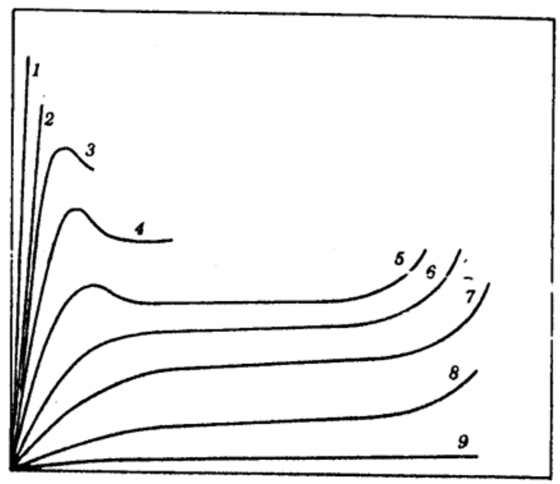
STRESS - STRAIN RESPONSE OF POLYMERS

stress



strain

amorphous polymer ↑

T increases from 1 → 9

1, 2 << T_g

1, 2, 3, 4 < T_g

9 > T_f

1, 2 — quasi-Hookean behavior

others much affected by $\dot{\epsilon}$, viscous flow

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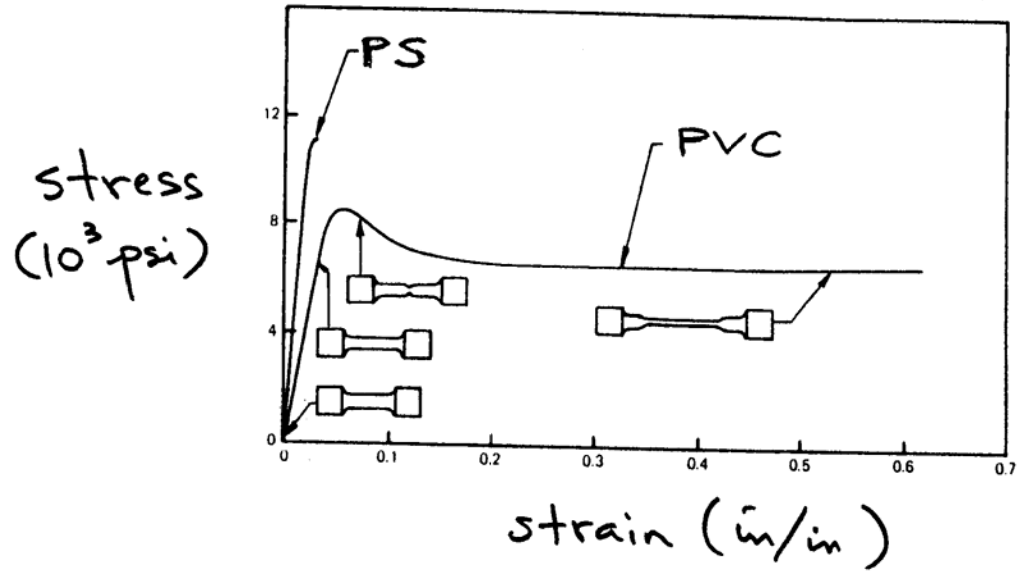
comparison of two amorphous polymers:



initial region — bond angle deformation & bond stretching; essentially instaneously recoverable

yield region — uncoiling and straightening of polymer chains; partially recoverable

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post yield region — falling stress with increasing strain; slippage of chains past one another; slow, incomplete recovery

drawing region — necked region propagates along length of specimen; necked material extensively deformed (chain orientation) & stronger than adjacent material

final region — rising stress with increased strain; strain hardening due to increased drawing (orientation) of polymer chains

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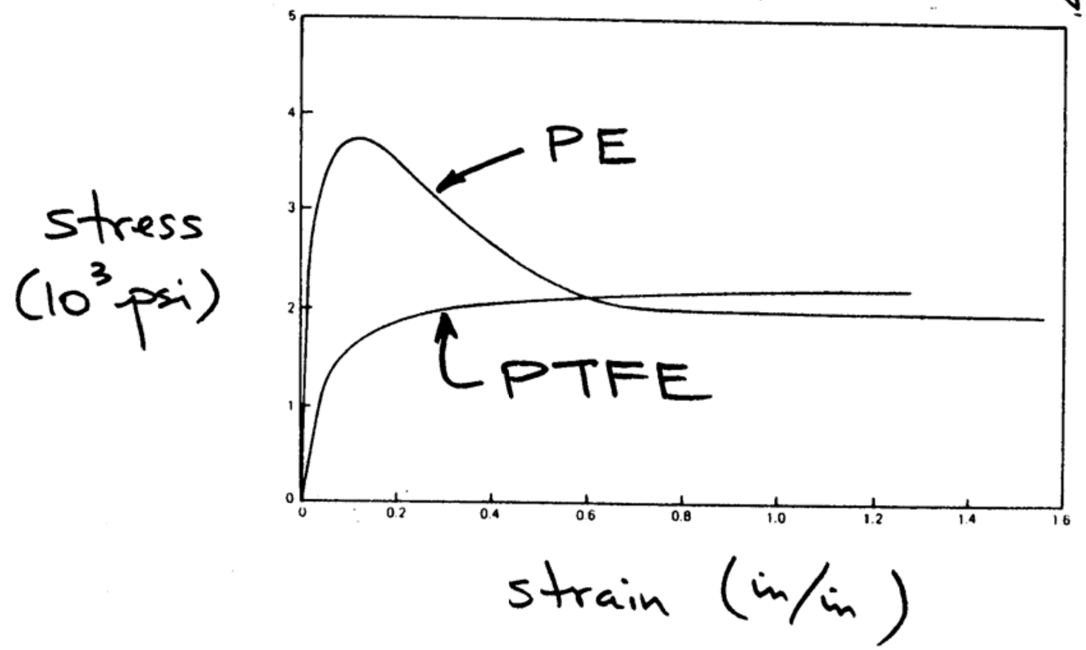
two examples of semicrystalline polymers:



stress-strain behavior -

may vary widely depending on % crystallinity, polar nature of polymer, spherulite size, temperature, etc.

Thomas H Courtney, Mechanical Behavior of Materials 2nd Ed. (2000)

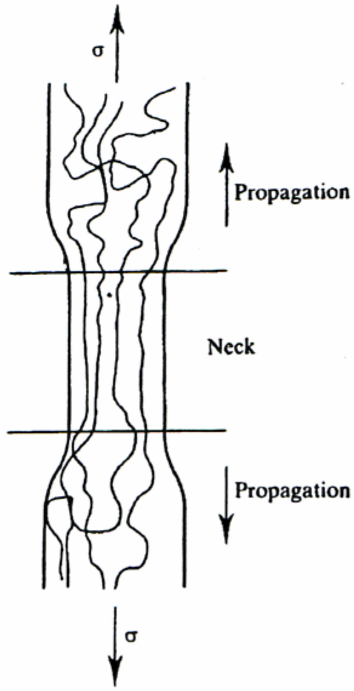


Figure 8.17
Schematic of process of molecular alignment during neck propagation of a glassy polymer. Extensive alignment takes place in the neck as this strong region propagates along the gage length and converts the less deformed and aligned material into the molecularly oriented structure.

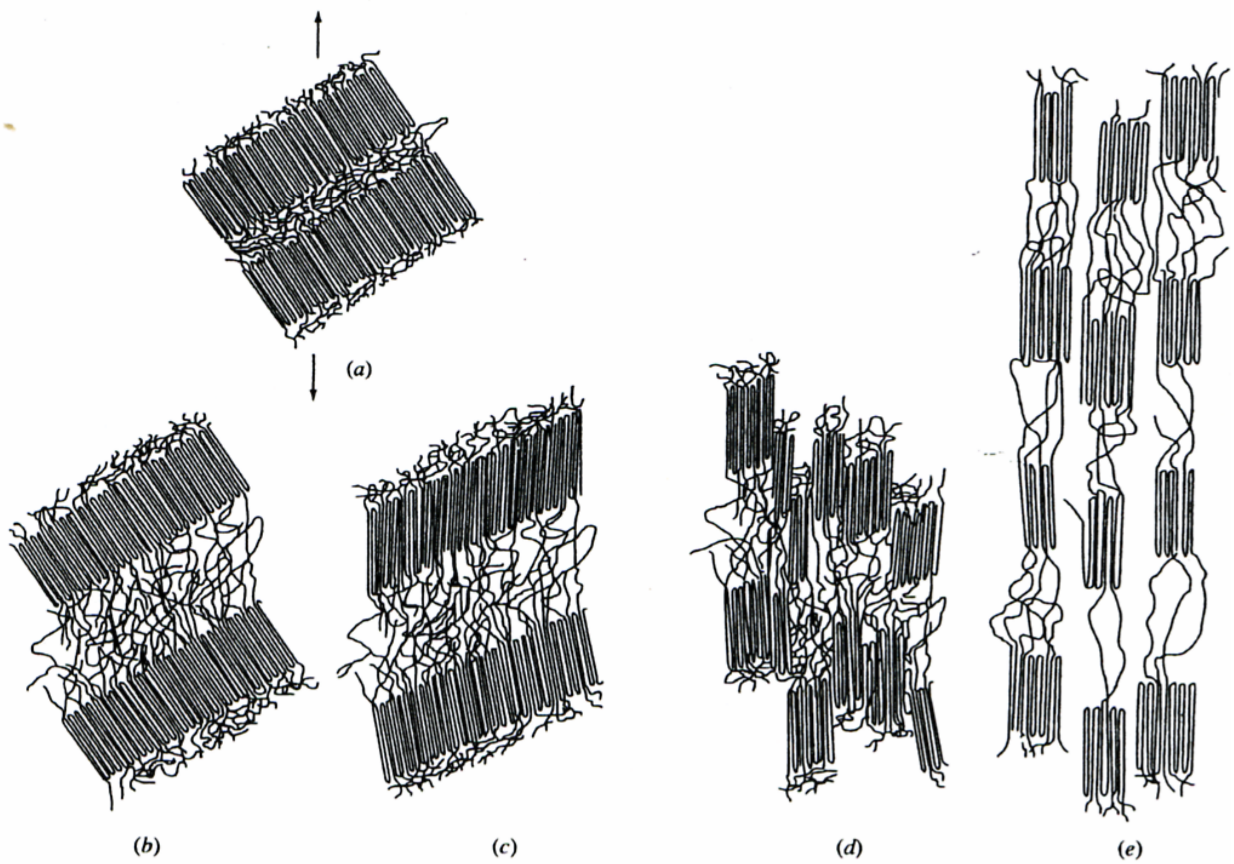


Figure 8.30
Schematic of stages of tensile deformation of a semicrystalline polymer. (a) The initial structure in which crystalline regions are connected by amorphous ones. Note that molecules in the amorphous region constitute the "ties." (b) The initial stages of deformation in which elongation of the amorphous tie molecules occurs. (c) With increasing strain the crystalline segments rotate, aligning themselves with the tensile axis. (d) The crystal segments undergo "fragmentation" by intersegmental displacement at a later deformation stage. (e) Orientation of the crystalline segments and the tie molecules in the last stages of deformation. (*From J. M. Schultz, Polymer Materials Science, Prentice-Hall, Englewood Cliffs, N.J., 1974, p. 500.*)

Factors Affecting the Mechanical Properties of Polymers

Factor	Change in Factor	Modulus	Strength	Ductility	Remarks
Loading Rate/Strain Rate	↑	↑	↑	↓	
Temperature	↑	↓	↓	↑	
Secondary bond strength	↑	↑			Stronger secondary bonding generally increases stiffness. Also, stronger secondary bonding leads to increased ability to crystallize.
Chemical Structure					Steric factors - backbone: phenyl groups stiffen & strengthen; O atom flexibilizes & softens pendant groups: bulky/close to backbone stiffen & strengthen
Polar Substituents					Polar groups cause increase stiffness & strength.
Molecular Weight	↑	↑	↑	↓	Most effective at lower MW.
Crystallinity	↑	↑	↑	↓	
Spherulite Size					Large spherulite size can lead to brittle fracture.
Prior History					Orientation as a result of processing can dramatically alter all mechanical properties and they are anisotropic.
Plasticizer	↑	↓	↓	↑	Recall that water is often a significant plasticizer.
Crosslinking	↑	↑	↑	↓	
Irradiation	↑	↑	↑	↓	For example: uv irradiation of thermoplastics.
Fillers & reinforcements	↑	↑	↑	↓	Examples: talc, calcium carbonate, carbon black, mica, glass beads/fibers.
Copolymerization					Copolymerization can dramatically alter all mechanical properties. Also, effects are different for random copolymer and block copolymer.