

Chapters 16

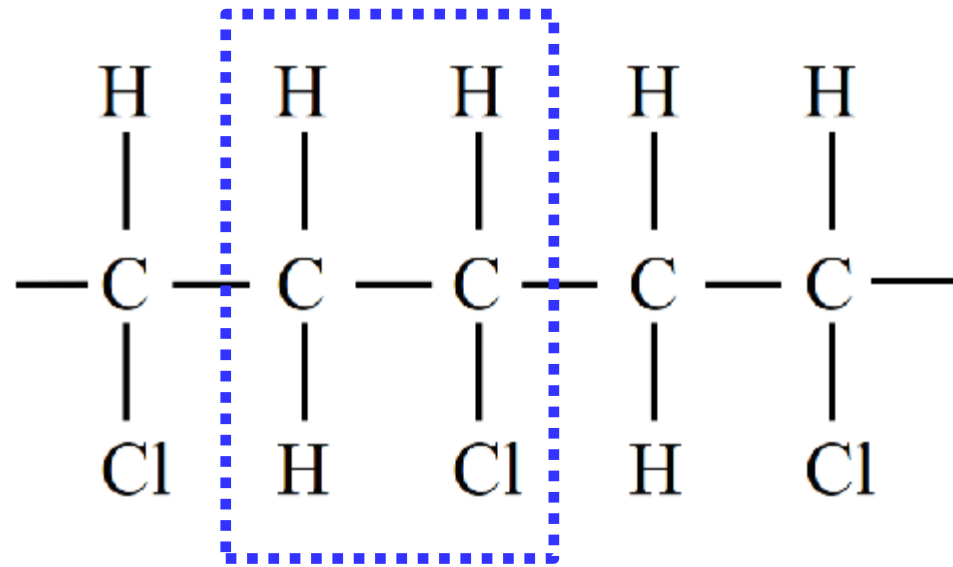
Polymers

Dr. Zhe Cheng

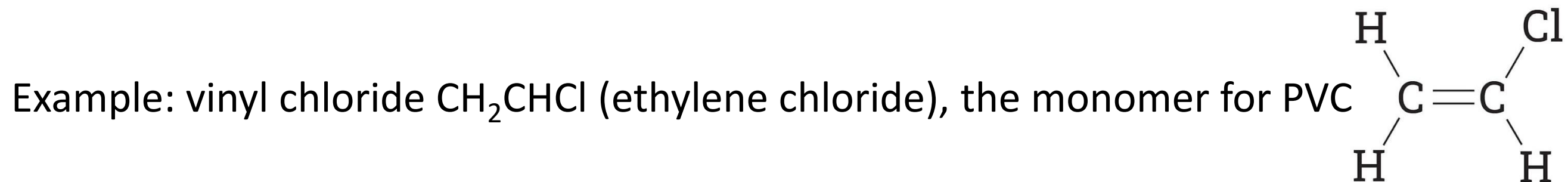
Polymer & Monomer

- Substance of very **large molecules consisting of many repeating units**, most often **organic** based on C as well as other elements such as H, O, and S.
i.e., **poly + mer**

Example: polyvinyl chloride (PVC)

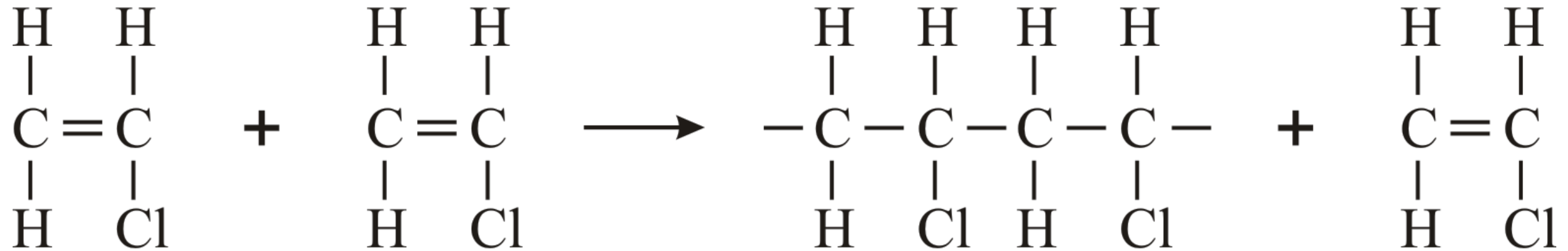


- **Monomer:** (a single) small molecule from which a polymer is formed

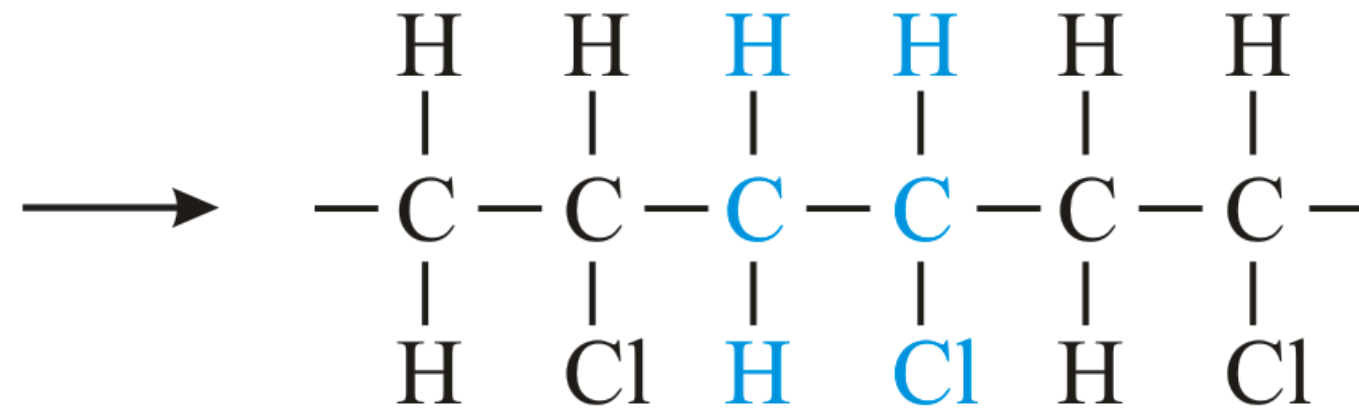


From Monomer to Polymer - Polymerization Reaction

From vinyl chloride (CH_2CHCl) to PVC



vinyl chloride monomers



poly(vinyl chloride)

Natural Polymers

➤ Many natural polymers have been used for long

Wood



<https://www.kretzlumber.com/cherry-logs/>

Cotton



<https://www.agriharvest.tw/archives/95536>

Wool



<https://westwoodhart.com/blogs/westwood-hart/how-sheeps-wool-is-transformed-into-high-quality-fabrics-for-custom-suits>

Silk



<https://www.ahi-intl.farm/post/silkworm-farming>

Leather



<https://www.myfurnituremarket.com/hides-and-horns-brazilian-leather-hides/hh015-p20456/iteminformation.aspx>



<https://leatherhidestore.com/rich-cognac-leather-hide.html>

Rubber

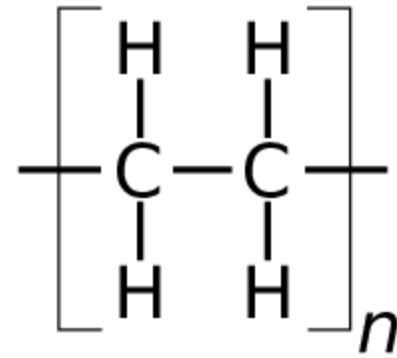


<https://erca.cefic.org/how-is-rubber-made/>
<https://www.tirerack.com/content/tirerack/desktop/en/homepage.html>

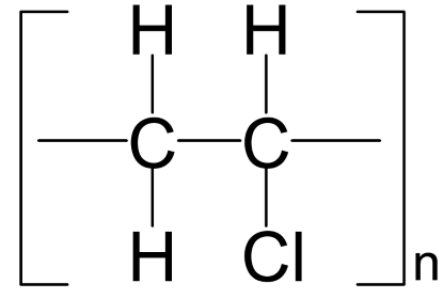


Common Synthetic Polymers (1)

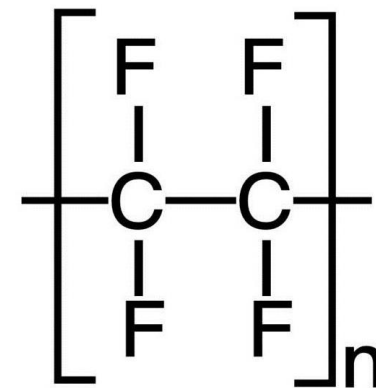
Polyethylene (PE)



Poly vinyl chloride (PVC)

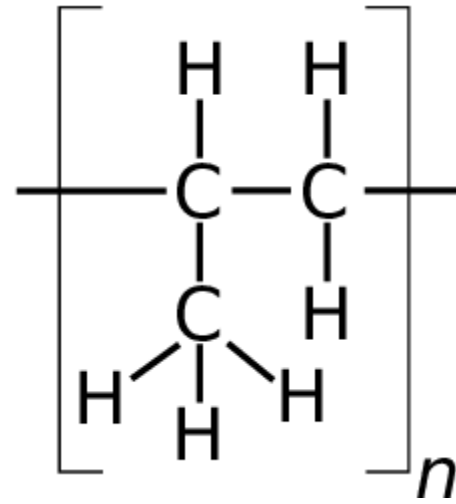


Poly tetrafluoroethylene (PTFE or Teflon®)

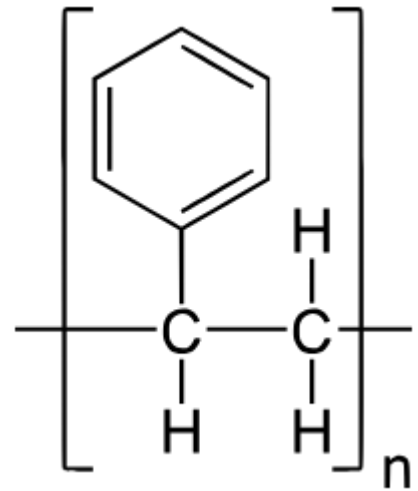


Common Synthetic Polymers (2)

Poly propylene (PP)

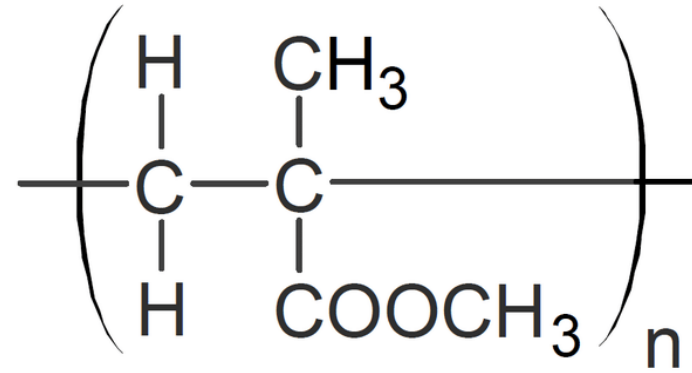


Poly styrene (PS)



Common Synthetic Polymers (3)

Poly methyl methacrylate (PMMA)



Nylon 6, 6

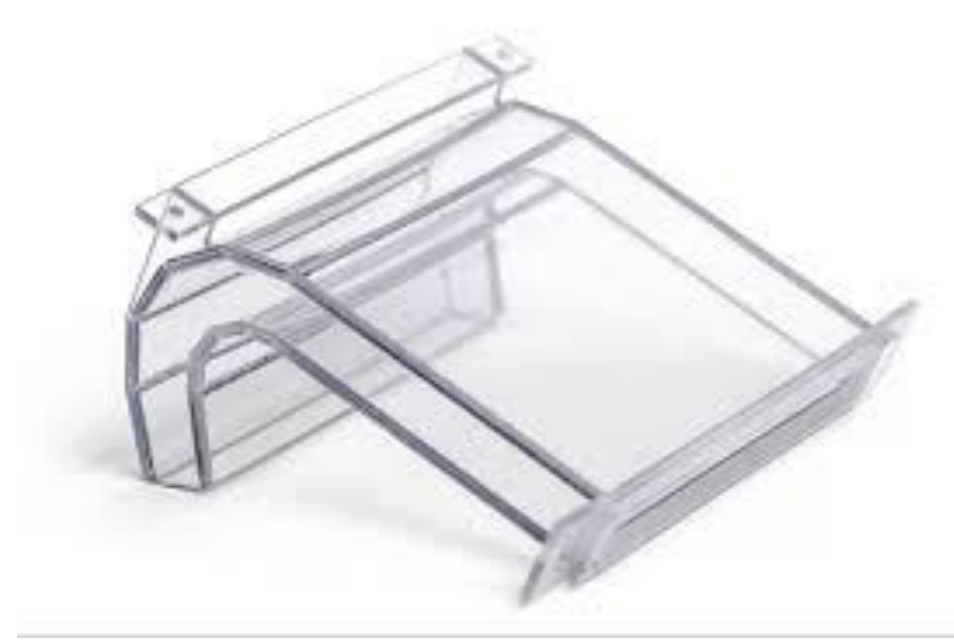


PET

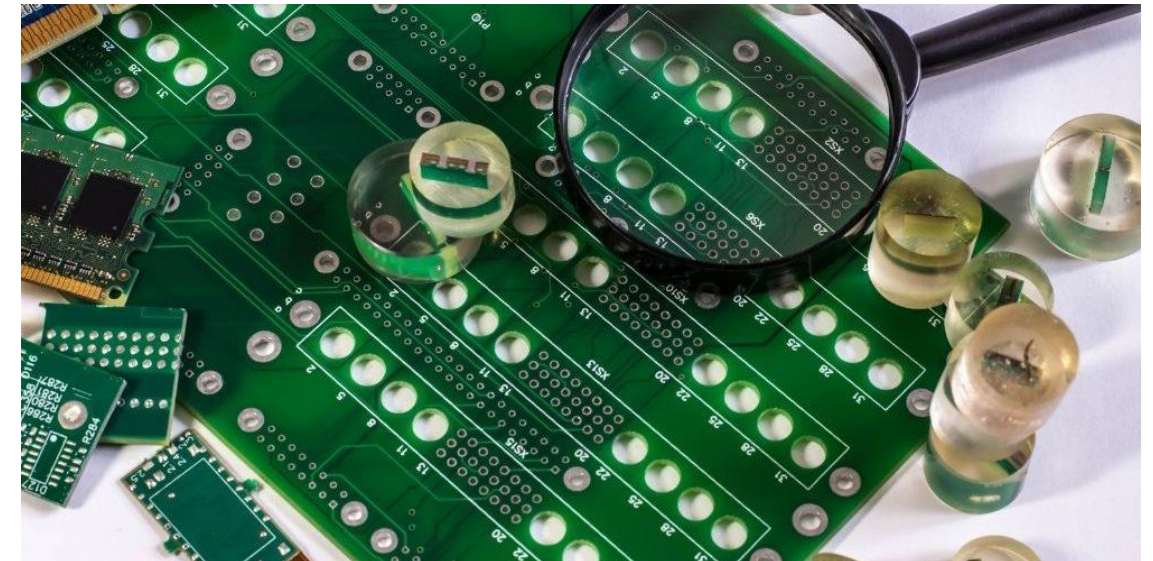


Common Synthetic Polymers (4)

Poly carbonate (PC)



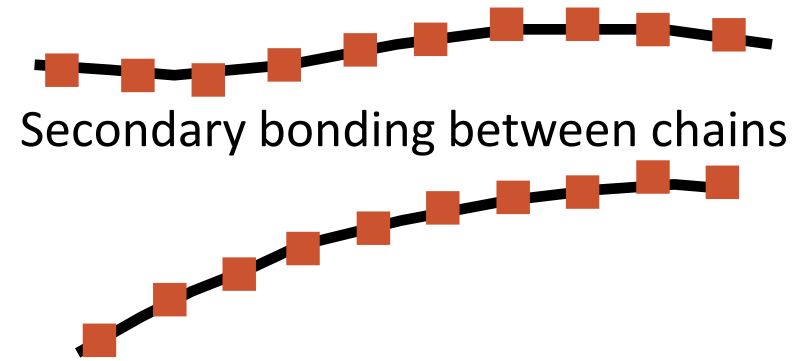
Phenol formaldehyde
(phenolic resin or Bakelite)



Molecular Structures for Polymers

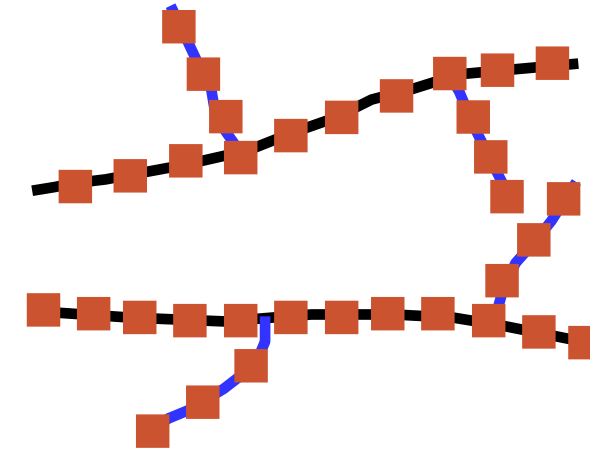
Linear

e.g., PE, PVC, PMMA, PTFE



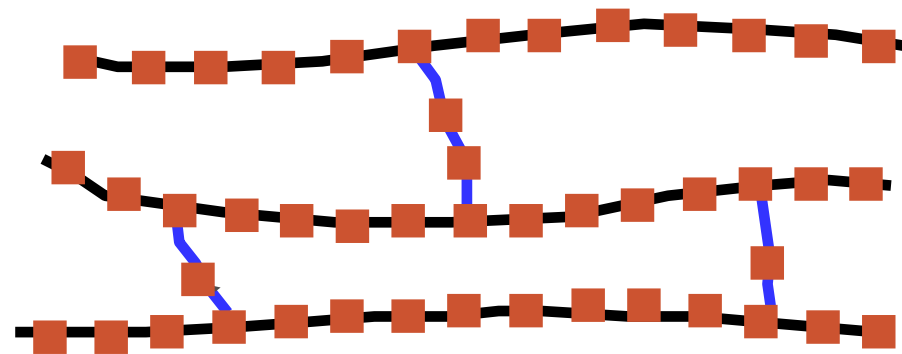
Branched

e.g., LDPE



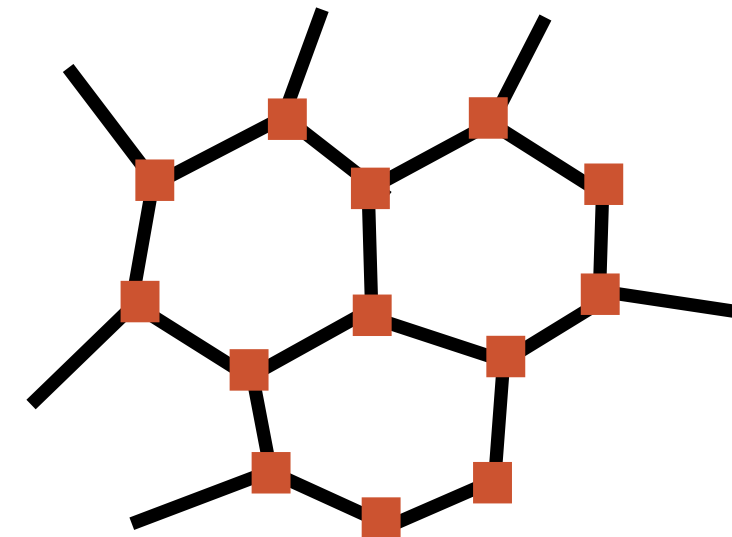
Cross-linked

e.g., Cross-linked rubber



Networked

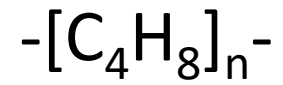
e.g., Epoxy, phenolic resin



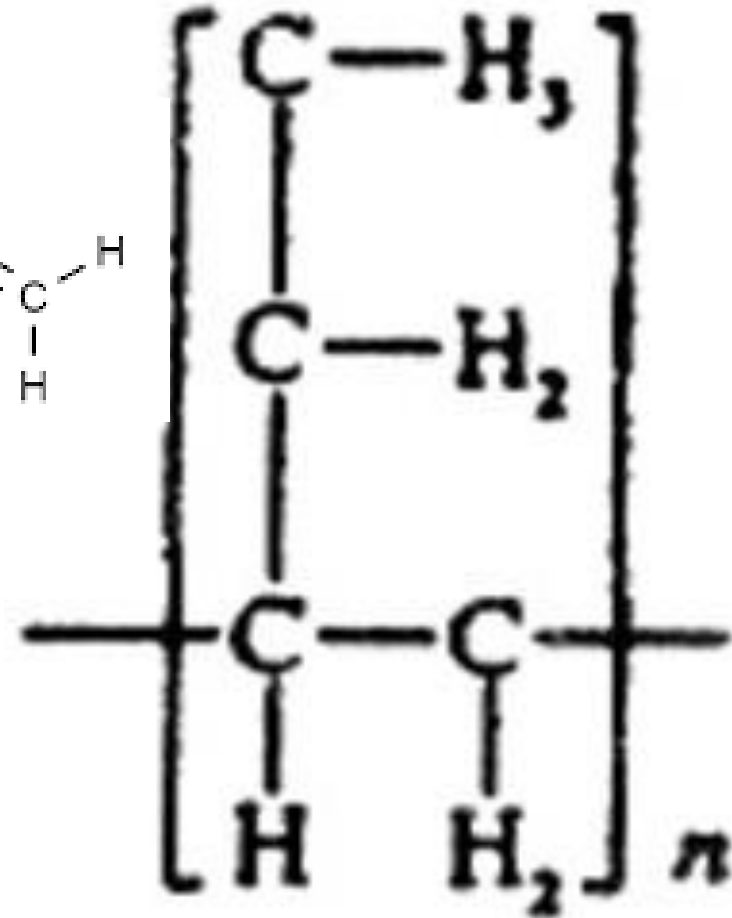
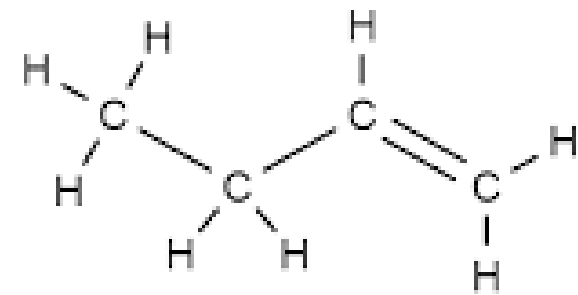
Complexity in Polymer Structure (1)

- Geometric arrangement of side groups can vary due to symmetry of monomer

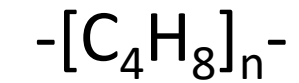
Poly-butylene



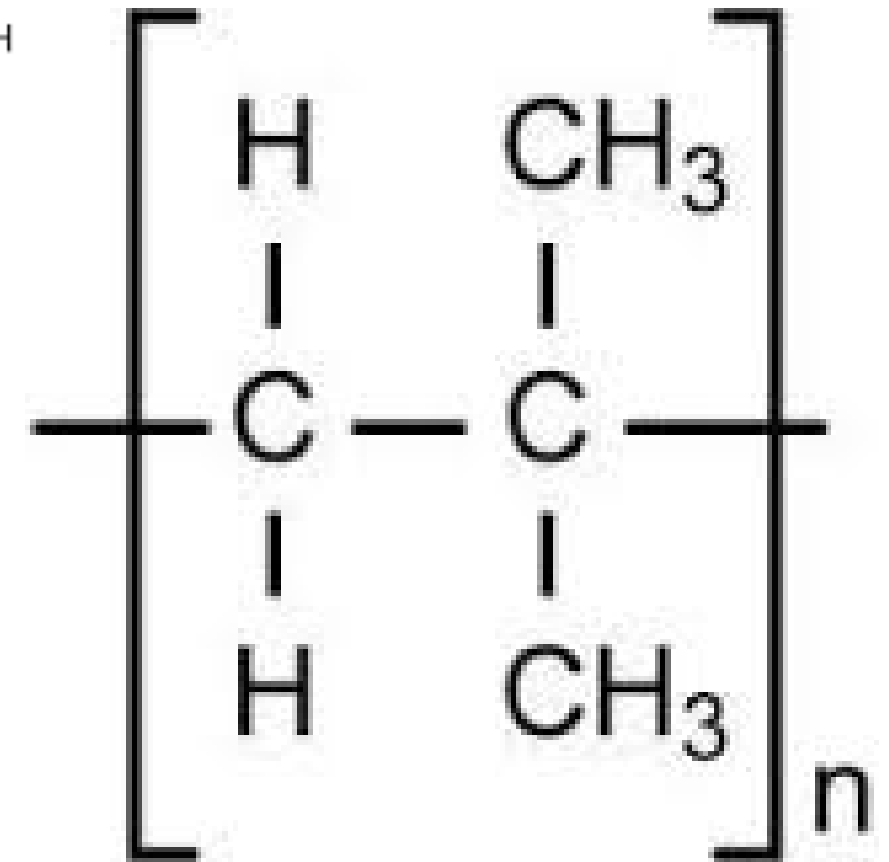
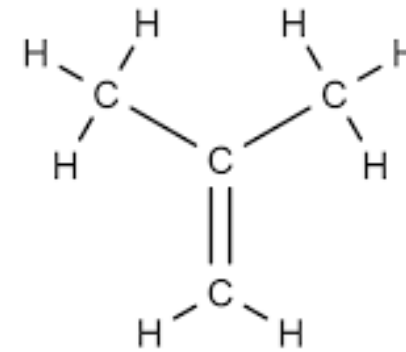
n-butylene



Poly-**iso**-butylene



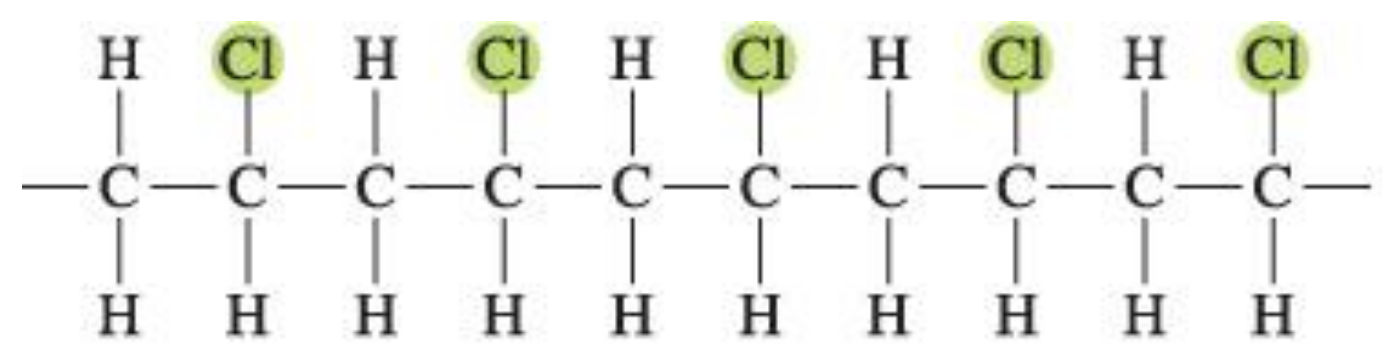
iso-butylene



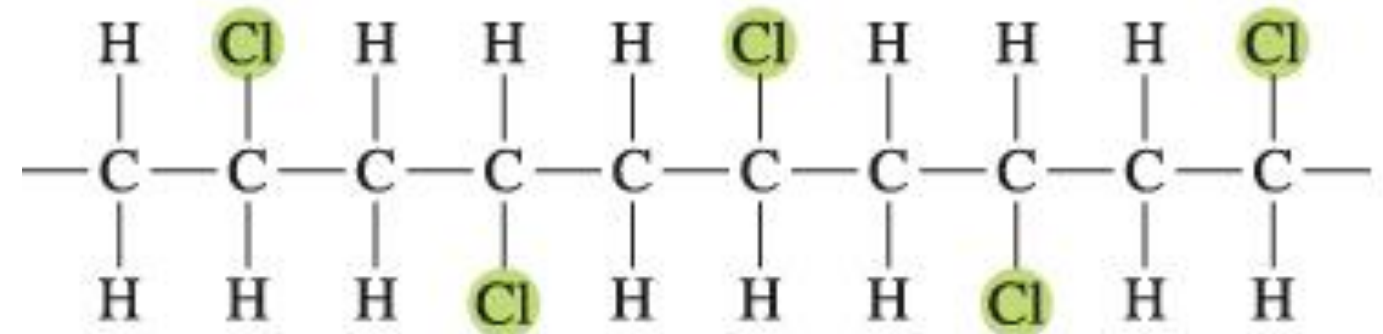
Complexity in Polymer Structure (2)

➤ Geometric arrangement of side groups can vary due to placement of side groups

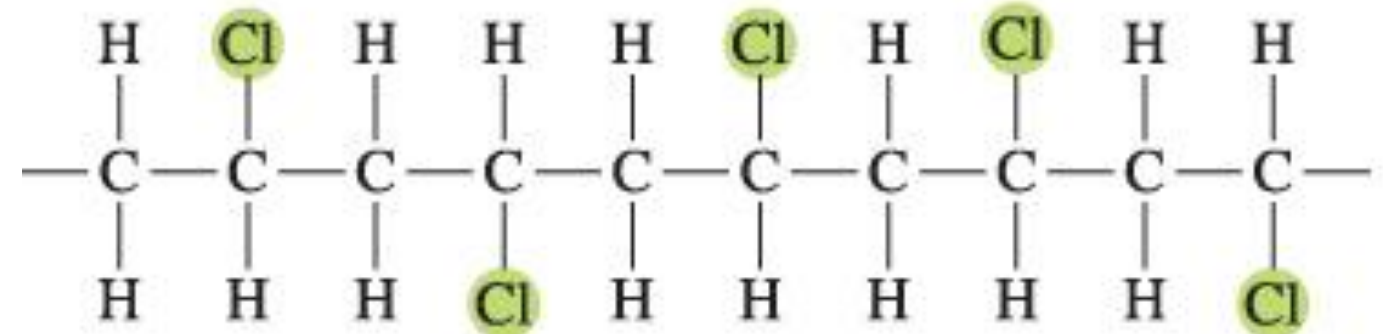
➤ Example:
Placement of -Cl group in PVC



Isotactic



Syndiotactic

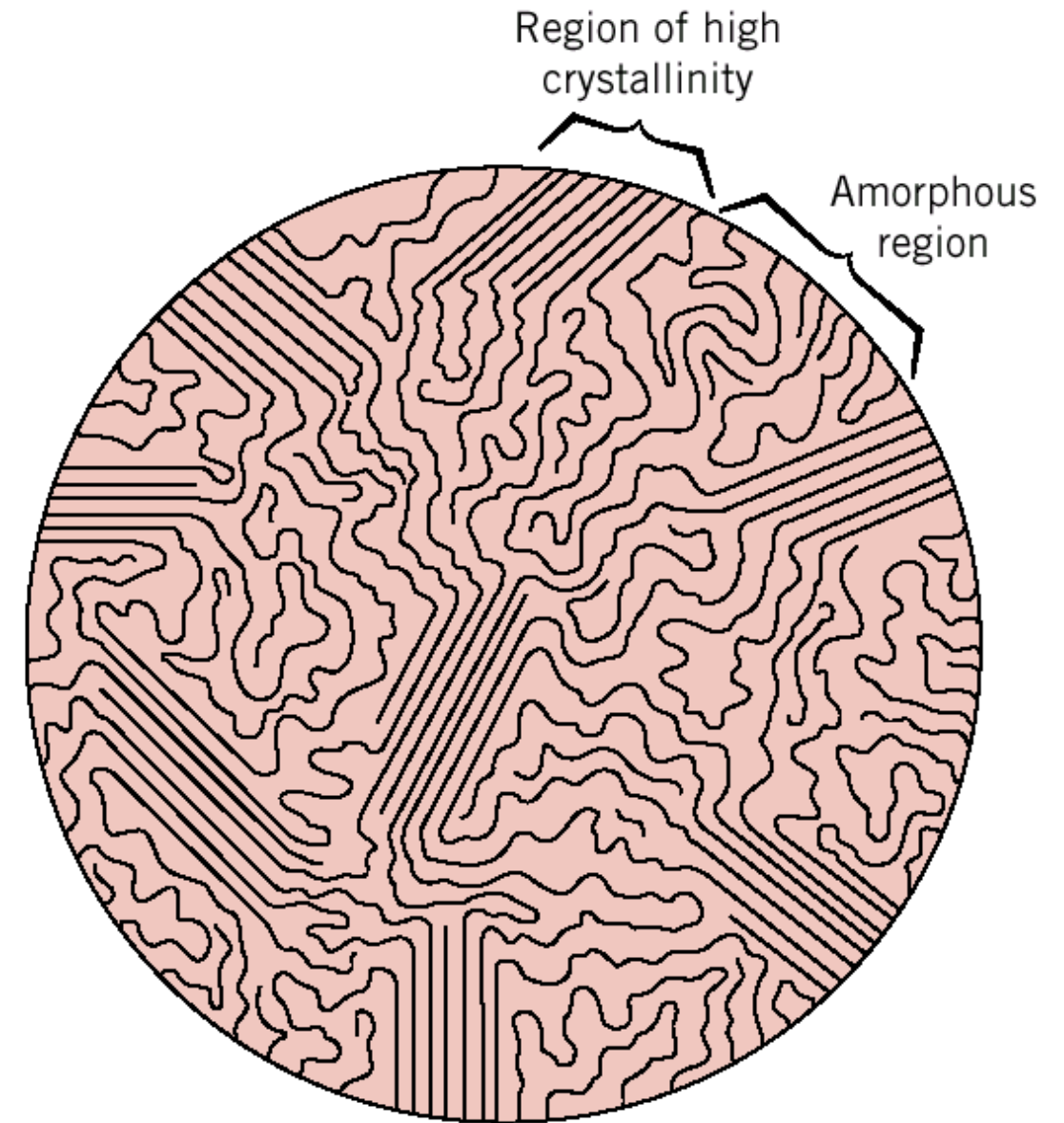
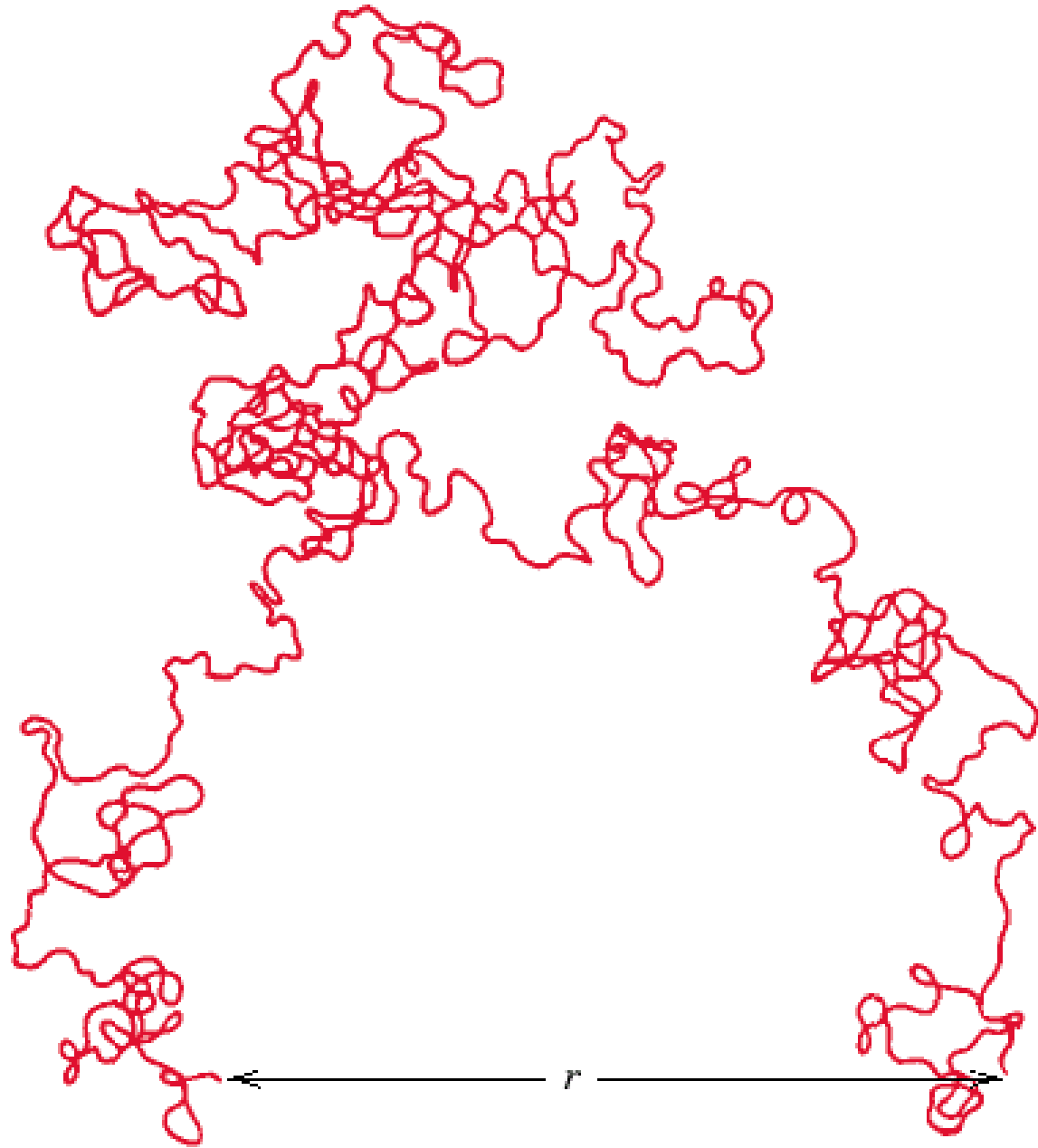


Atactic

Complexity in Polymer Structure (3)

➤ Messy chain structure

➤ Often mixture of crystalline regions and amorphous regions



Complexity in Molecular Weight for Polymers

Molecular weight or M : Mass of a mole of a polymer molecules

Low M 

High M 

Average molecular weight for polymers

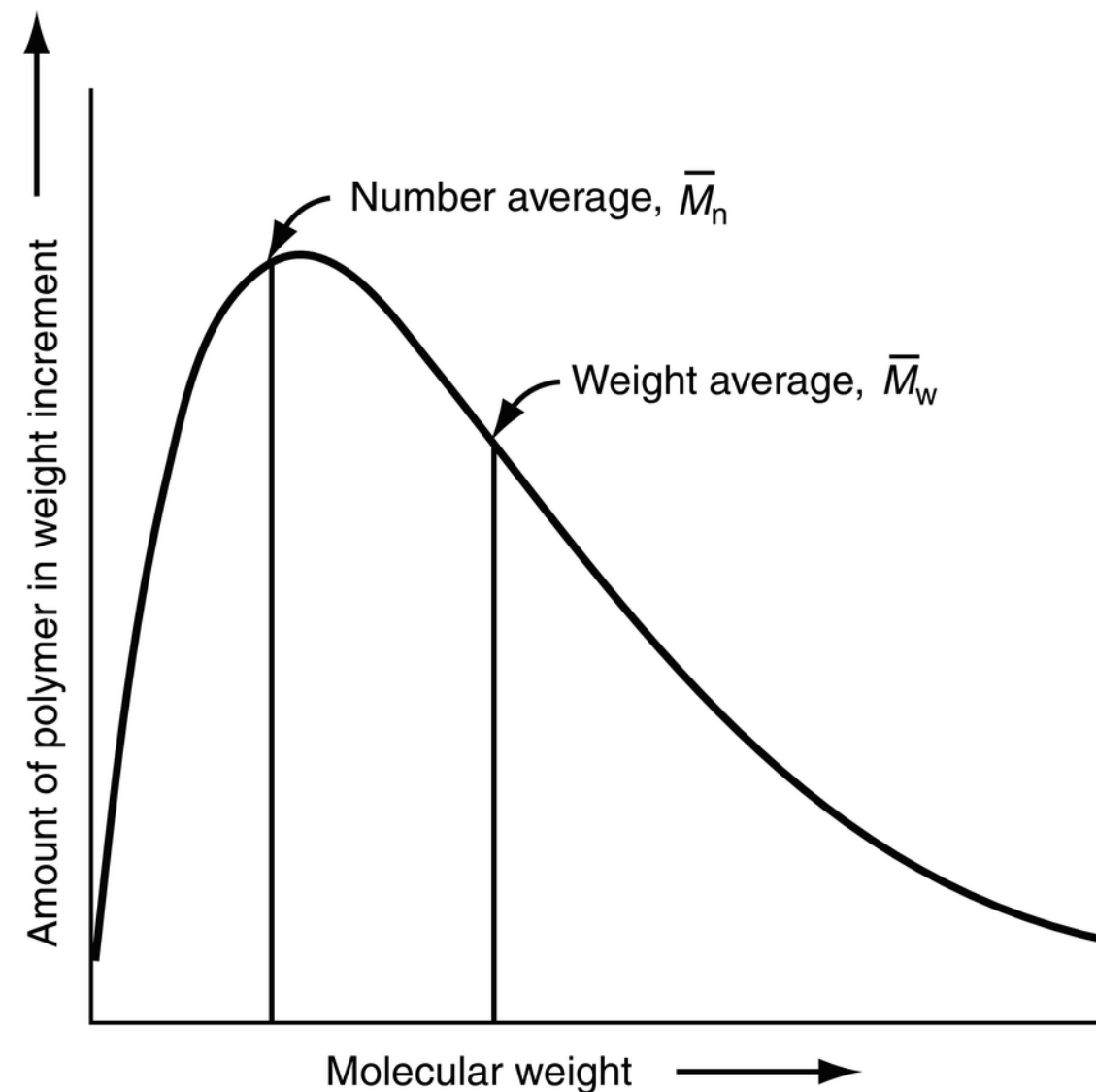
- The “same” polymer often has varying chain length, meaning there is a distribution of molecular weights
- Need to define “average” molecular weight, by number or weight or volume, etc.

e.g., number “averaged”
molecular weight:

$$\bar{M}_n = \sum x_i M_i$$

M_i Mass for chains in the i th range

x_i Number fraction of chains in the i th range



Thermoplastics vs Thermosets vs. Elastomers

➤ Thermoplastics

Polymers that softens and change shape plastically when heated

- Can be reversibly reheated and recycled
- Mostly straight or simple branch-like structures
- Examples: polyethylene (PE), poly propylene (PP)



➤ Thermosets

Polymers that, after one-time heating for shaping purpose, go through extensive cross-linking reactions within it and become “set” in shape

- Cannot be re-shaped by heating and recycled – degradation would occur
- Examples: phenolic resin, polyurethane



➤ Elastomers

Polymers that, after one-time heating for shaping purpose, goes through some cross-linking reactions/thermoset reactions, allowing large elastic deformation

- Cannot be re-shaped by simple heating
- Examples: natural rubber



Melting & Glass Transition for (Thermoplastic) Polymers

- Polymers often contain both crystalline and glassy/amorphous regions
- Like inorganic glasses, 2 critical temperatures:

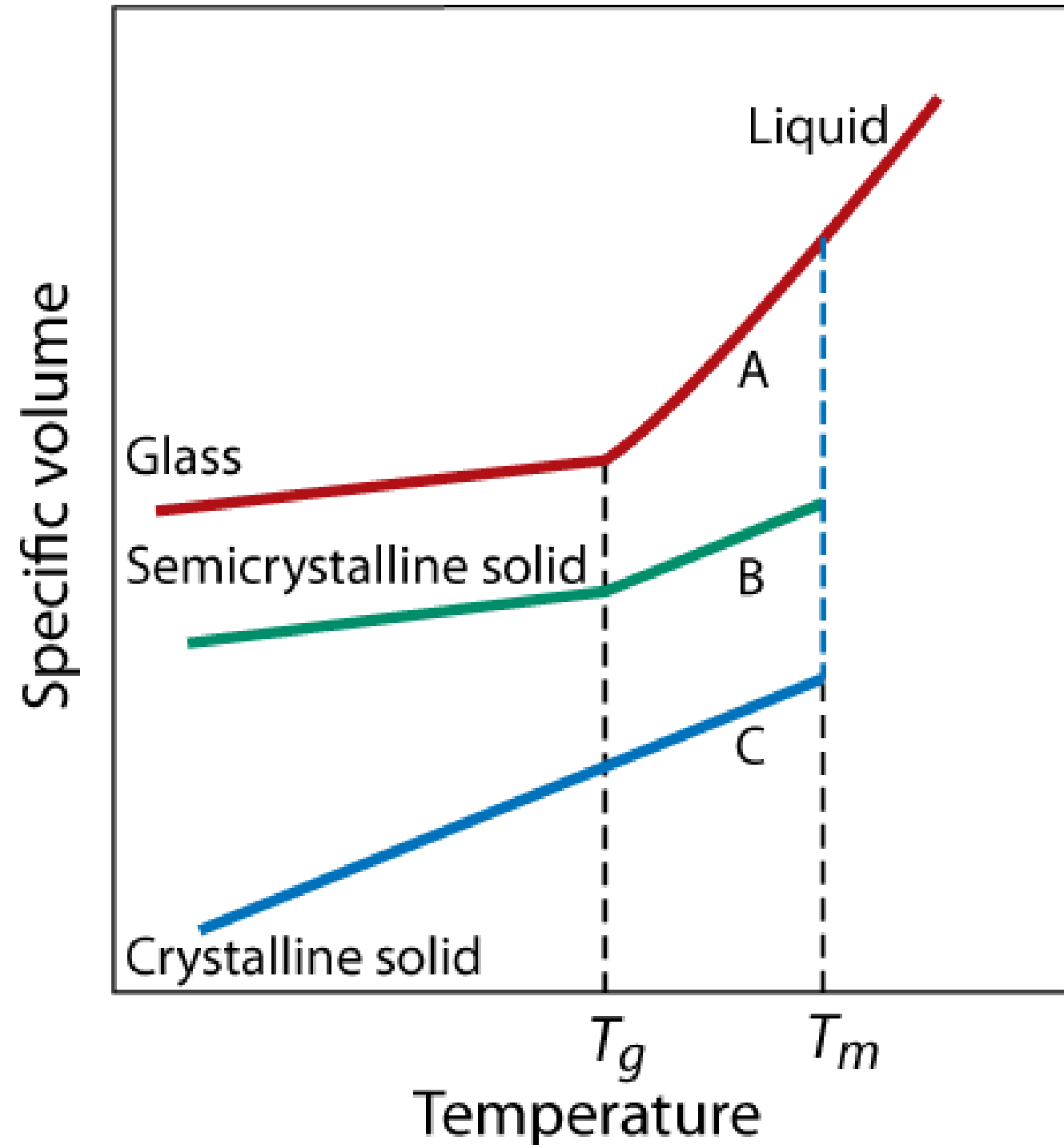
T_m Melting temperature

For crystalline material, the temperature at which phase transition between (free flowing) liquid and crystalline solid happen

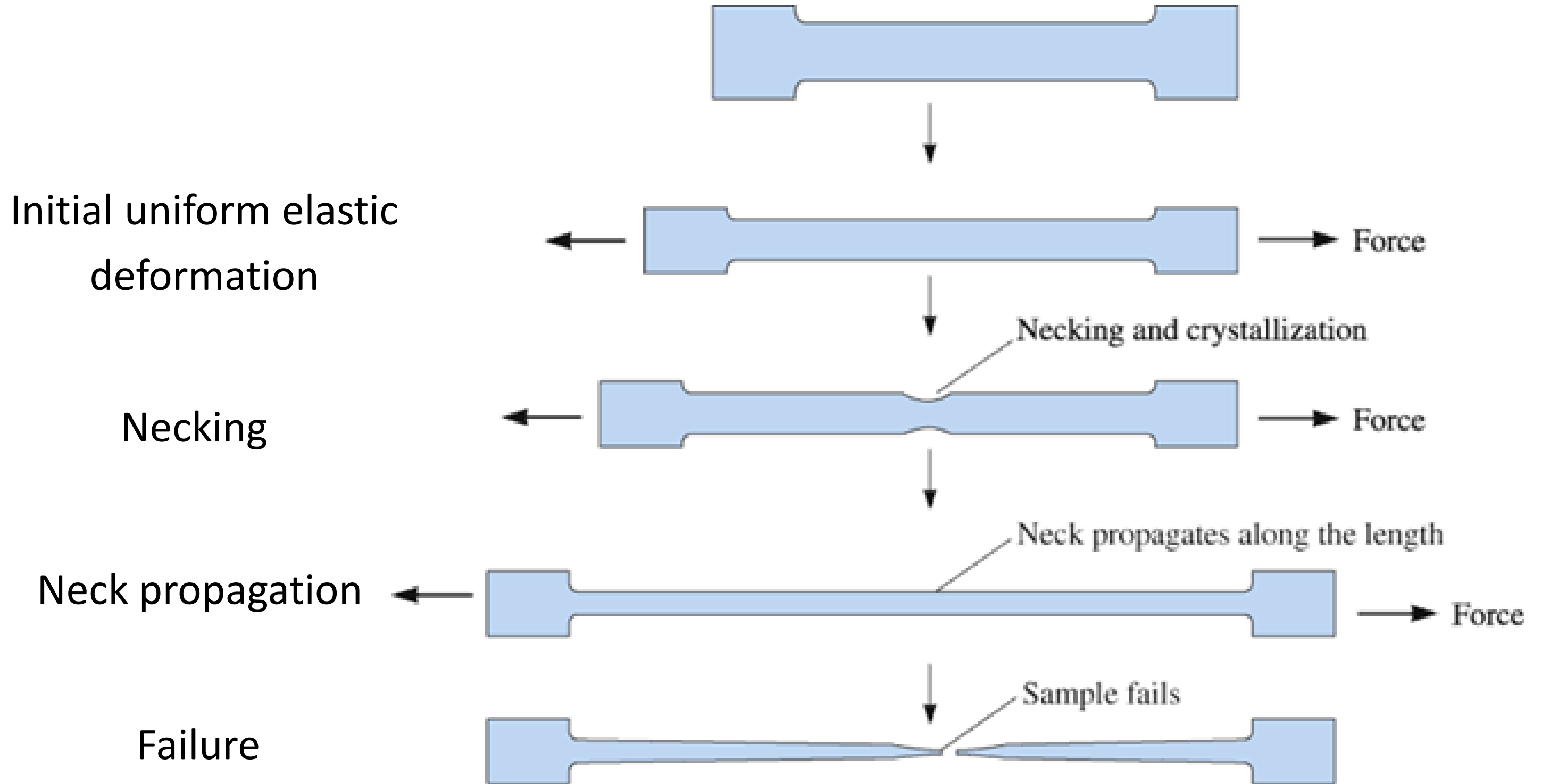
T_g Glass transition temperature

For glassy material (thermoplastic polymer here), the temperature at which the highly viscous, under-cooled liquid transforms to rigid amorphous solid, accompanied by sudden change in other physical/chemical properties

$$T_m > T_g$$



Sample Deformation in Tensile Test for Thermoplastics



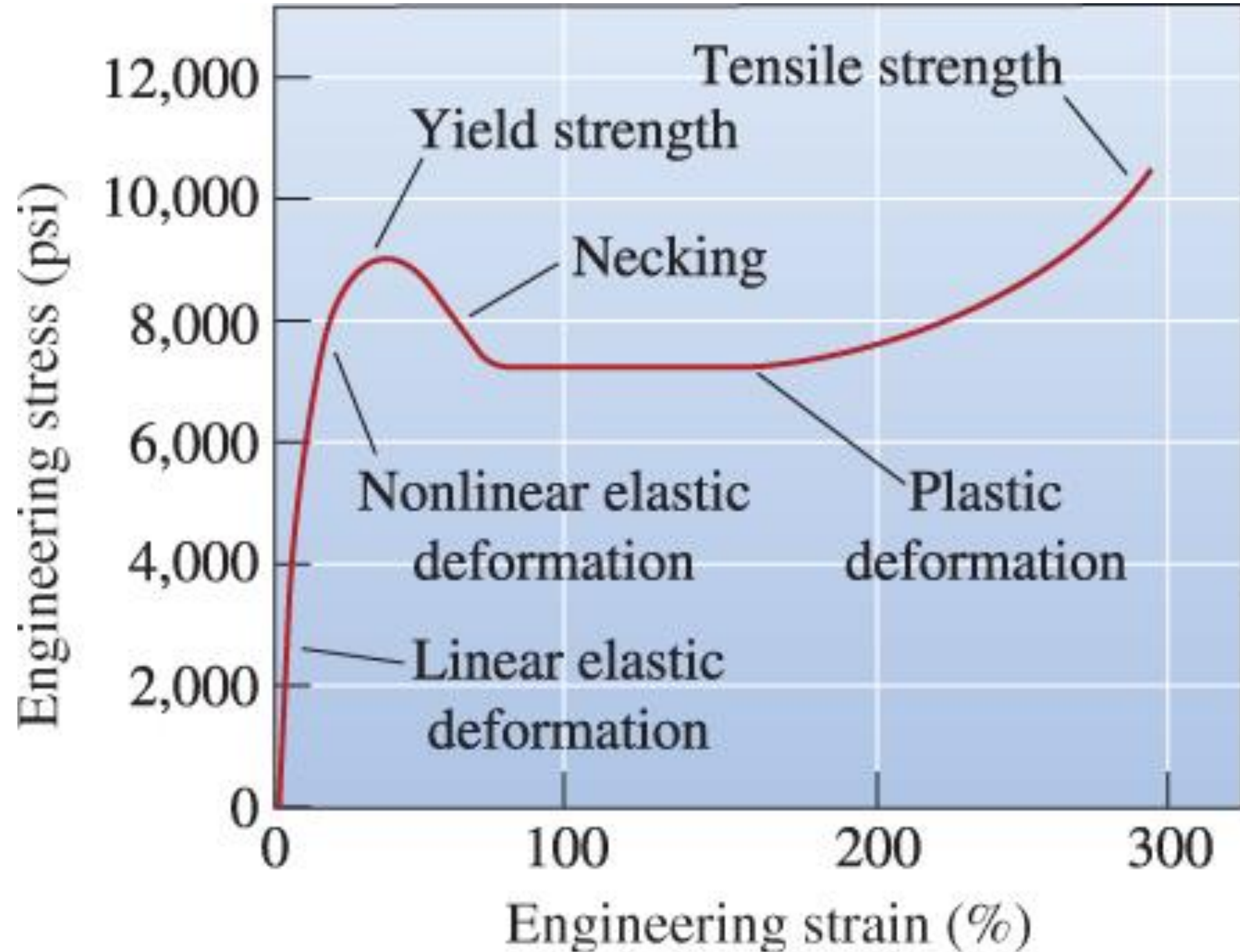
Tensile Curve for Thermoplastic at RT - Nylon 6, 6 Example

Initial viscoelastic behavior:

- Elastic part: polymer chain stretch/distort under applied stress → quick & full recovery
- Viscous flow part – entire polymer chains slide → slow, even incomplete, recovery

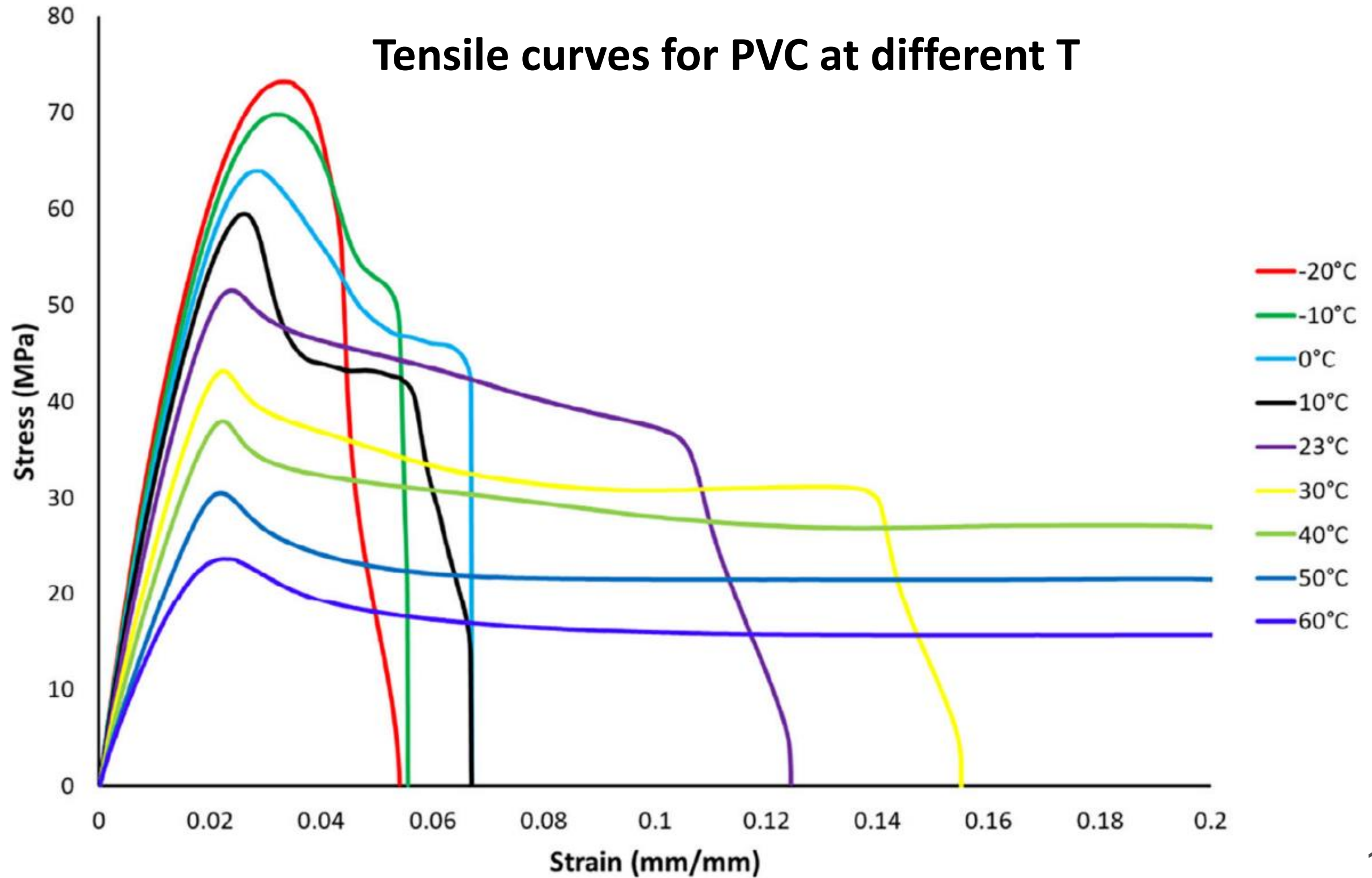
Subsequent plastic behavior:

- Polymer chains disentangle, slide, and align under stress → no recovery



Tensile Curve Changes w/ Temperature for Thermoplastics

Significant drop
in E , σ_y & σ_U ,
yet increase in
%EL as T
increases



Thermoplastic Polymer Mechanical Behavior - T Effect (1)

Temperature strongly impacts structure of polymers and, as a result, mechanical properties

➤ Above T_m

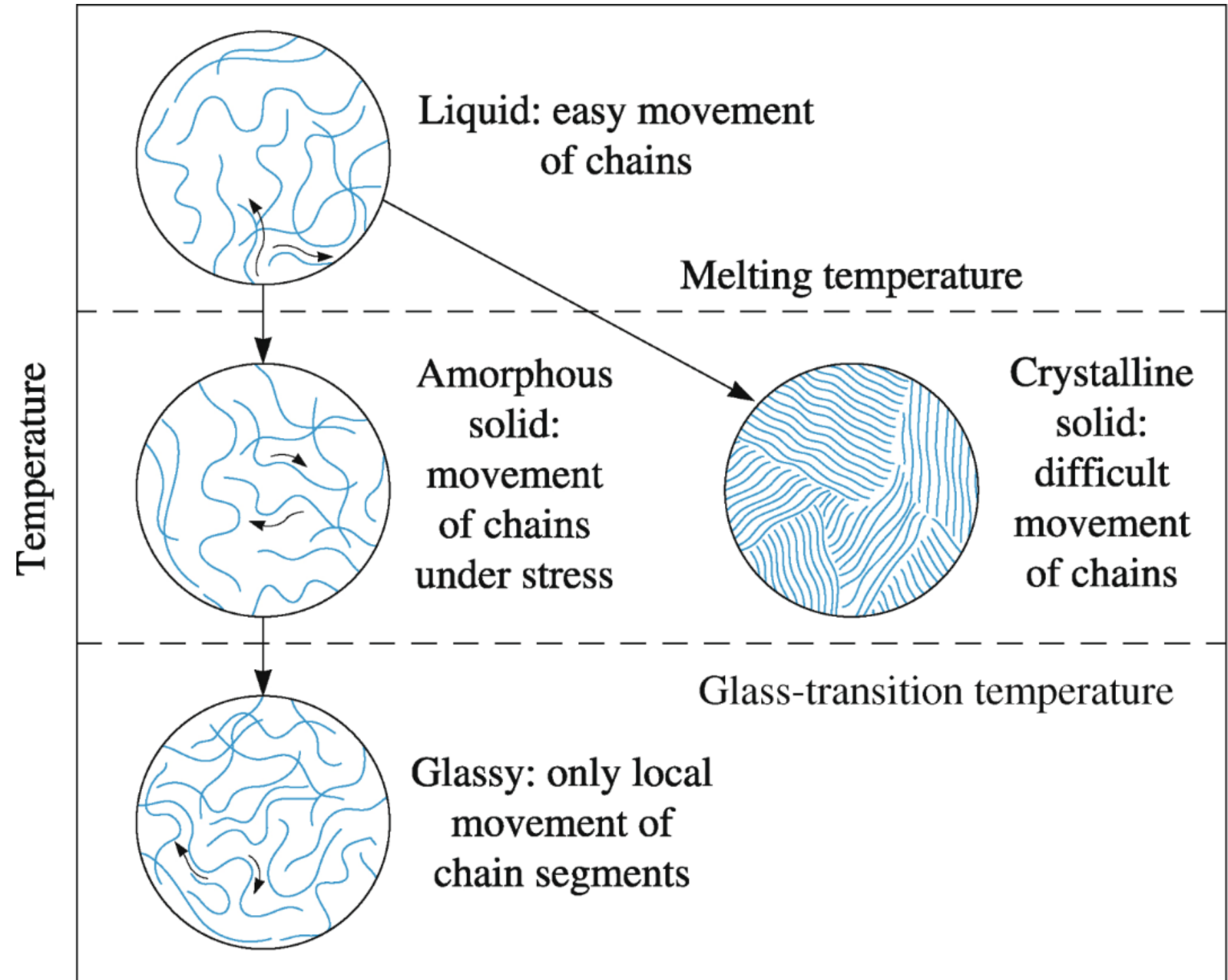
- Free flowing liquid

➤ Between T_m and T_g

- Amorphous regions - high viscosity (semi-) liquid that move under applied stress
- Crystalline regions

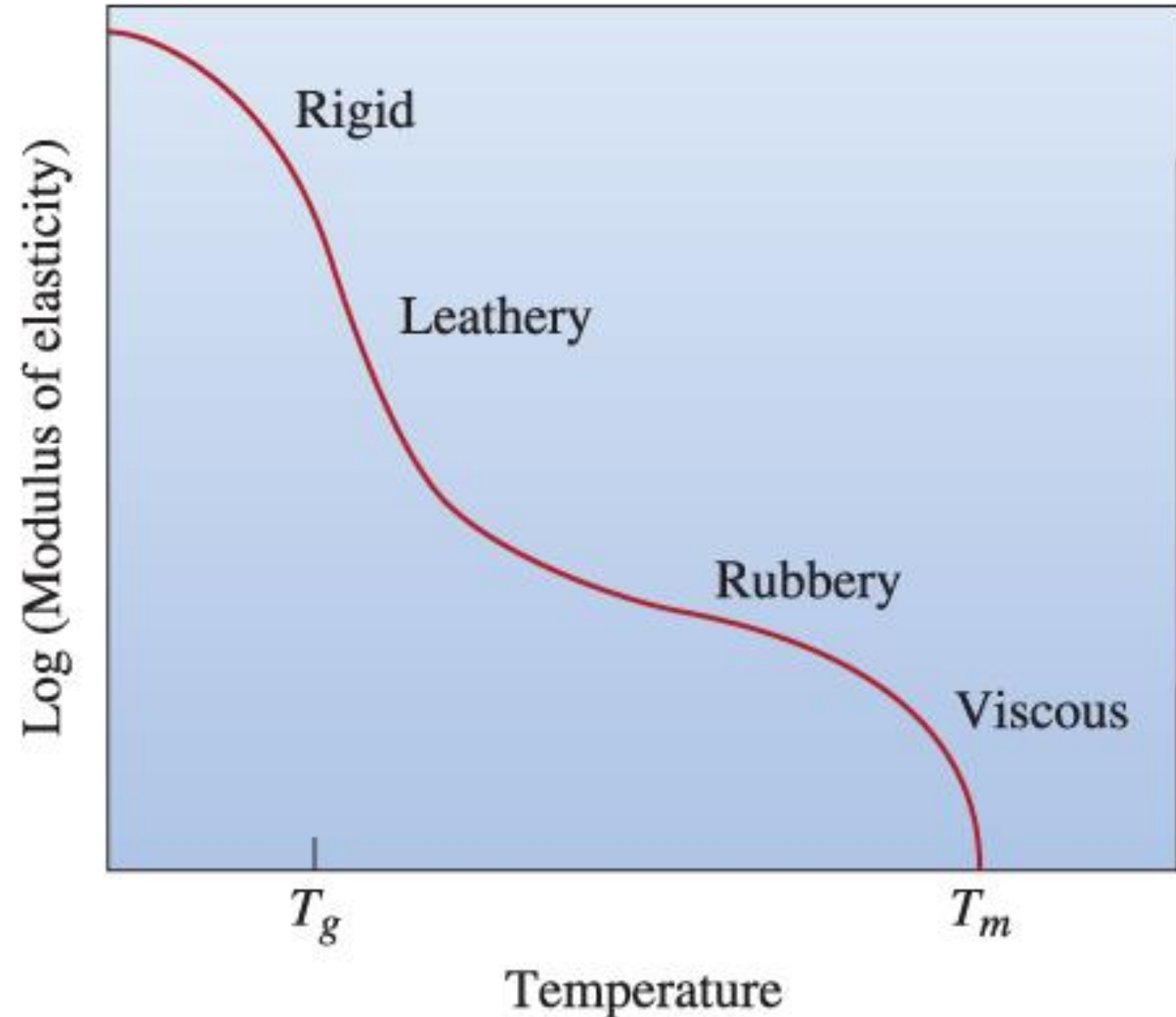
➤ Below T_g

- Amorphous regions become brittle and do not flow



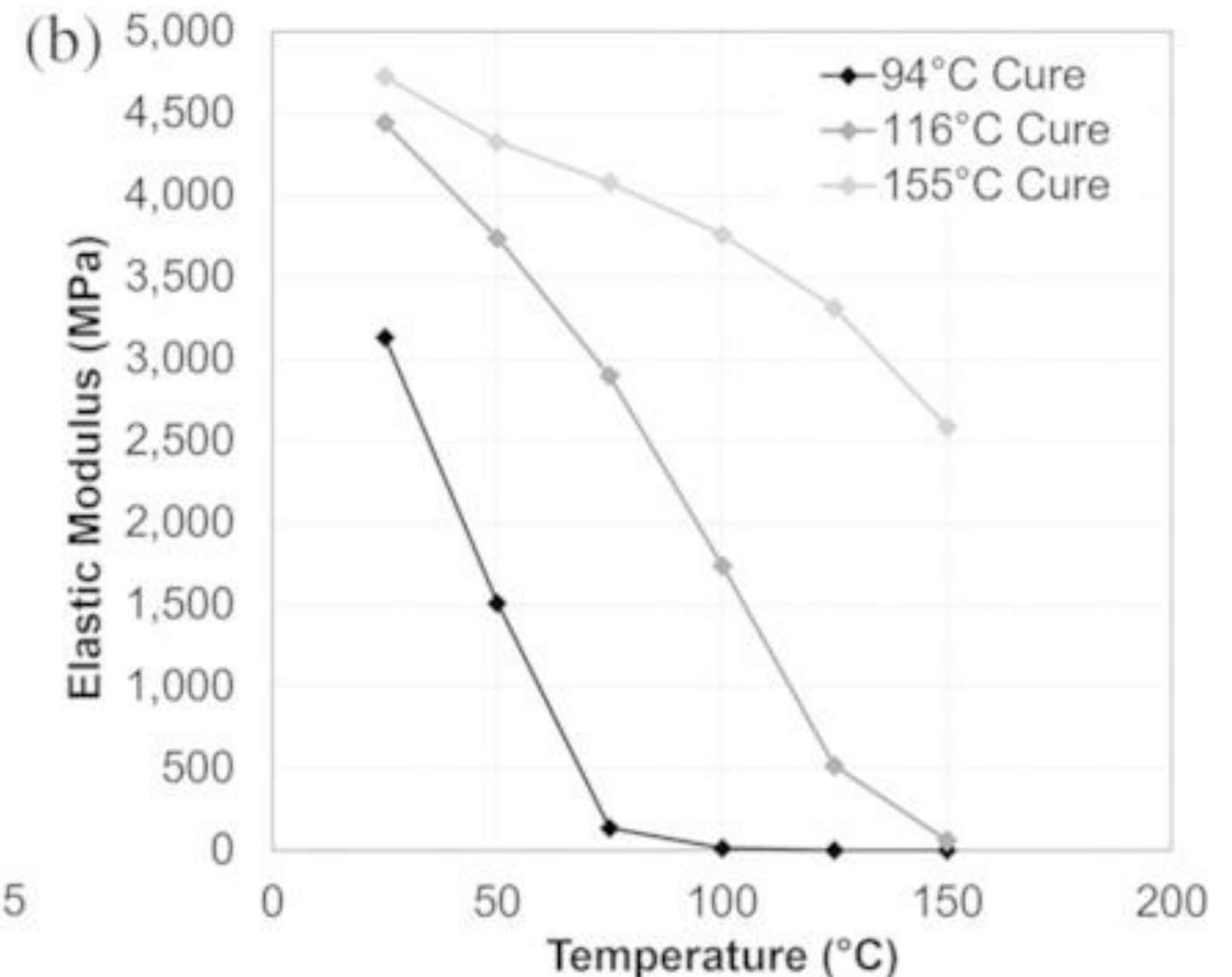
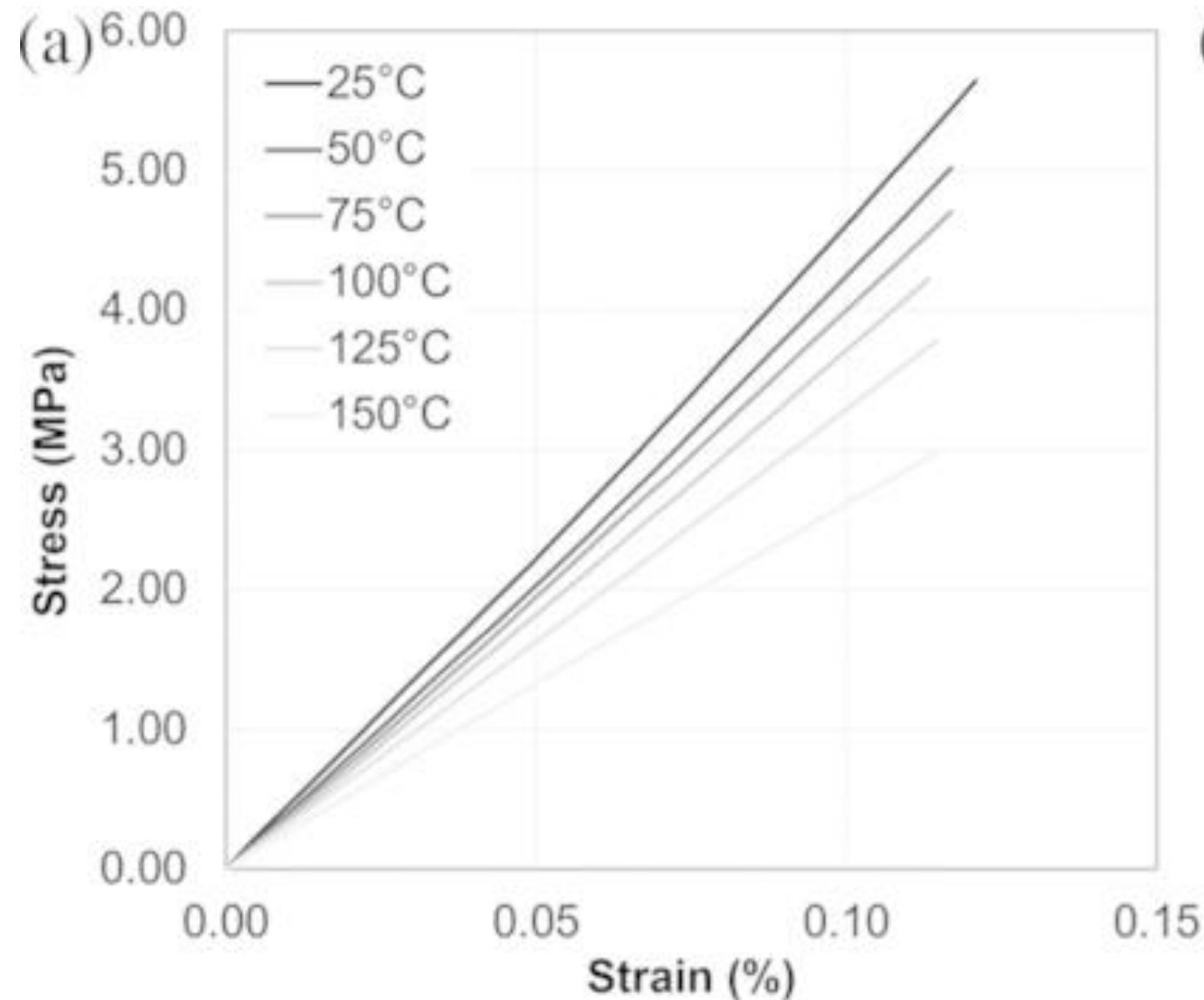
Thermoplastic Polymer Mechanical Behavior - T Effect (2)

- **Above T_m**
Free flowing liquid, $E \ll 10^{-3}$ MPa
- **Around T_m**
Amorphous regions flow as viscous liquid (like cold honey),
 $E \sim 10^{-3} - 10^{-2}$ MPa
- **Below T_m , but well above T_g**
Large motion between chains possible - highly elastic like rubber,
 $E \sim 10^{-1} - 1$ MPa
- **Slightly above and around T_g**
Small motion between chains possible - flexible yet tough like leather
 $E \sim 1 - 10^2$ MPa
- **Well below T_g**
Rigid brittle solid like glass, $E > \sim 10^3$ MPa



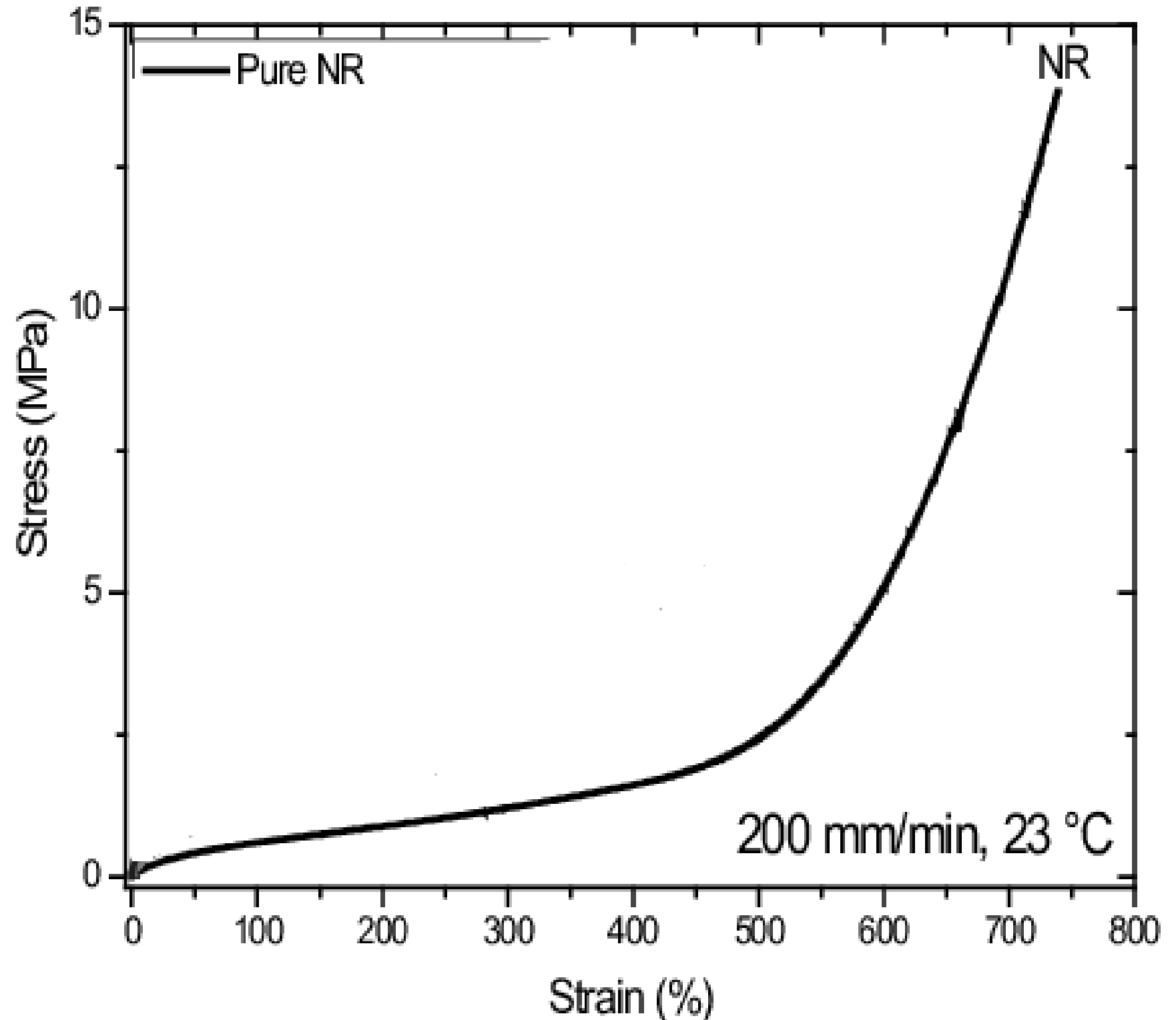
Mechanical Behavior for Thermoset Polymers

- Significant cross-linking (10 to 50%), forming networked structure for thermosets
- Examples: epoxies, polyester resin, **phenolic resin** (see figures below)
- Rigid & brittle; more cross-linking (higher cure T) → less plasticity; E still drops as $T \uparrow$



Mechanical Behavior for Elastomers (Rubbers)

- Very low modulus:
~1 MPa (0.001 GPa) for natural rubber
- May appear stronger due to stretching & alignment of polymer chains
- Examples: natural rubber (see right)



Thermal & Mechanical Properties of Some Polymers at RT

Polymer Material	Type	T_m (°C)	T_g (°C)	E (GPa)	σ_y (MPa)	σ_U (MPa)	%EL (%)	K_{1c} (MPa•m ^{0.5})
PE	thermoplastic	115	-100	0.2	10	15	400	0.4
PVC	thermoplastic	/	80	3.0	50	50	100	2.5
PTFE	thermoplastic	327	-60	0.6	/	25	400	3
PS	thermoplastic	/	100	3.2	35	40	30	1.2
PMMA	thermoplastic	/	105	3.2	60	70	5	1.7
Nylon 6, 6	thermoplastic	255	50	2.9	80	95	40	3.5
PET	thermoplastic	260	75	3.0	65	70	100	3.0
Phenolic resin	thermoset	/	/	7	/	45	1	0.7
Natural rubber	elastomer	65	-65	0.003	0	15	500	2

- Low density (~1 - 2 g/cc), due to light elements (C, H, O, etc.) and not very dense packing
- Low T_m & T_g , as well as low E , σ_y & σ_U due to weaker, secondary bonding
- Higher %EL (ductility) than metals due to stretching of & sliding between polymer chains
- Polymers w/ highly cross-linked structure show lower %EL, but still much higher than ceramics

Comparison of Tensile Curves for Some Common Polymers

Elastic modulus E :

Thermoset > Thermoplastic > Elastomer

Thermosets/highly cross-linked

PR Phenolic resin

Thermoplastics

PMMA Polymethylmethacrylate

PA6 Polyamide (Nylon 6)

ABS Acrylonitrile Butadiene Styrene

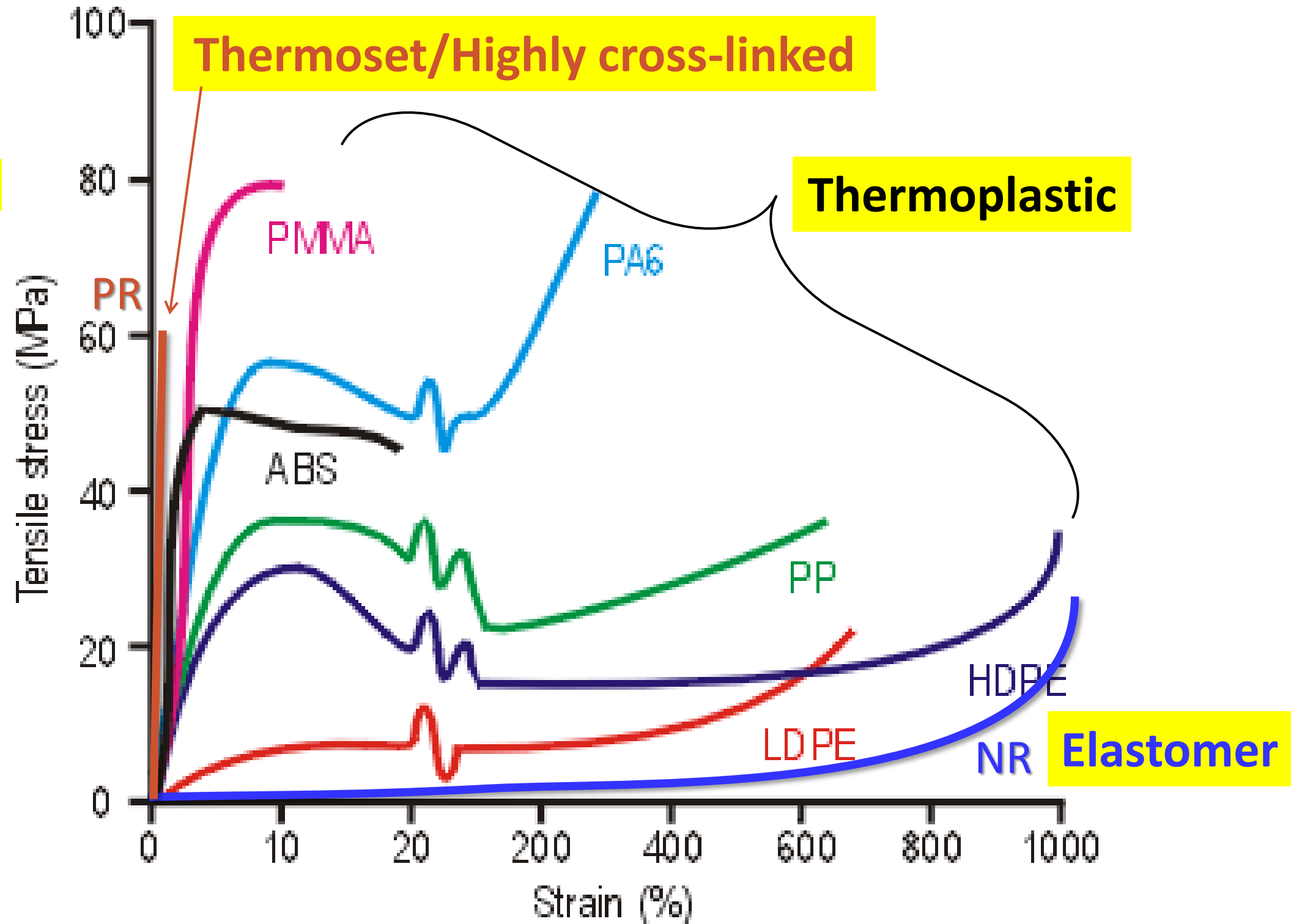
PP Polypropylene

HDPE High density polyethylene

LDPE Low density polyethylene

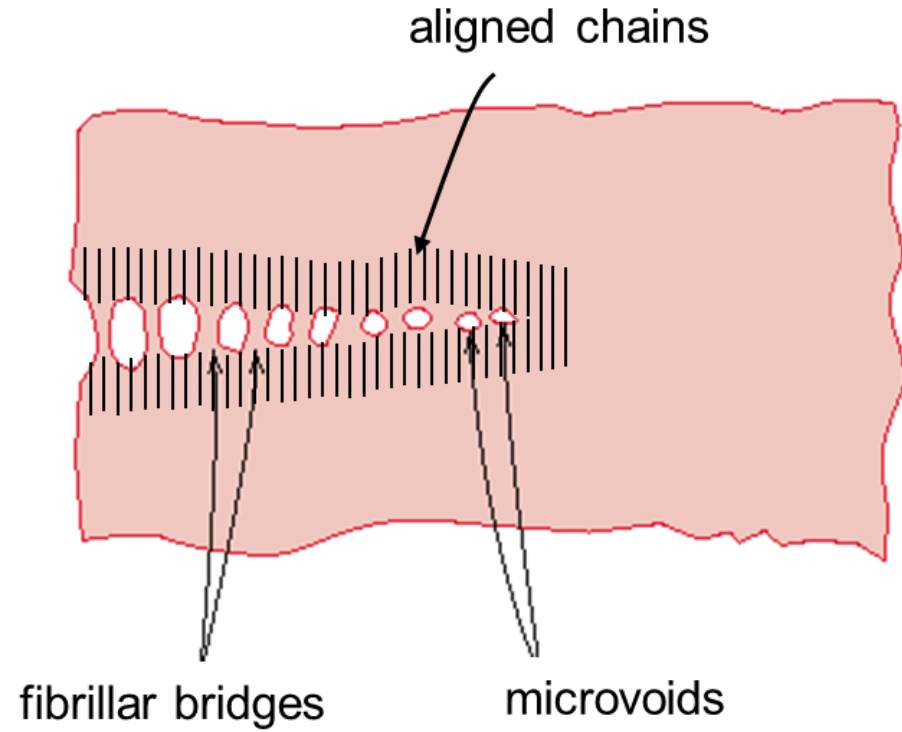
Elastomer

NR Natural rubber

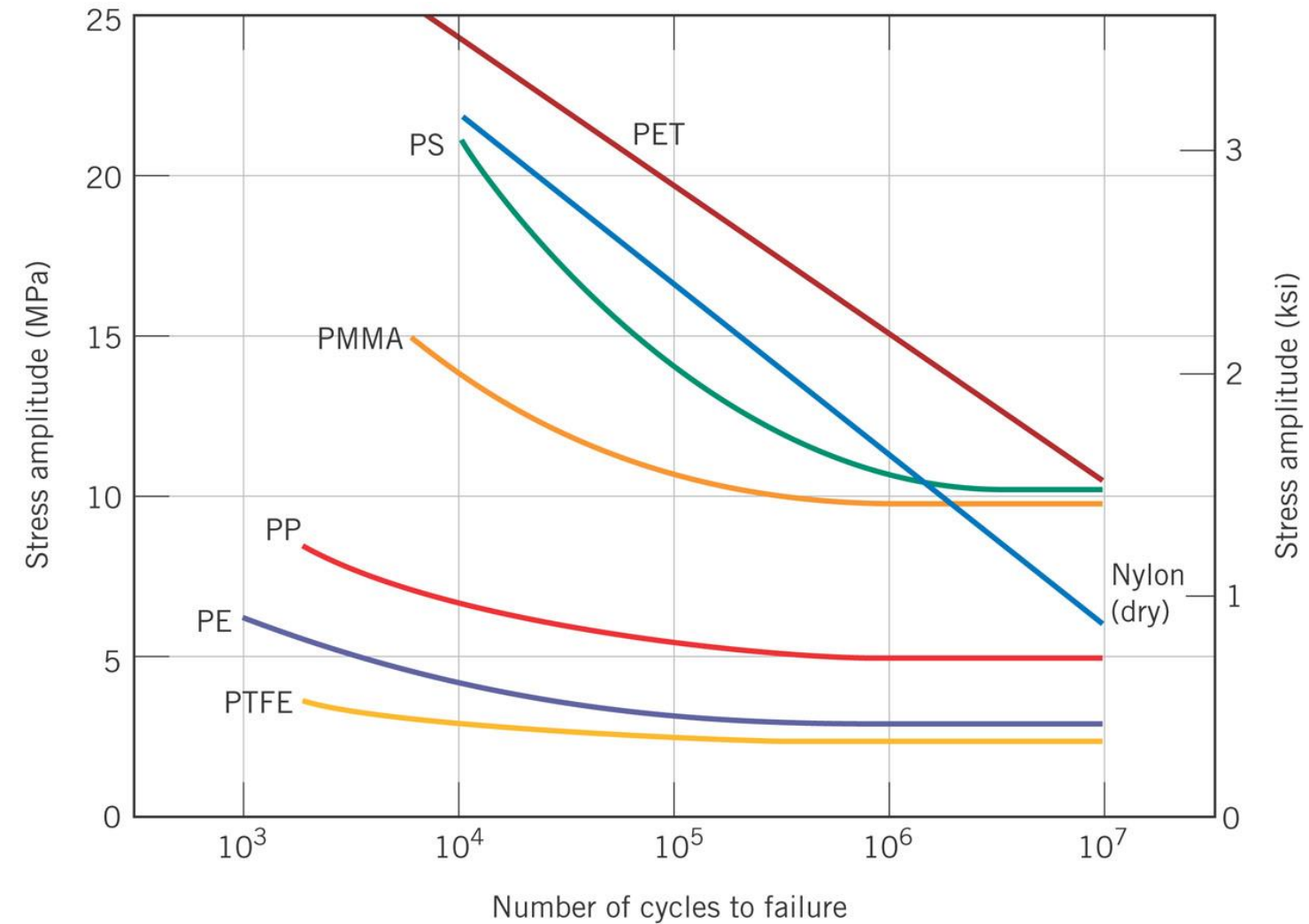


Failures in Polymer

Fracture



Fatigue



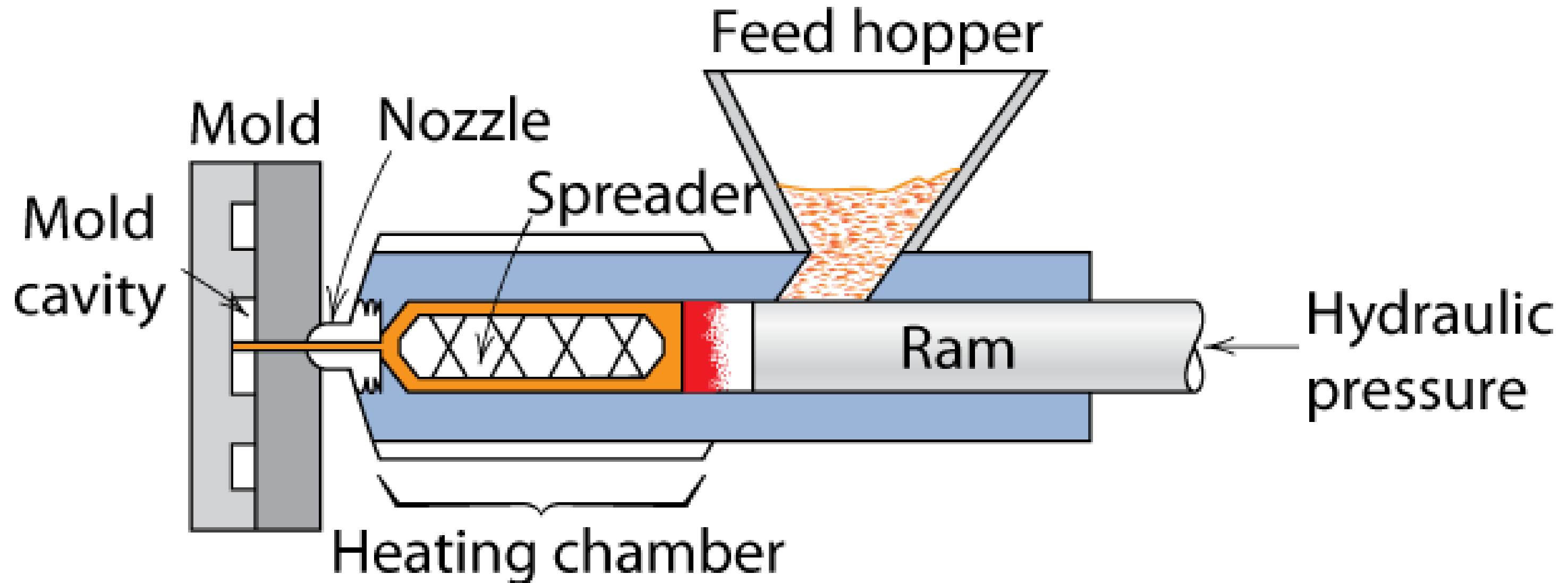
Creep

Often, due to low T_m/T_g , and viscoelasticity

Polymer Processing (2) - Injection Molding

For thermoplastics and some thermosets

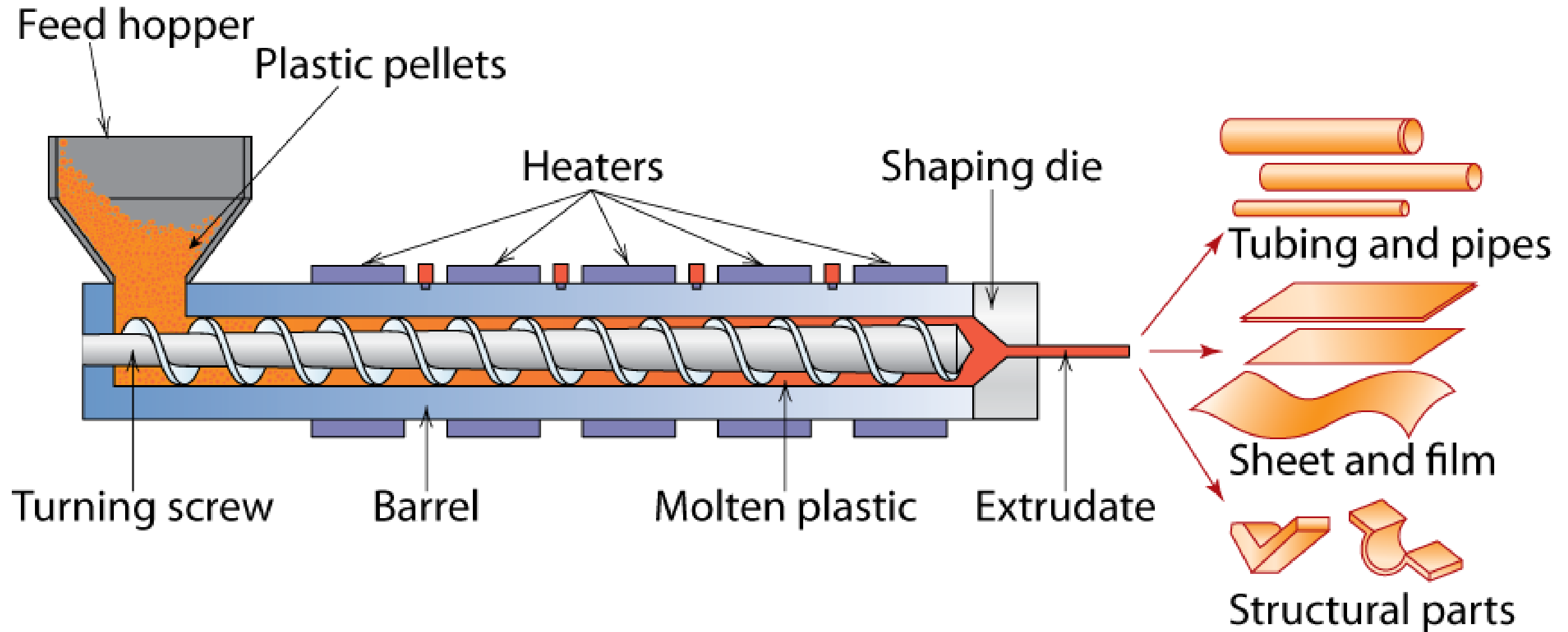
- Ram forces plastics into heating chamber where the plastic melts
- Molten plastics forced/injected into the mold cavity



Polymer Processing (3) - Extrusion

Thermoplastics only

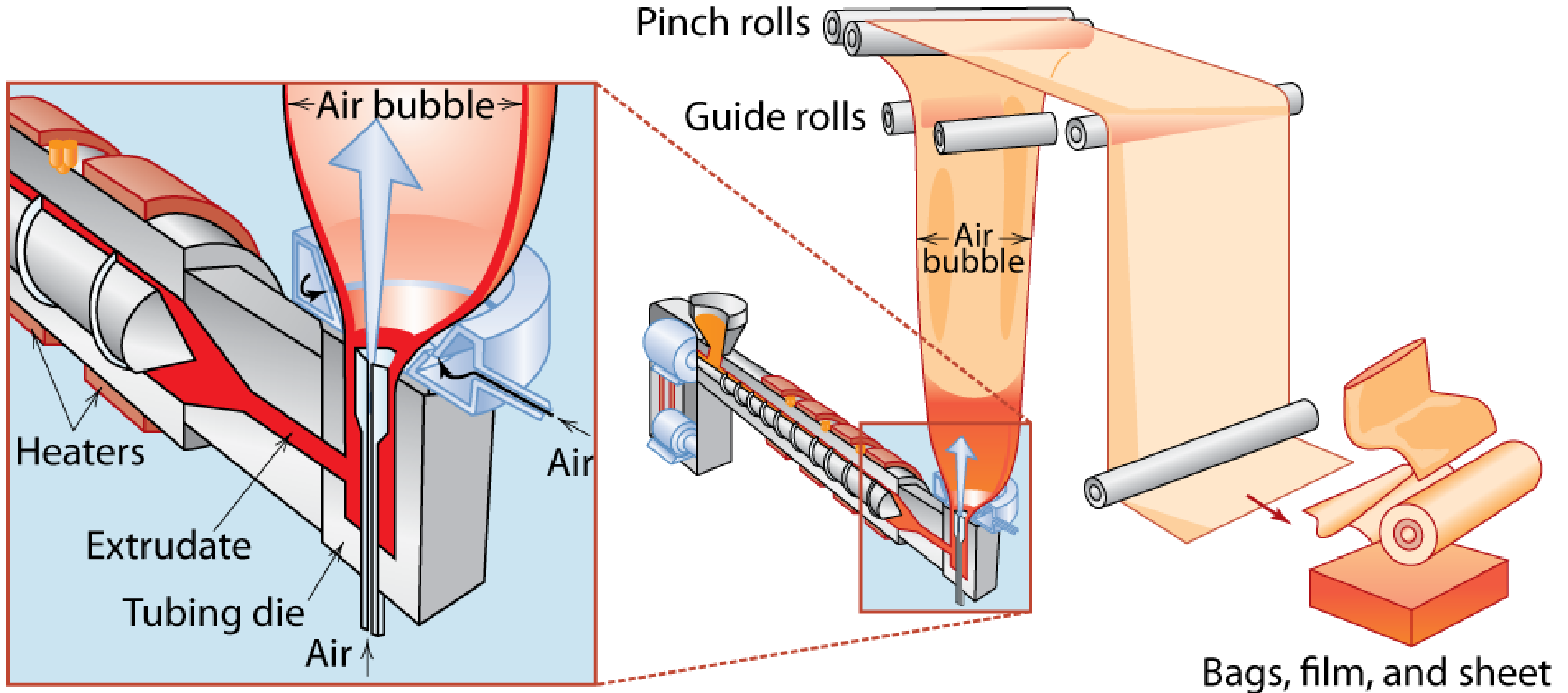
- Plastic pellets feed from hopper into the heater, pushed by with screw
- Molten polymer forced through the die to form the final product



Polymer Processing (4) - Blow-Film Extrusion

Thermoplastics only

- Make thin, plastic sheets



END

Homework 0

Carefully review chapter 16 lecture slides and, if interested, read textbook sections of Askeland 16 and give an honor statement confirming the reading