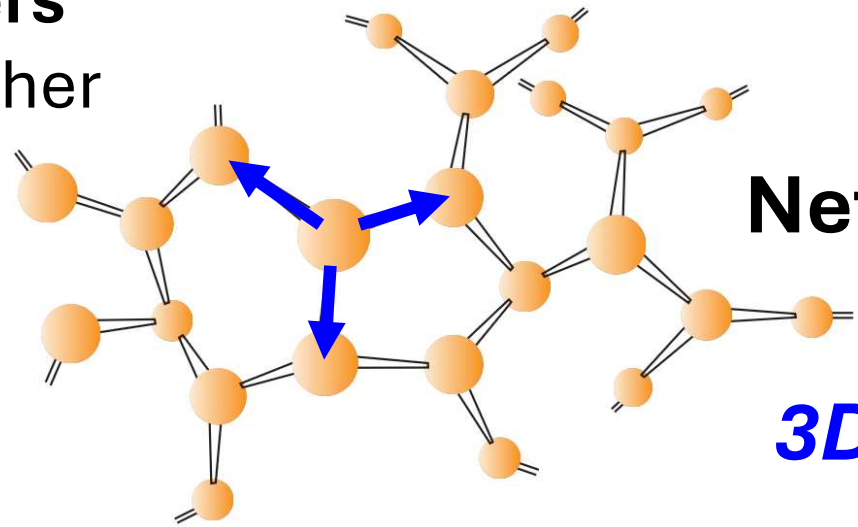


Thermoplastics are often linear: these are polymers that soften/melt quite easily under heat



Thermosetting polymers are network: much tougher

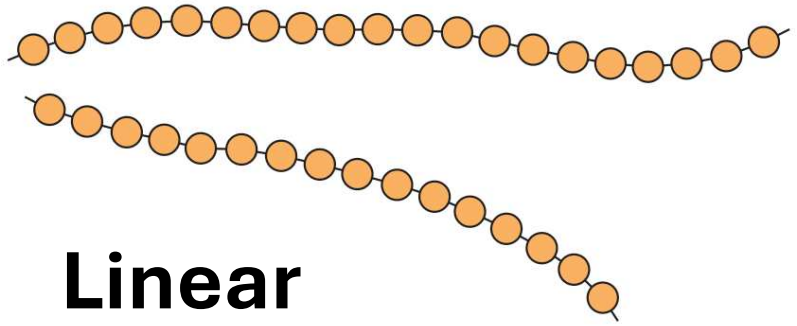




Network

***3D** linking*

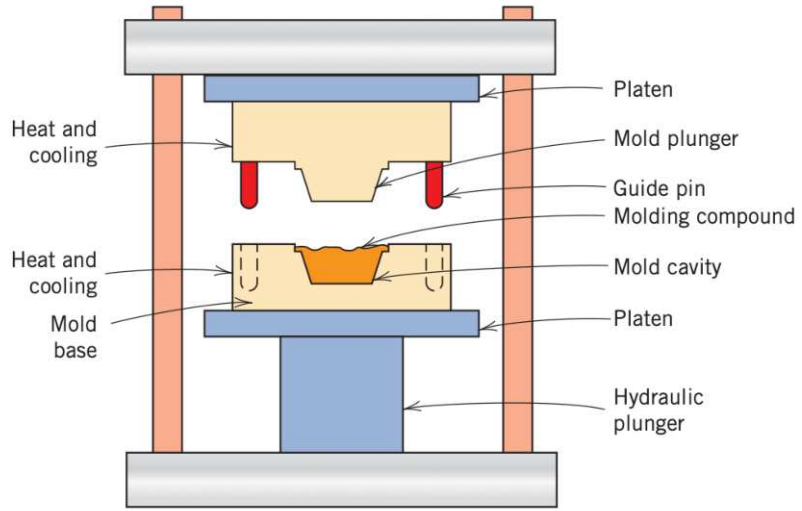
Polymer processing



Linear



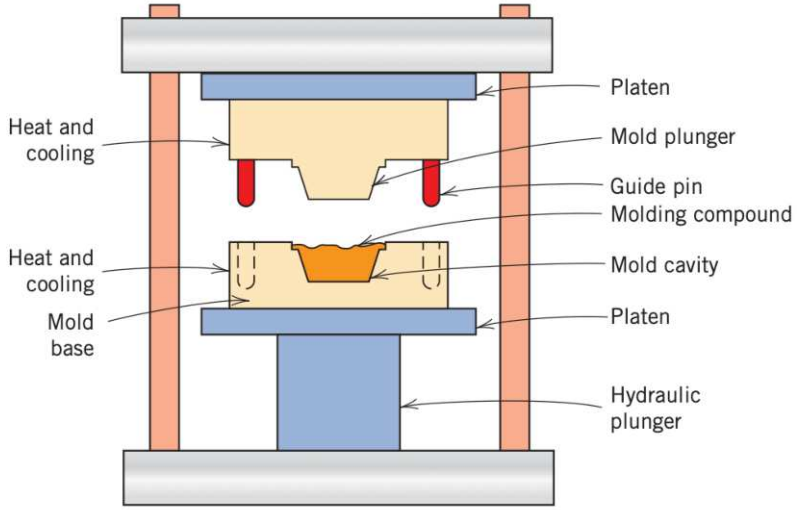
Thermoplastics are often linear: these are polymers that soften/melt quite easily under heat



These can be easily melted and formed in the mold. No extra steps required.

Recall from last time

Polymer processing

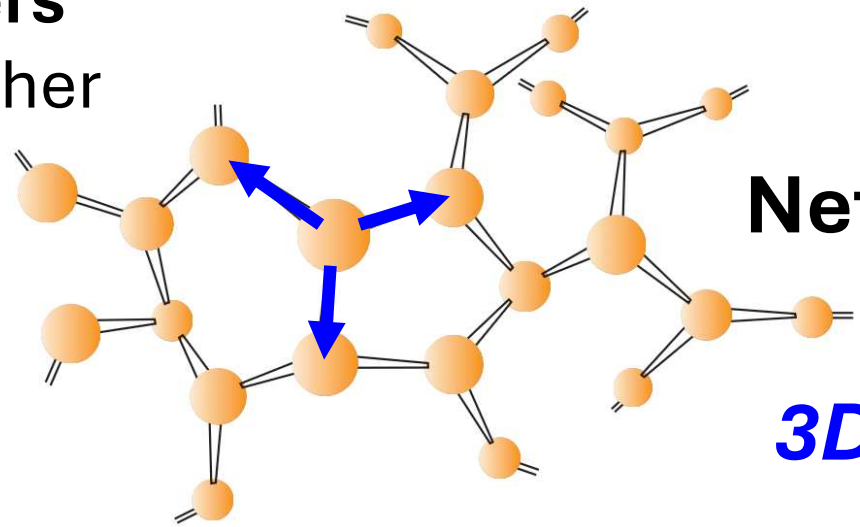


These are generally molded as linear polymers, then *cured* in a second step to form the network



Thermosetting polymers
are network: much tougher

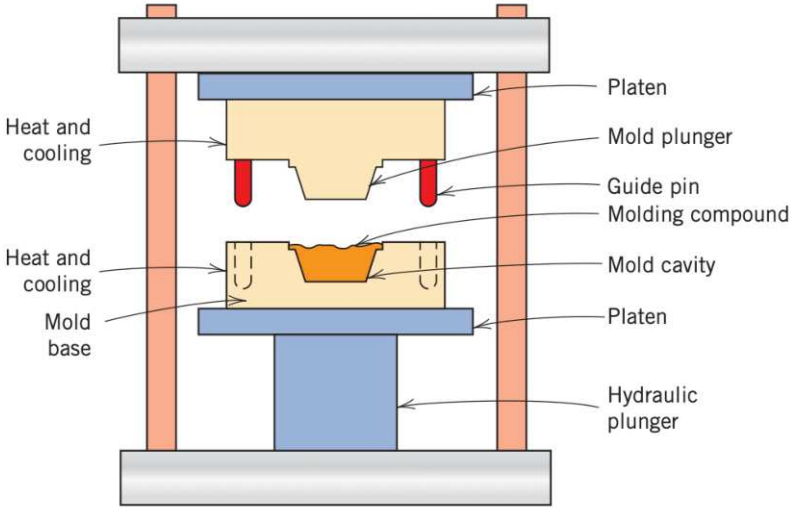




Network

***3D** linking*

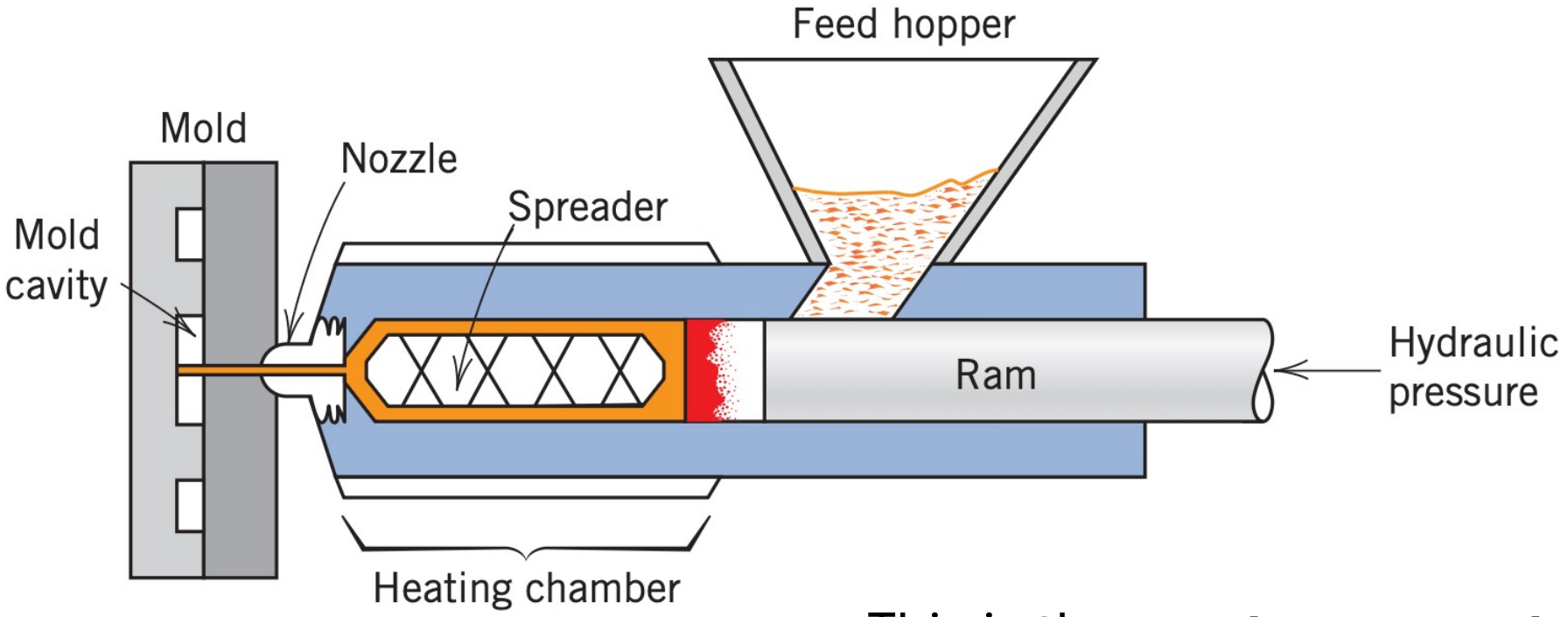
Polymer processing



What if our desired product has an irregular shape?

Polymer processing

Injection molding uses pressure to fill the mold with a melted polymer material

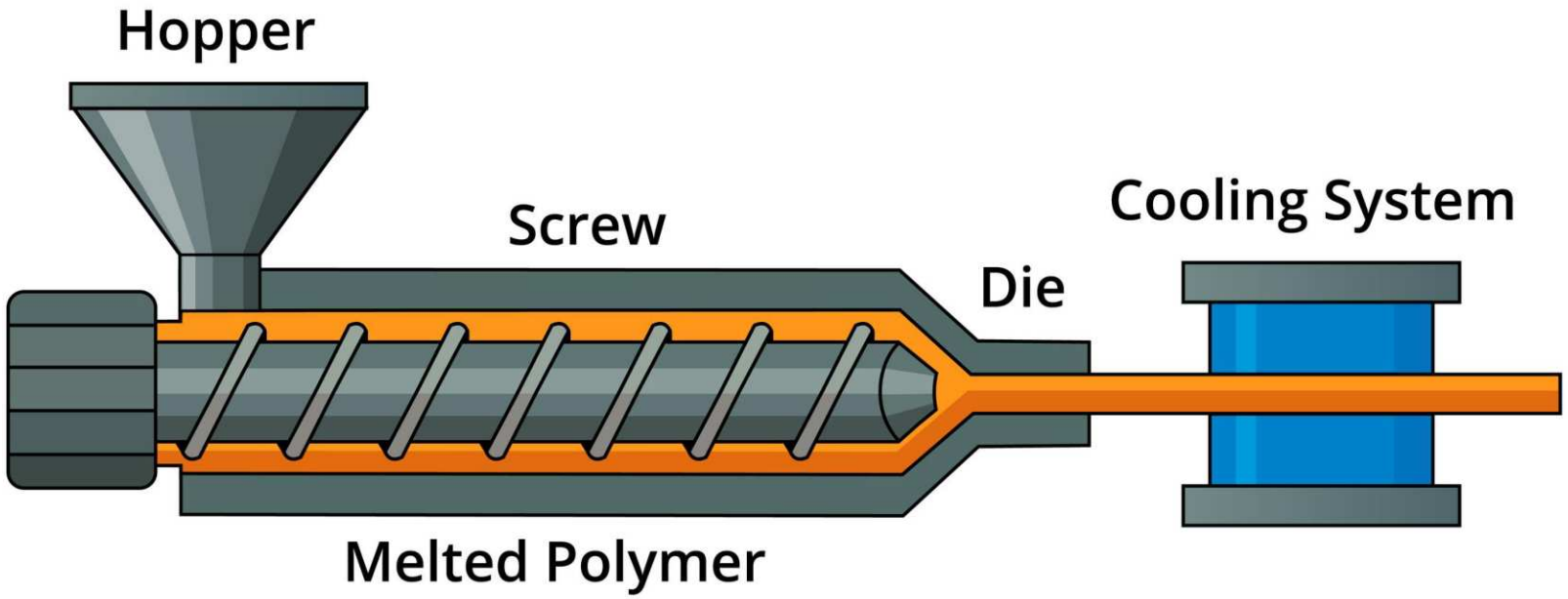


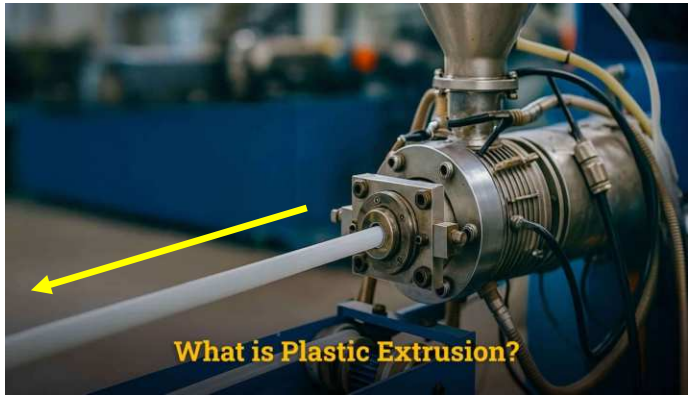
This is the **most common technique** for most plastics – it is very fast!



Polymer processing

Extrusion uses a screw to press the material through a small opening, where it solidifies with air cooling. This is like injection molding but without the mold.





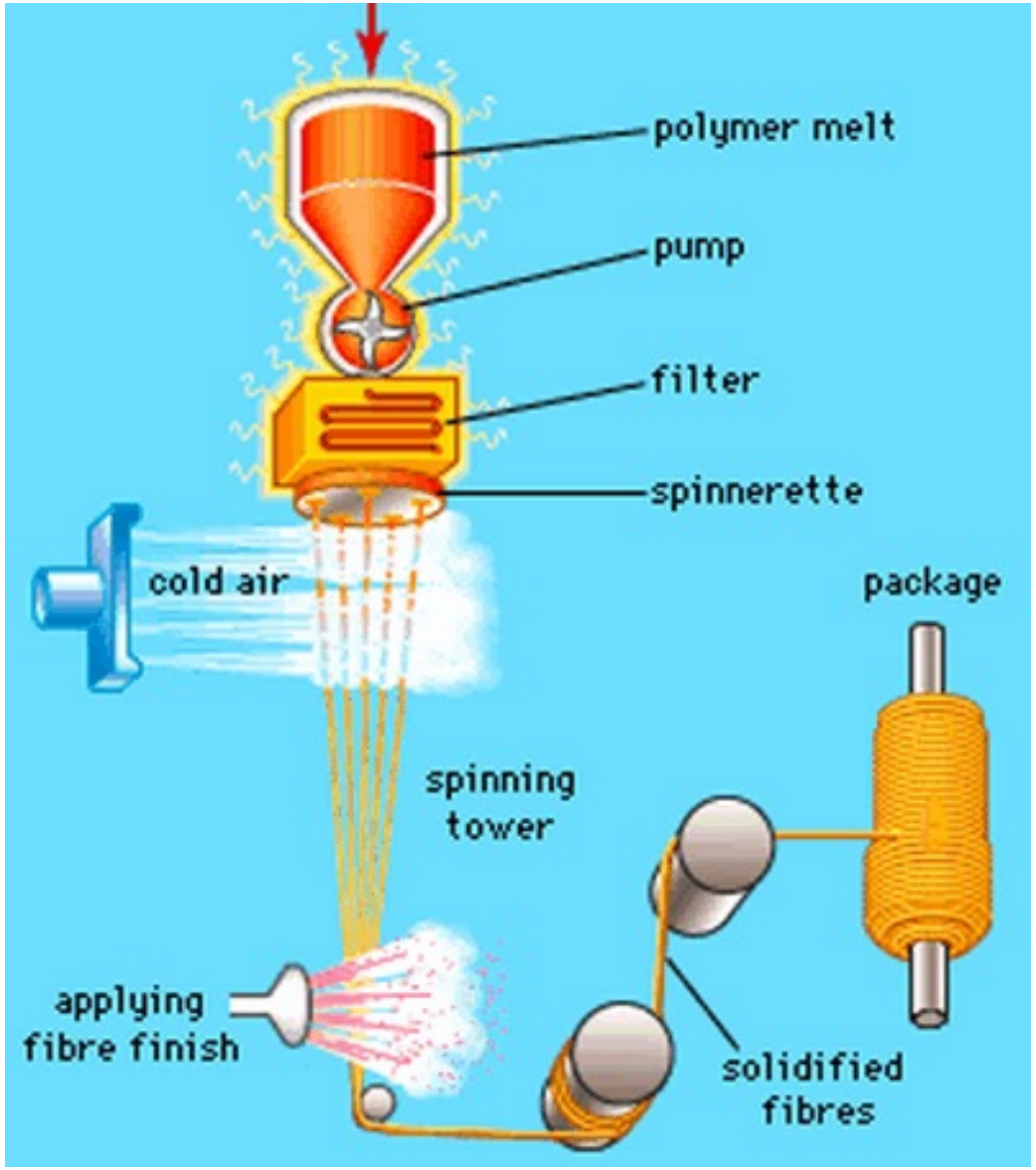


Useful for making rods, tubes, hoses, and filaments (fixed cross-section)

Polymer processing

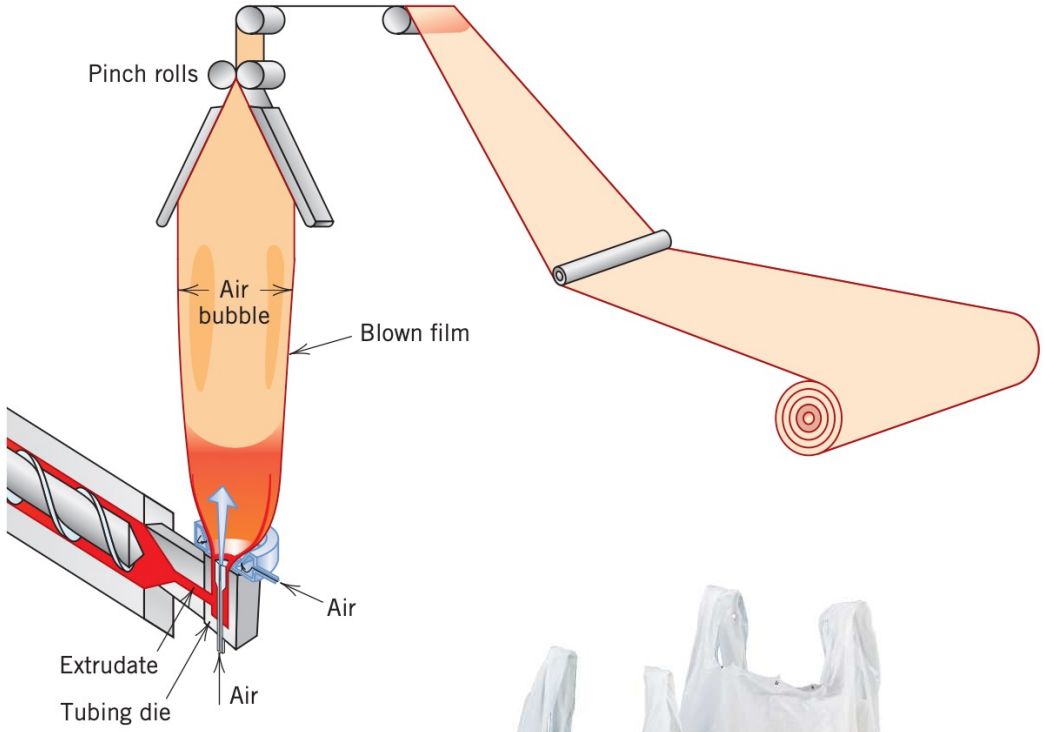
Melt spinning is used to make **fibers** that are used in clothing/textiles.





Polymer processing

Blown-film extrusion is used to make **films** (*e.g.*, for plastic bags)









Questions on processing methods?

Things to know from today

- Viscoelasticity of polymers
- Temperature and strain dependence
- Glass transition temperature