Chemical Engineering 378

Science of Materials Engineering

Lecture 18

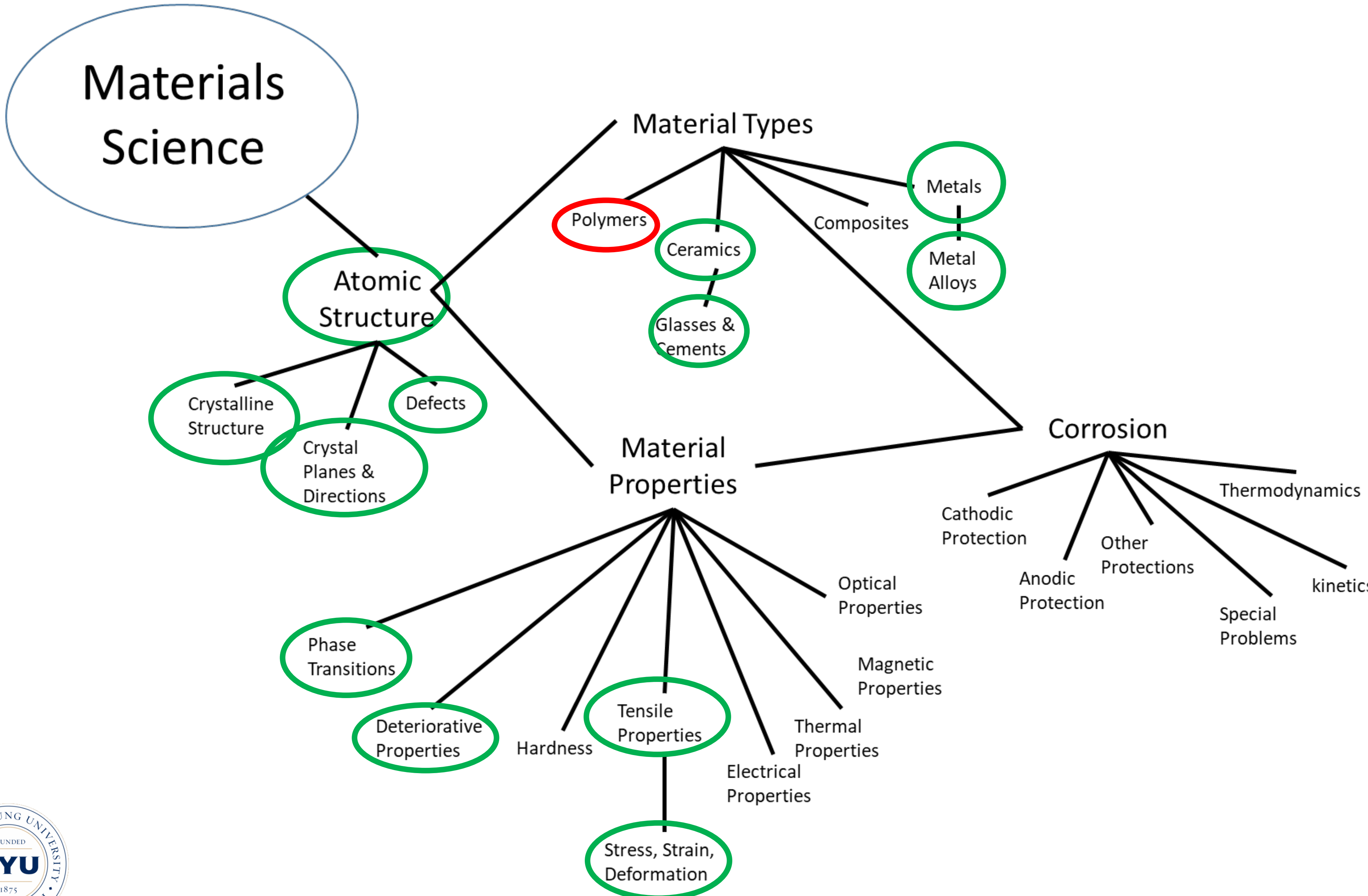
Polymers and Applications II

Spiritual Thought

D&C 101:16

Therefore, let your hearts be comforted concerning Zion; for all flesh is in mine hands; be still and know that I am God.

Materials Roadmap



OEP

- https://www.youtube.com/watch?v=7YIxDLIQWdI&t=67s

OEP #6

The Amazing Spider Man

Group work okay, Due 10/19/22 at beginning of class

(Don't be afraid to "Google" for reasonable assumptions; just provide references!)

So… could a spider pull a jet?

Of all the Spiderman movies (of which there are MANY), this one is perfect for us, because Peter actually develops web shooters, rather than having his DNA do this for him. Spiderman webbing is of course a polymer, and there are some interesting claims made (or shown) in this movie. In particular, using this clip and supporting references, determine a) the yield strength of Spiderman webbing, and b) the diameter needed of a Spiderman silk strand that will just support Peter while swinging from a skyscraper in New York.

Condensation Reaction I

$$H_2N-(CH_2)_6-NH_2 \; + \; ClOC-(CH_2)_8-COCl$$

Hexamethylenediamine

Sebacoyl chloride

$$\downarrow$$

$$\ldots\; HN-(CH_2)_6-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_8-CO \;\ldots$$

$$+2HCl$$

NYLON 6,10

Condensation Reaction II

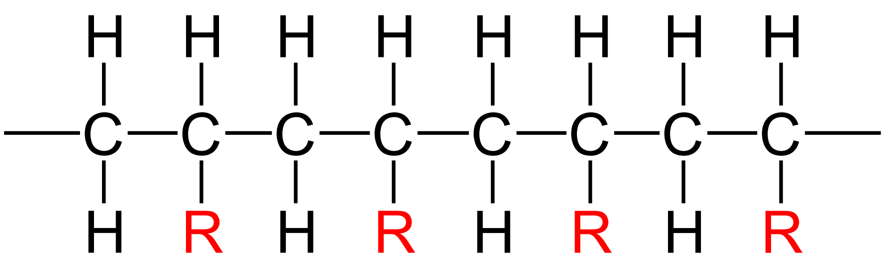
https://www.youtube.com/watch?v=INWc6xUf6U4

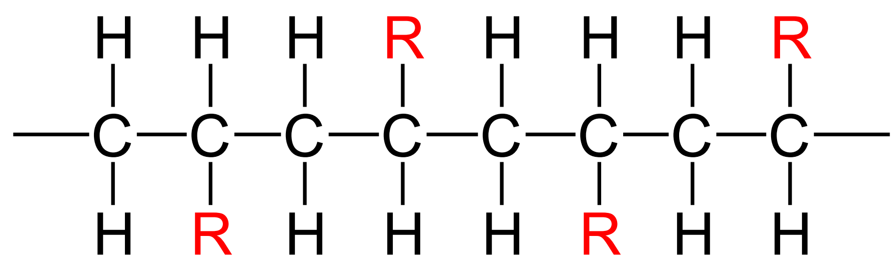
Tacticity

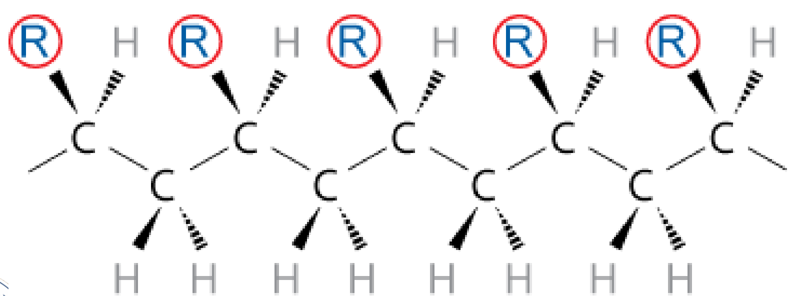
Tacticity – stereoregularity or spatial arrangement of R units along chain

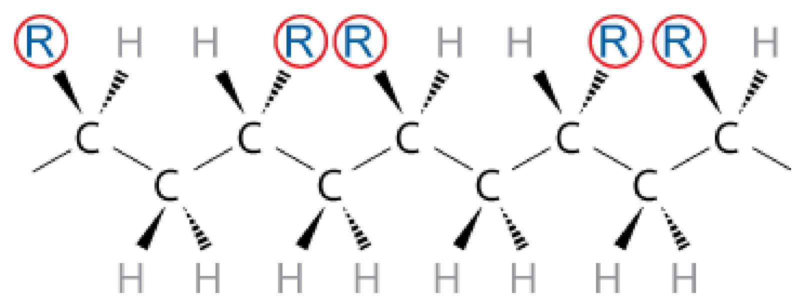
isotactic – all R groups on same side of chain

syndiotactic – R groups alternate sides



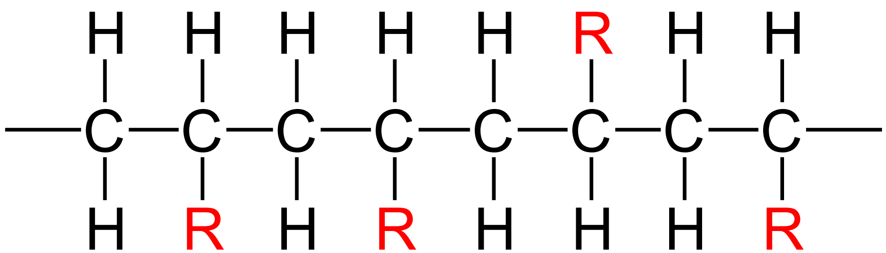


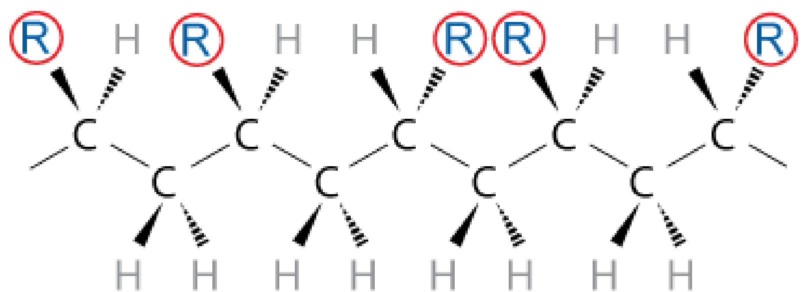




Tacticity (cont.)

atactic – R groups randomly positioned

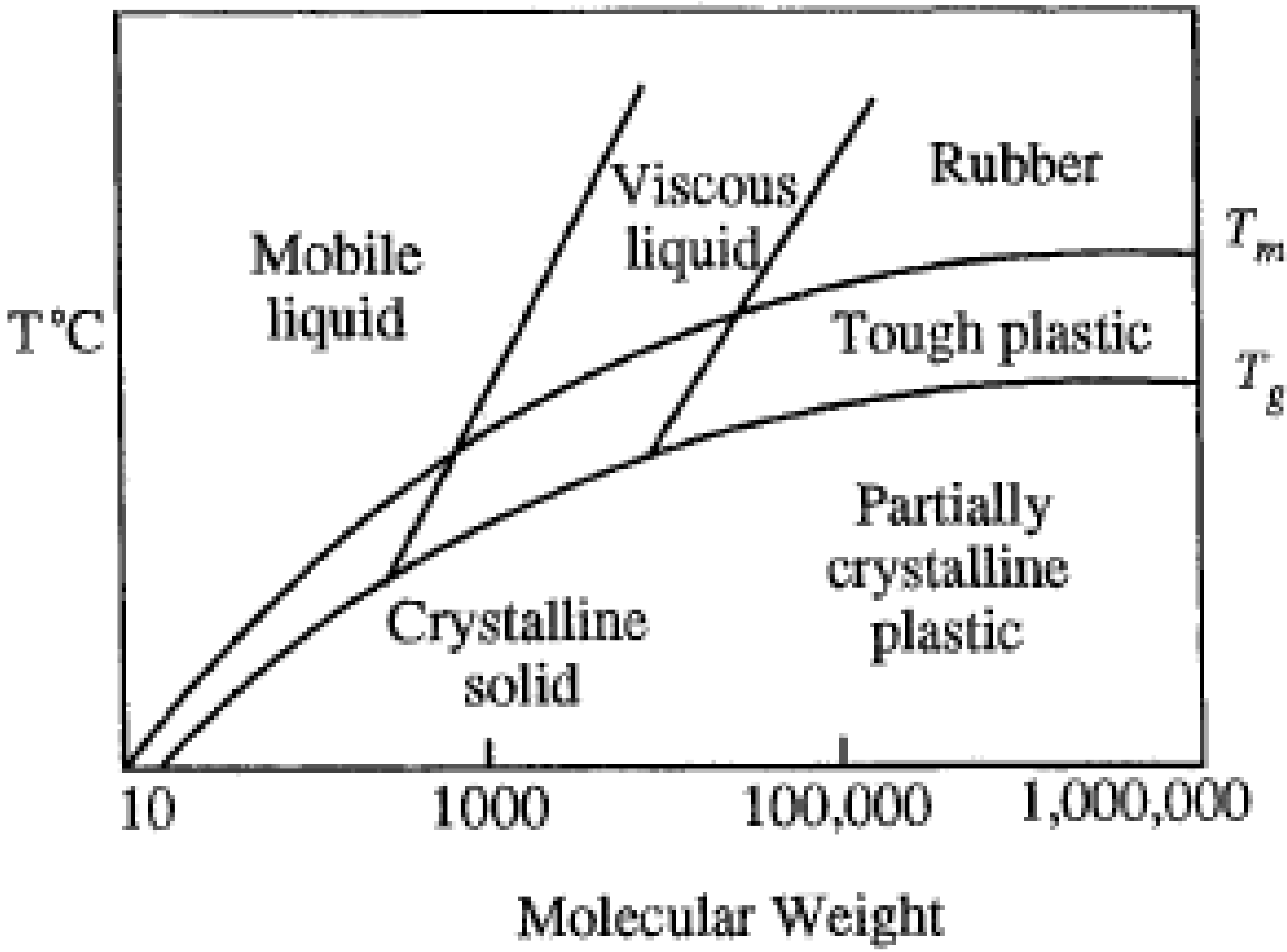




Structure and properties

- Crystallinity?
  - Isotactic
    - Partially Crystalline
  - Syndiotactic
    - Partially Crystalline
  - Atactic
    - Amorphous
- Melting Point? (highest to lowest)
  - Isotactic
  - Syndiotactic
  - Atactic

General Trends



General

Table 1. Properties of Common Thermoplastics and Thermosets [data from Callister, 1994; Fried, 1995; Shackelford, 1996; Smith, 1996].

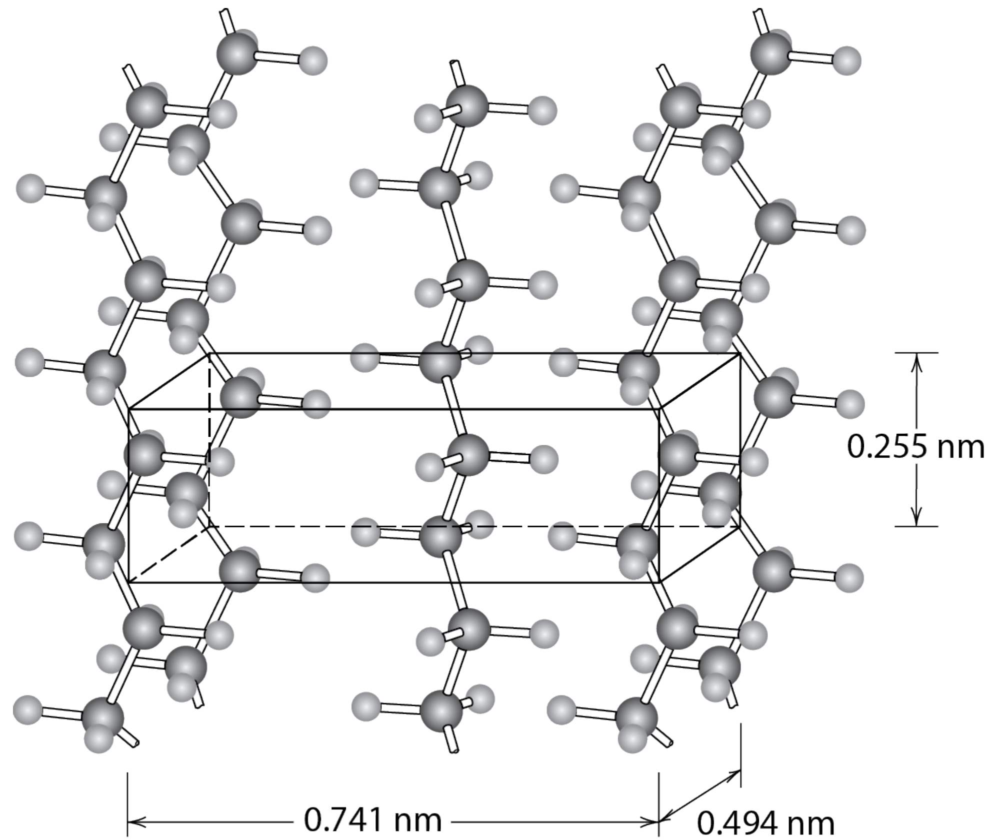
polymer	mer structure	structural state	tens.streng. (MPa)	impact strg (J/m)[a]	density (g/cm^3)	T_g[b] (°C)	T_{max}[c] (°C)	bulk price $/kg	Applications
<u>thermoplastics</u>									
ABS	copolymer of acrylonitrile, butadiene and styrene	glassy coply with rubbery domains	40	200-600	1.03	--	71-93	2.82-3.04	refrigerator linings, lawn & garden equipment
polyamides (nylon 6,6)	-NH-$[CH_2]_6$-NH-C-$[CH_2]_4$-C-	highly crystalline, spherulitic struct., H-bonding	75	100	1.15	57	82-150	2.97-7.60	bearings, gears, cams, bushings, tool handles, wire coatings
polycarbonate	-O-ϕ-C-ϕ-O-C-	stiff molecular structure	63-72	650-850	1.20	150	120	4.80-6.35	machine parts, car parts, propellers, instrument panels, CDs
polyethylene, LD[d]	[-CH_2-CH_2-]	branched (60% C)[f]	8-16	50-700	0.92	-110	82-100	1.21-1.32	flex.sheet, bottle, toys
polyethylene, HD[e]		linear (95% C)	26-33	25-100	0.95	-90	80-120	1.32-1.39	batteries, tanks, ice trays
polypropylene	[-CH_2-C(CH_3)H-]	isotactic (amorp.)	31-41	25-100	0.91	-10	107-150	1.21-1.32	bottles, packing, TV cabinets
polystyrene	[-CH_2-C(ϕ)H-]	isotactic (crystal.)	36-52	12-20	1.05	100	104	1.32-1.45	Styrofoam, tile, battery cases, toys, lighting
polyvinyl chloride (PVC)	[-CH_2-C(Cl)H-]	largely amorphous	41-52	50-125	1.4-1.5	105	110	0.81-3.30	pipe, garden hose, electrical insulation
polyethylene terephthalate (PET)	-O-CH_2-CH_2-O-C-ϕ-C-	crystalline	49-72	12-35	1.15	70-80	80-120	3.61-3.85	fiber, film, magnetic tape carpet, clothing, tires
<u>thermosets</u>									
phenolic		amorphous, wood and glass reinforced	52	12-900	1.3-1.9		150-288	1.36-2.20	electrical equip. , motor housings, insulators, brake and transmission parts
polyester	CH-O-C-$(CH_2)_x$-C-OH	amorphous, glass reinforced (fiber-glass)	40-90	400-800	1.7-2.3		150-177	1.43-1.67	car panels and body parts, boat hulls, indoor constr. panels, pipes tanks, ducts

[a]Based on notched Izod test. [b]Glass to liquid transition temperature. [c]Maximum use temperature (no load). [d]Low density. [e]High density. [f]C is crystallinity.

Crystallinity in Polymers

Fig. 14.10, *Callister & Rethwisch 10e.*

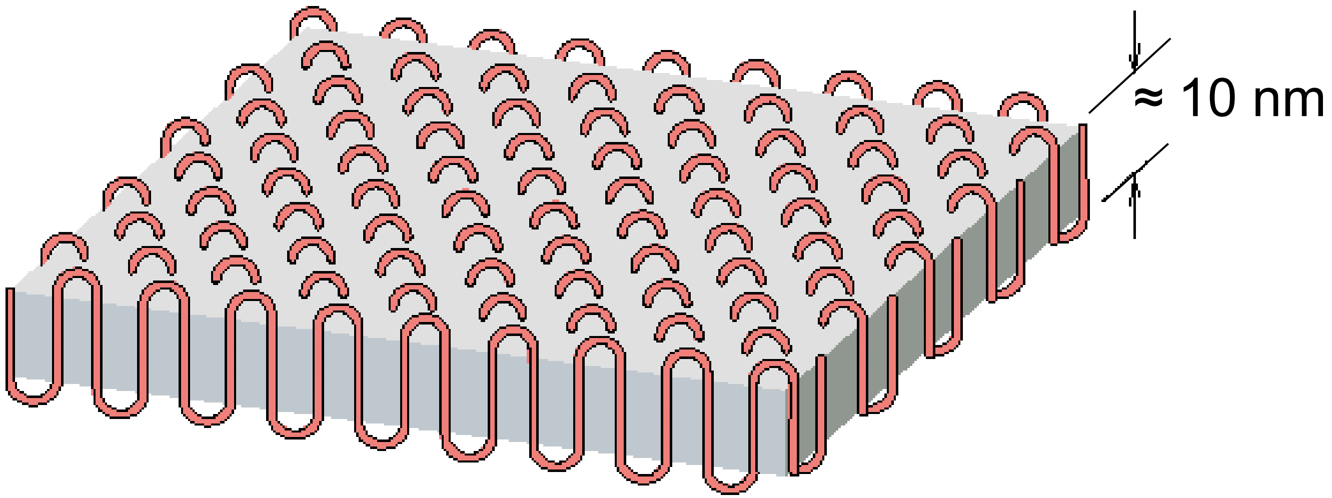
- Ordered atomic arrangements involving molecular chains
- Crystal structures in terms of unit cells
- Example shown
  - polyethylene unit cell



Polymer Crystallinity

- Crystalline regions
  - thin platelets with chain folds at faces
  - Chain folded structure

Fig. 14.12, *Callister & Rethwisch10e.*



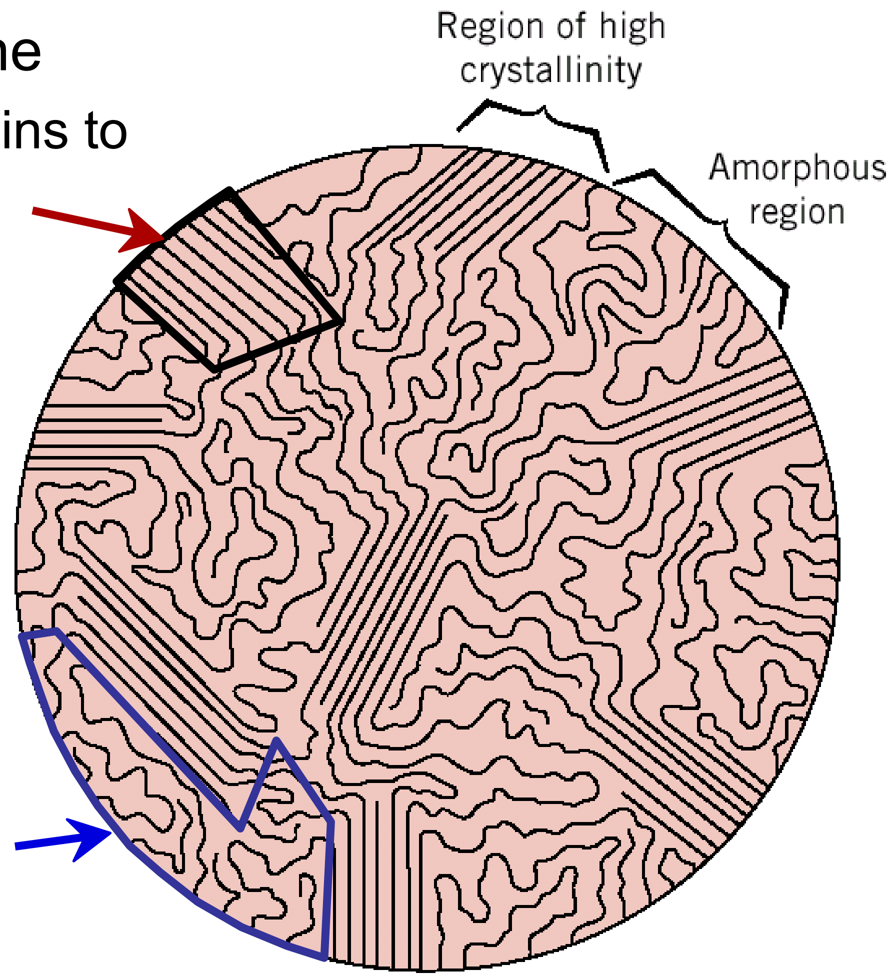
Polymer Crystallinity (cont.)

Polymers rarely 100% crystalline

- Difficult for all regions of all chains to become aligned

crystalline region

- Degree of crystallinity expressed as % crystallinity.
  -- Some physical properties depend on % crystallinity.
  -- Heat treating causes crystalline regions to grow and % crystallinity to increase.

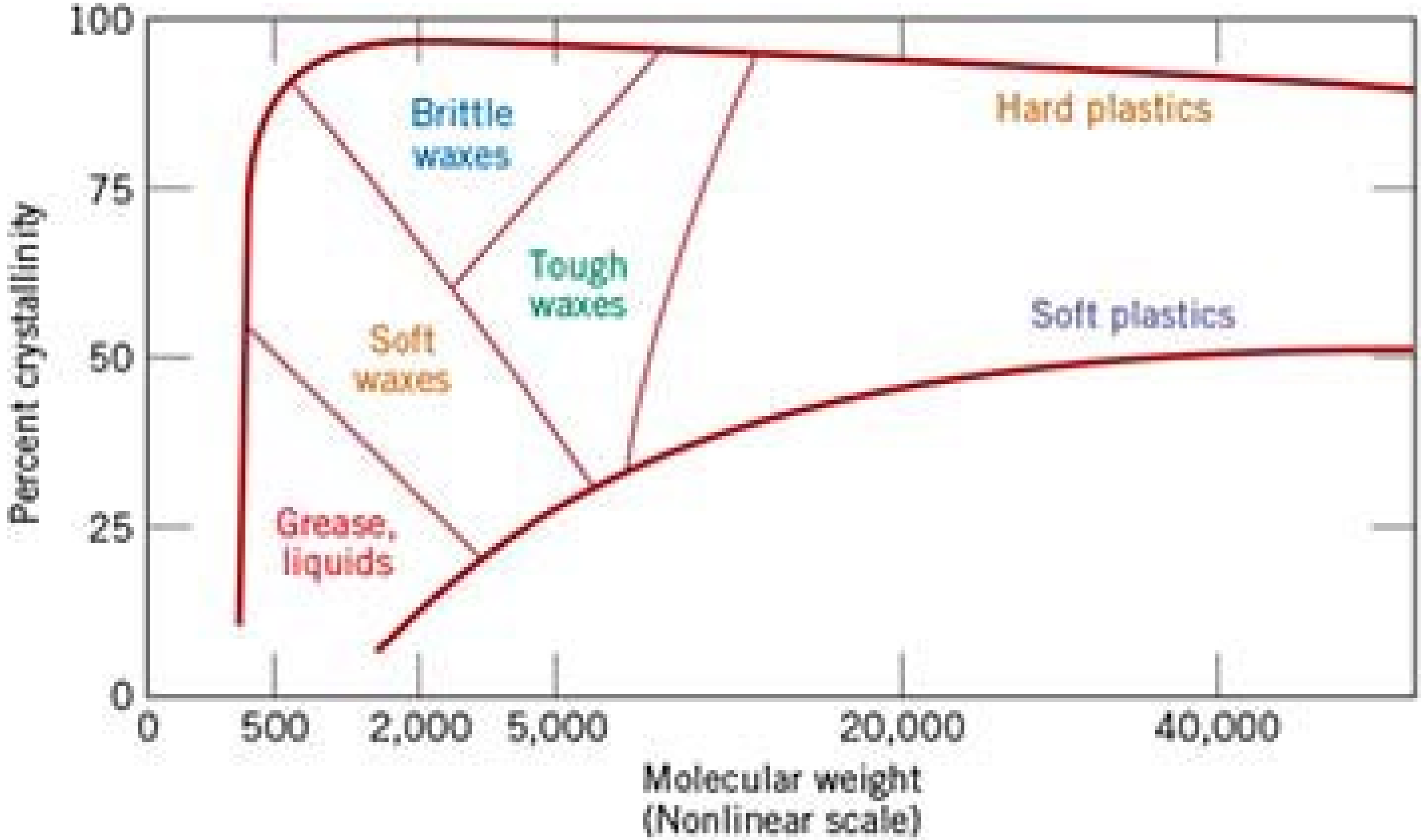


amorphous region

$$\%Crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Fig. 14.11, *Callister 6e.* (From H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

Impact of Crystallinity



From R. B. Richards, "Polyethylene—Structure, Crystallinity and Properties," *J. Appl. Chem.*, 1, 1951, p. 370.

Polymer Single Crystals

- Electron micrograph – multilayered single crystals (chain-folded layers) of polyethylene
- Single crystals – only for slow and carefully controlled growth rates

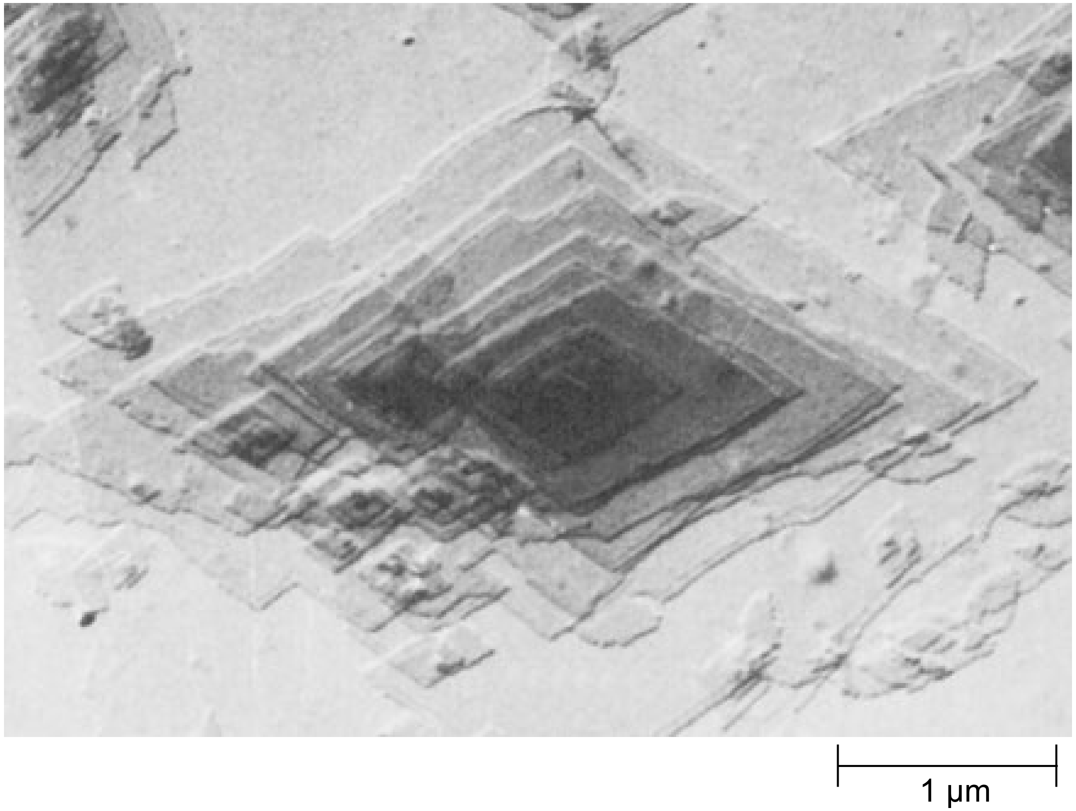
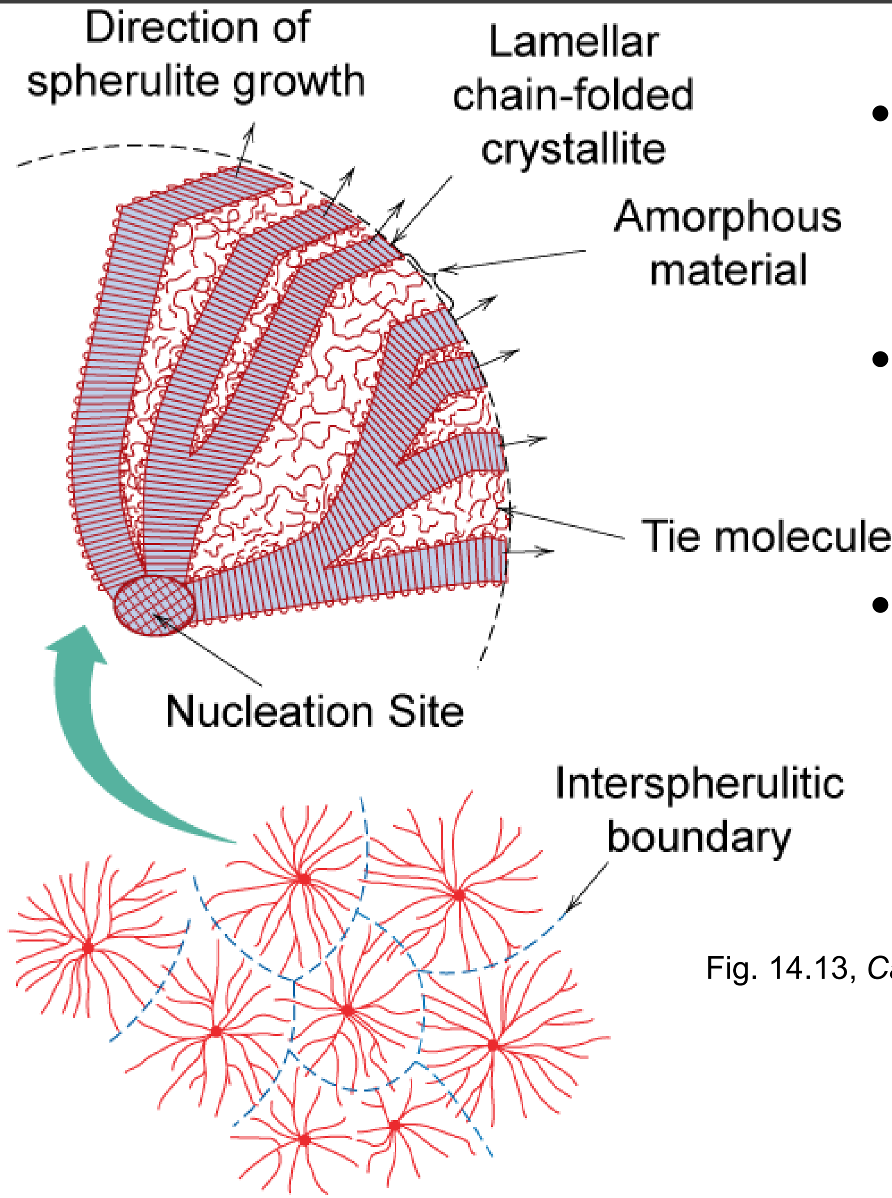


Fig. 14.11, *Callister & Rethwisch 10e.*
[From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Eds.), Growth and Perfection of Crystals. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498. Reprinted with permission of John Wiley & Sons, Inc.]

Semicrystalline Polymers

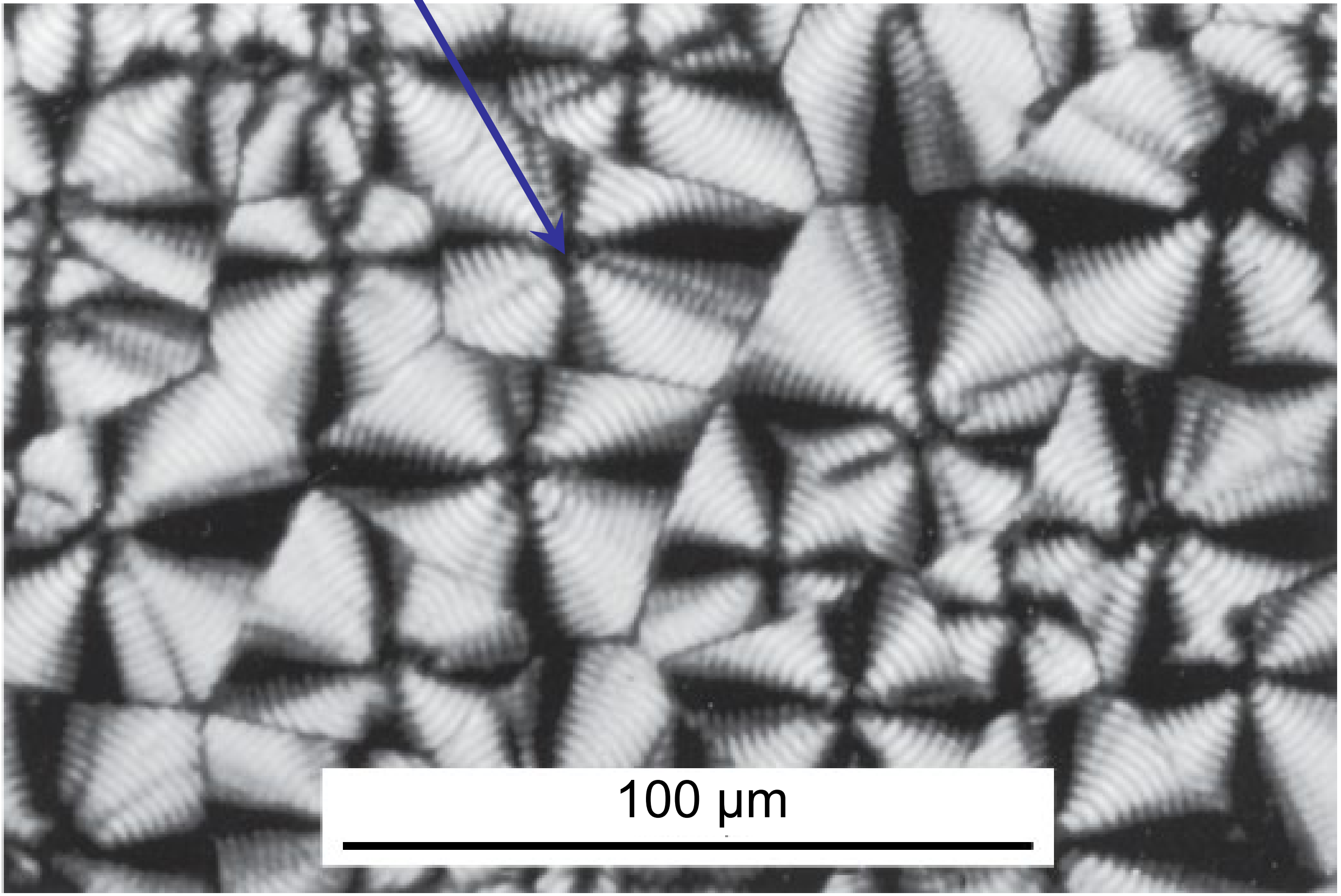


- Some semicrystalline polymers form spherulite structures
- Alternating chain-folded crystallites and amorphous regions
- Spherulite structure for relatively rapid growth rates

Fig. 14.13, *Callister & Rethwisch 10e.*

Photomicrograph – Spherulites in Polyethylene

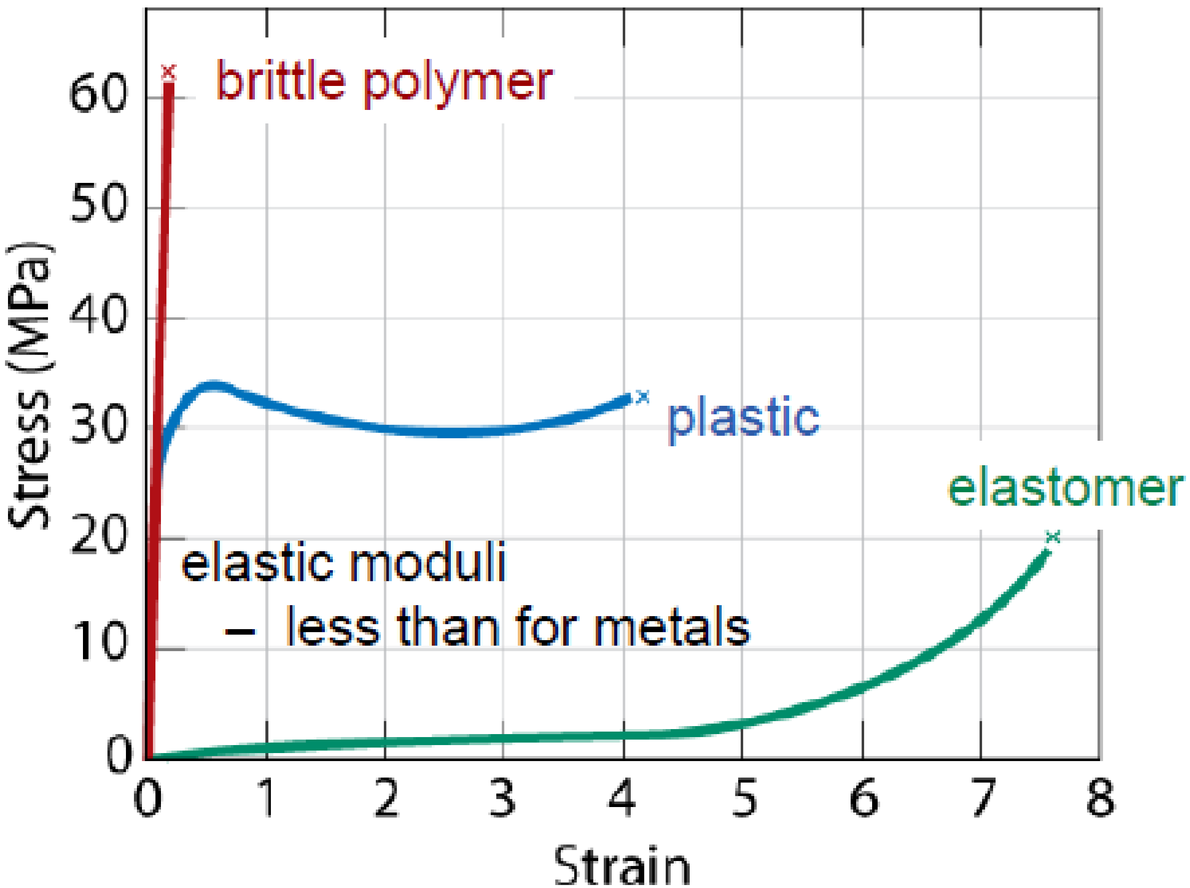
Cross-polarized light used
-- a maltese cross appears in each spherulite



Courtesy F. P. Price, General Electric Company

Fig. 14.14, *Callister & Rethwisch 10e.*

Stress Strain Behavior

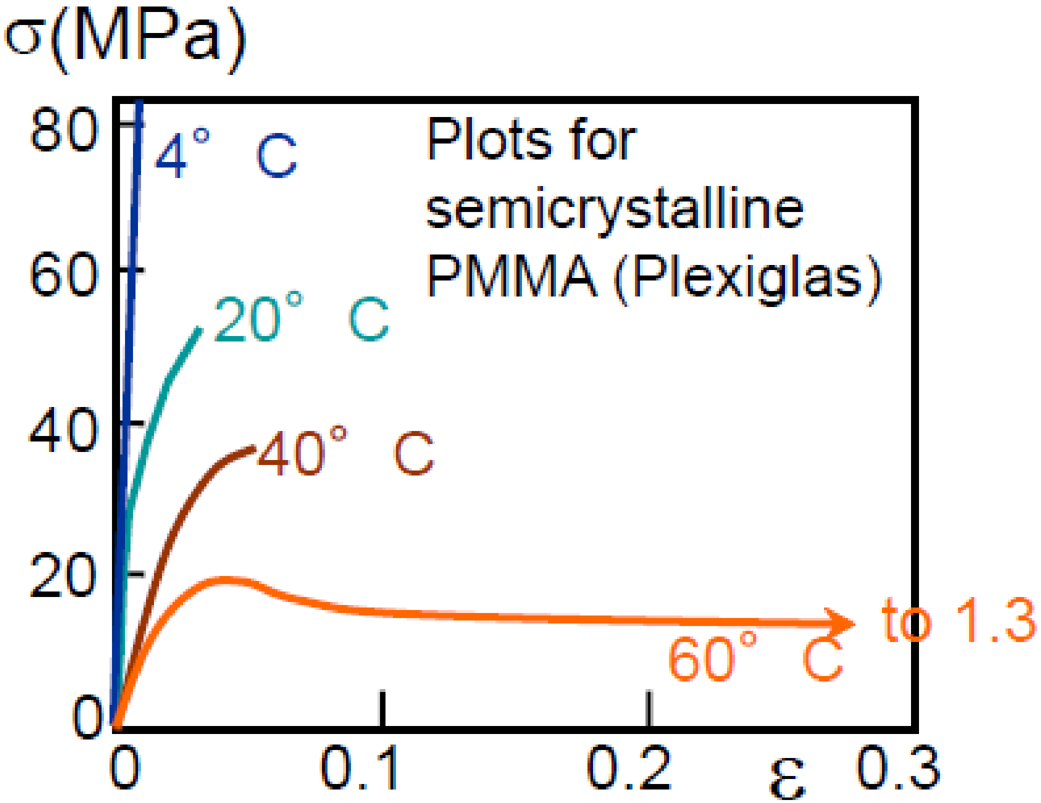


- Fracture strengths of polymers ~ 10% of those for metals
- Deformation strains for polymers > 1000%
  - for most metals, deformation strains < 10%

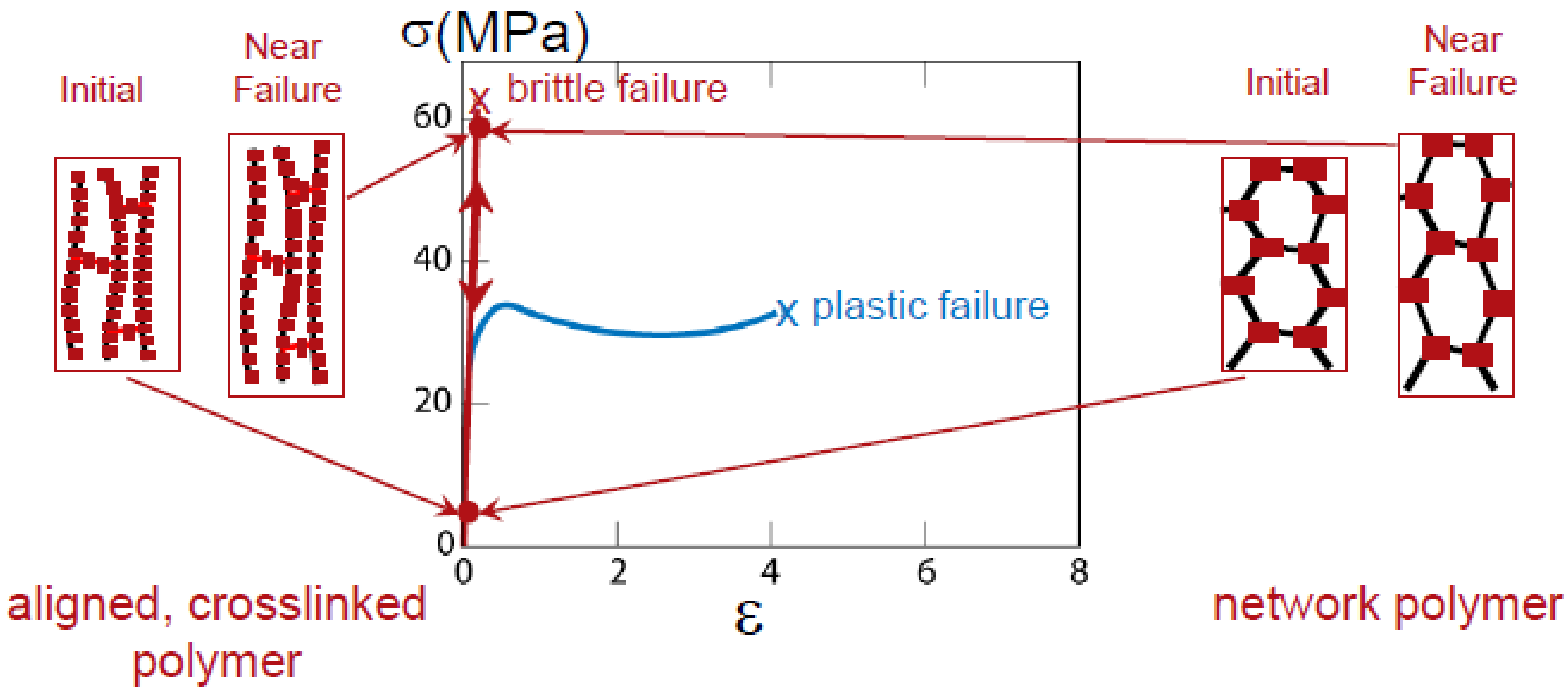
Influence of T and Strain Rate on Thermoplastics

- Decreasing *T*...
  -- increases *E*
  -- increases *TS*
  -- decreases %*EL*

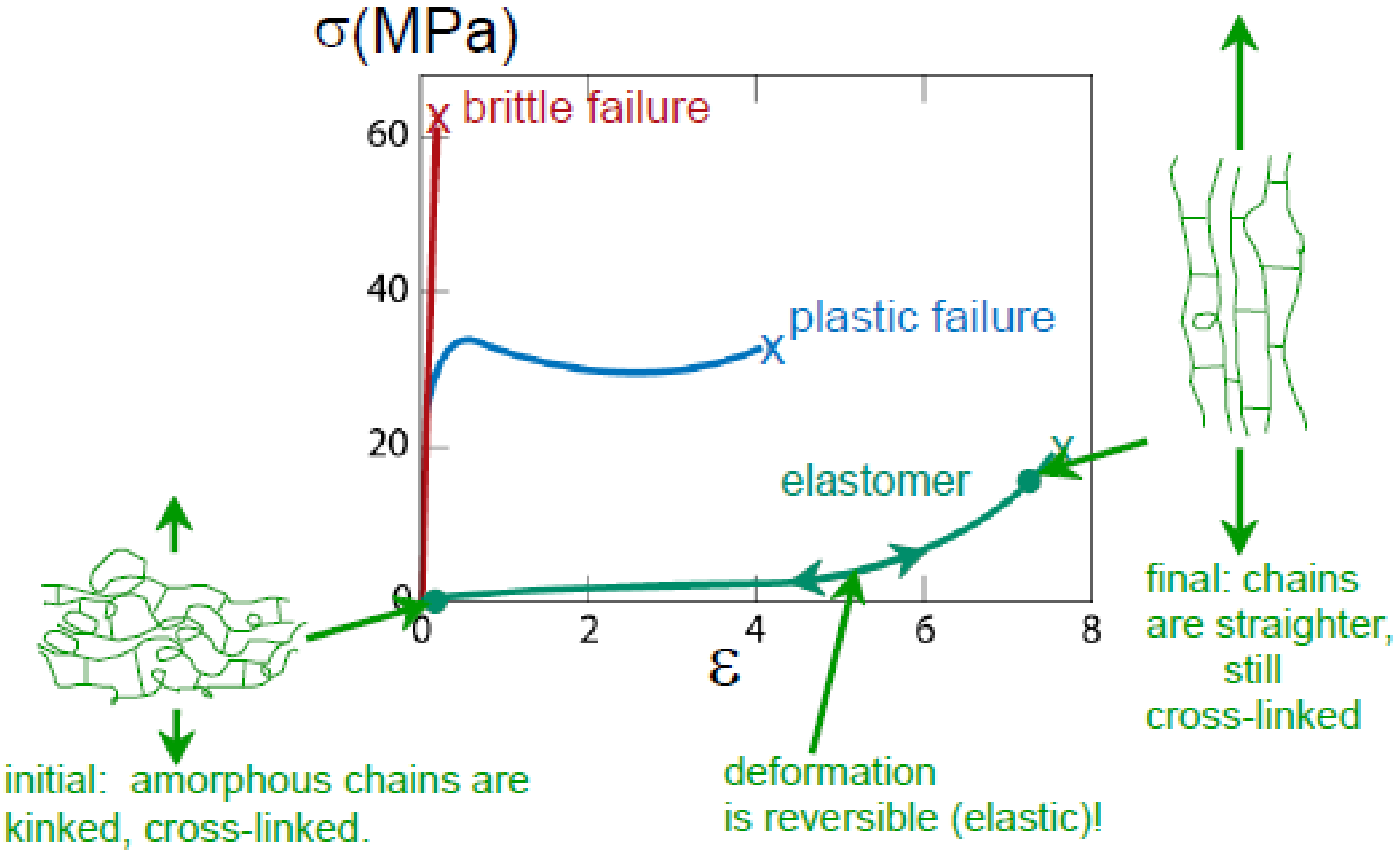
- Increasing strain rate...
  -- same effects as decreasing *T*



Mechanisms of Deformation (network)



Mechanisms of Deformation (Elastomers)



- Compare elastic behavior of elastomers with the:
  - -- brittle behavior (of aligned, crosslinked & network polymers), and
  - -- plastic behavior (of semicrystalline polymers)

Cracking and Fracture

Craze formation prior to cracking

- during crazing, plastic deformation of spherulites
- and formation of microvoids and fibrillar bridges