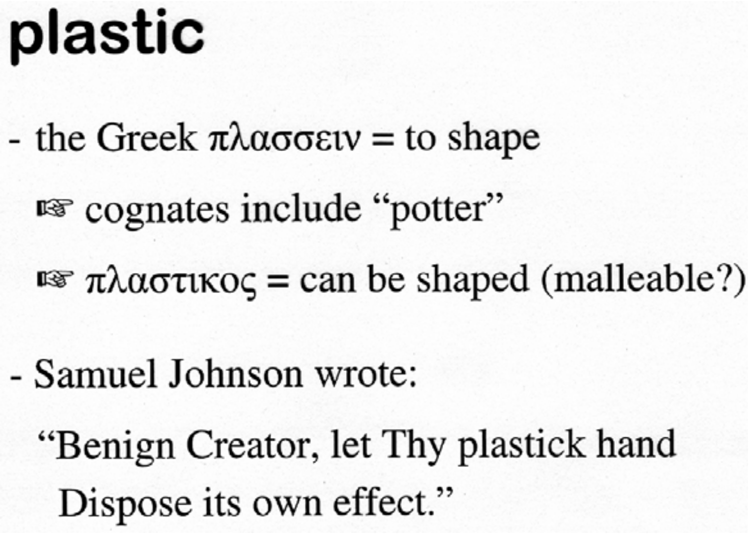
## Ancient Polymer History

- Originally natural polymers were used
  - Wood
  - Cotton
  - Leather
  - Rubber
  - Wool
  - Silk
- Oldest known uses
  - Rubber balls used by Incas
  - Noah used pitch (a natural polymer) for the ark

## Polymer History



**plastic**

- the Greek πλασσειν = to shape

  ☞ cognates include "potter"

  ☞ πλαστικος = can be shaped (malleable?)

- Samuel Johnson wrote:

  "Benign Creator, let Thy plastick hand
  Dispose its own effect."

## Polymer History

"I just want to say one word to you –just one word – 'plastics.'"

Advice to Dustin Hoffman's character in *The Graduate*

## Polymer History

US annual production of polymers:
- 50 million tons
- 3-4 million tons recycled

US Steel production
- 80 million tons new steel
- 60 million tons recycled

US Aluminum production
- 3 million tons new
- 1 million recycled

# Polymer History

## Carl S. “Speed” Marvel

- b. 1894
- d. 1988
- B.A. Illinois Wesleyan
- Ph.D. UIUC, 1916
- Chemical Warfare work during WWI
- Father of American Polymer Chemistry

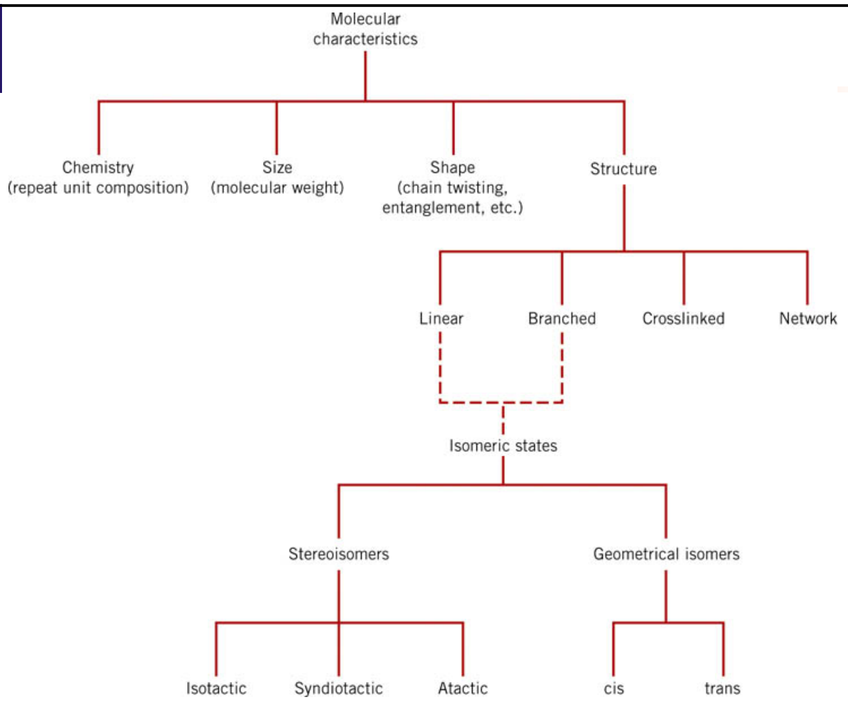
**“Speed could drink the hottest coffee and consume the largest amount of popcorn. He was fond of guiding his colleagues through the Greek alphabet and of interjecting Latin quotations. He teased us with statements of the wonderful chemistry they were doing at DuPont that he wished he could tell us about. In answer to our random complaints, he had lived through a bigger snowstorm, had had a worse graduate student (who improved dramatically) and a worse secretary (who responded to training), and always felt old (while doing the work of at least three young people). In remembrance of Speed Marvel, we smile for someone we really cared for and who cared for all of us. The lasting words that he gave me were "Remember that our major product is our students." ”**
**– Nelson Leonard**

---

# Polymer History

## Wallace Carothers

- b. April 27, 1896, Burlington, Iowa
- B.S., Tarkio College (gen. sci. & Eng.)
- Ph.D., U. of Illinois
- lecturer Harvard
- head of fundamental research in organic chemistry at DuPont; synthesis of long-chain molecules similar to cellulose and silk
- invented neoprene 1931: synthetic rubber
- invented nylon 1937: synthetic fiber
- m. February 1936
  62 technical publications
- d. April 29, 1937, Philadelphia
  69 patents



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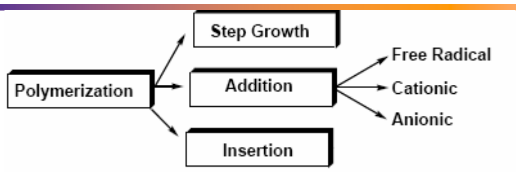
# Polymer Synthesis (more next time)



**Condensation or Step-Growth Polymerization**

Usually non-catalyzed chemical condensation reactions, with elimination of a low MW side-product (e.g., water).

Commonly involves –OH, –COOH, $–NH_2$

**Addition Polymerization**

Generally alkene monomers adding via chain reaction.

Radical or ion initiator.

Polymer contains all atoms of monomers.

**Insertion Polymerization**

Also usually of alkene monomers.

Monomer inserted into beginning of growing chain.

Catalyst mediated (usually organometallic).

Very high stereoregularity.

## Polymers

- **Types of polymers:**

  Thermoplastic

  Thermosetting

  Elastomers

---

## Polymers

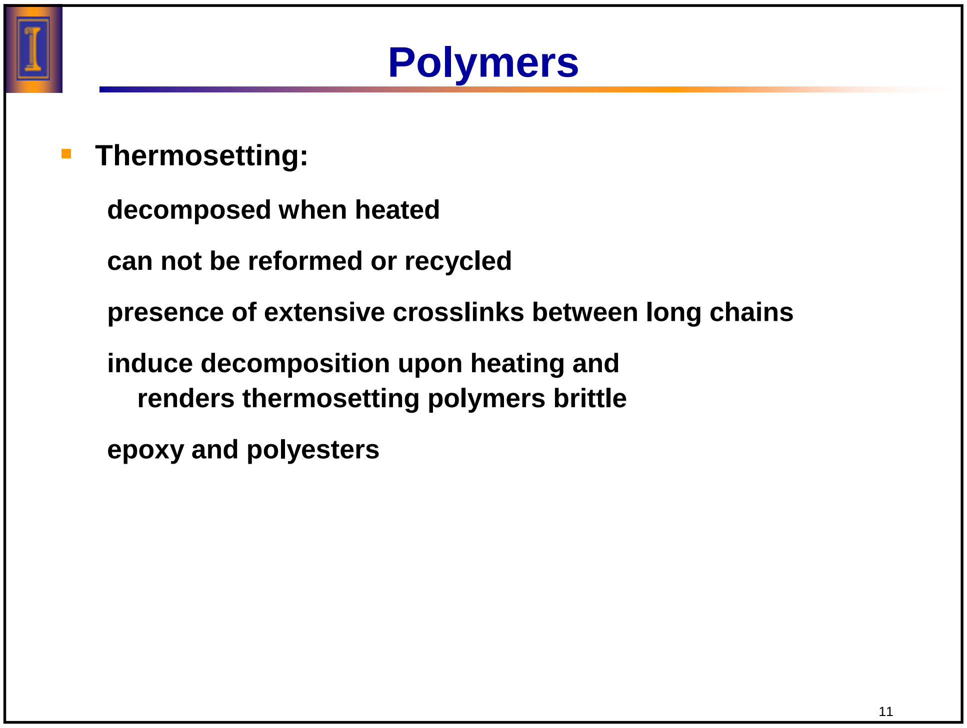
- **Thermoplastic:**

  **polymers that flow when heated**

  **easily reshaped and recycled**

  **due to presence of long chains with limited or no crosslinks**

  **polyethylene, polyvinylchloride**



## Polymers

- **Thermosetting:**

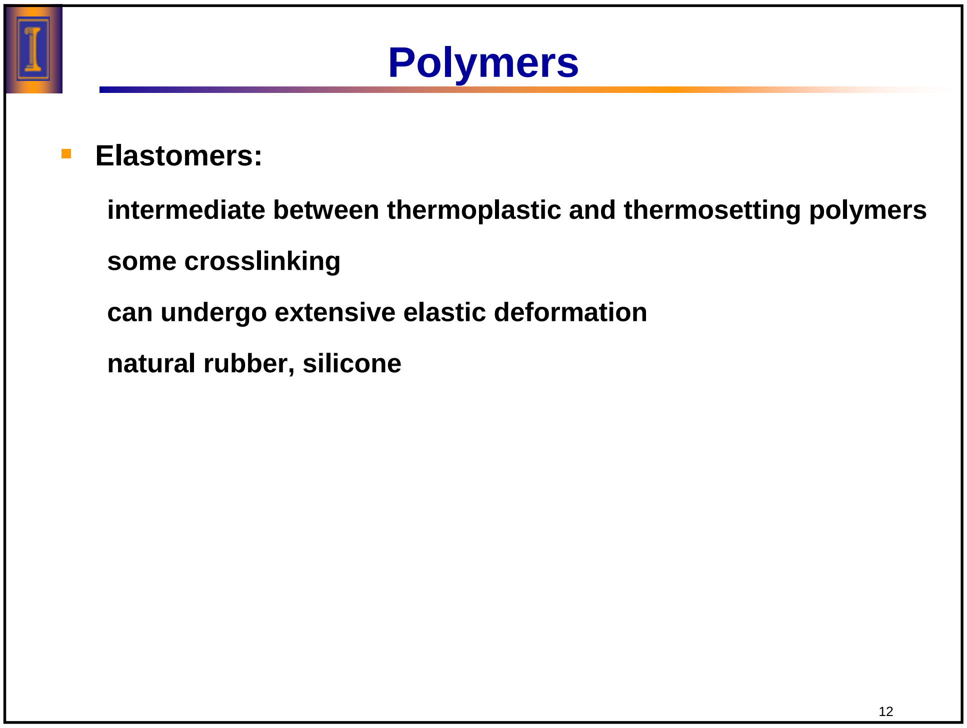
  decomposed when heated

  can not be reformed or recycled

  presence of extensive crosslinks between long chains

  induce decomposition upon heating and renders thermosetting polymers brittle

  epoxy and polyesters



## Polymers

- **Elastomers:**

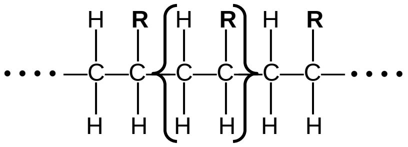
  intermediate between thermoplastic and thermosetting polymers

  some crosslinking

  can undergo extensive elastic deformation

  natural rubber, silicone

# Polymers



| Structure | Source-Based Name | Application |
|---|---|---|
| R = -H | Polyethylene | Plastic |
| R = $-CH_3$ | Polypropylene | Rope |
| R = -Cl | Poly(vinyl chloride) | "Vinyl" |
| X = -H, R = $-C_2H_5$ | Poly(ethyl acrylate) | Latex paints |
| X = $-CH_3$, R = $-CH_3$ | Poly(methyl methacrylate) | Plastic |
| R = -H | Polybutadiene | Tires |
| R = $-CH_3$ | Polyisoprene | Tires |
| X = -F, R = -F | Polytetrafluoroethylene | Teflon® |

# Bulk or Commodity Polymers

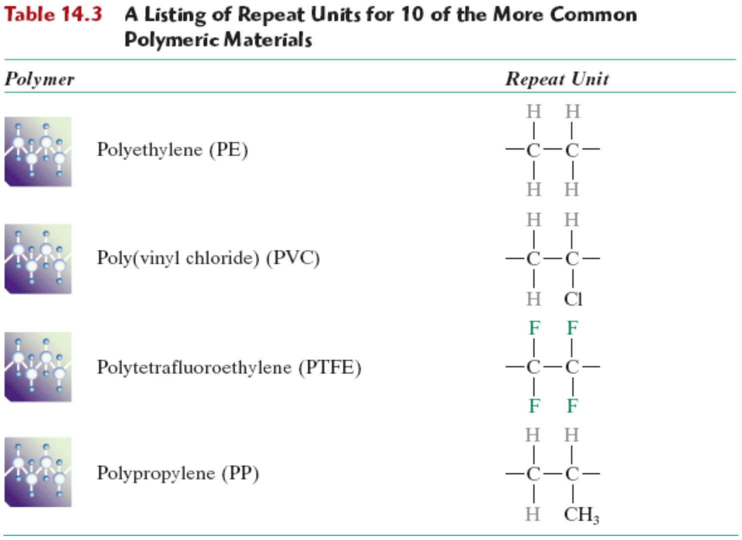
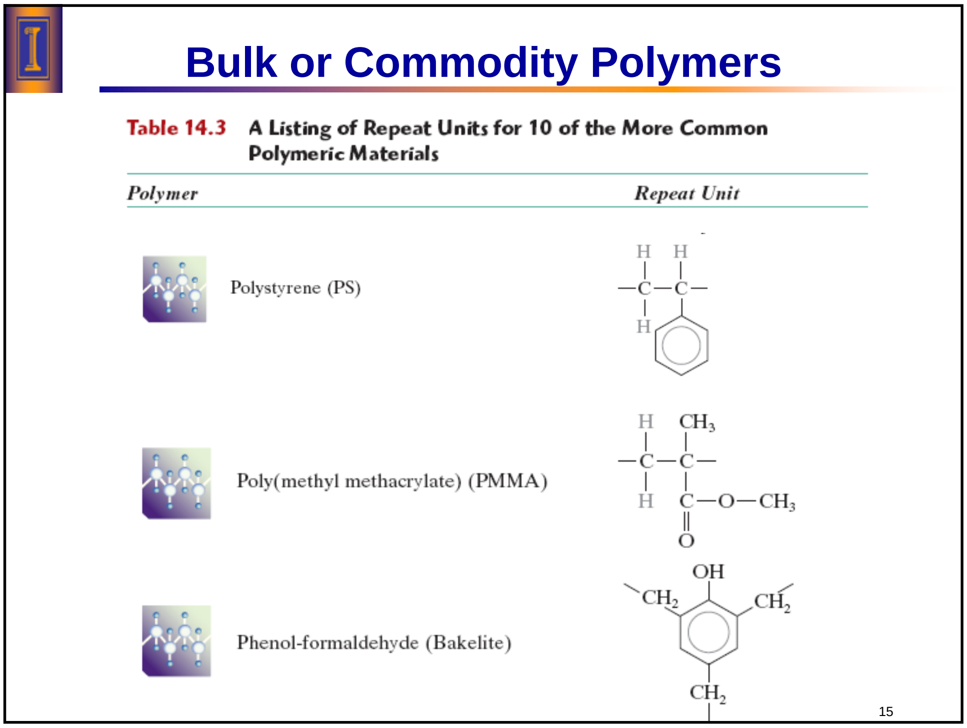


**Table 14.3** A Listing of Repeat Units for 10 of the More Common Polymeric Materials

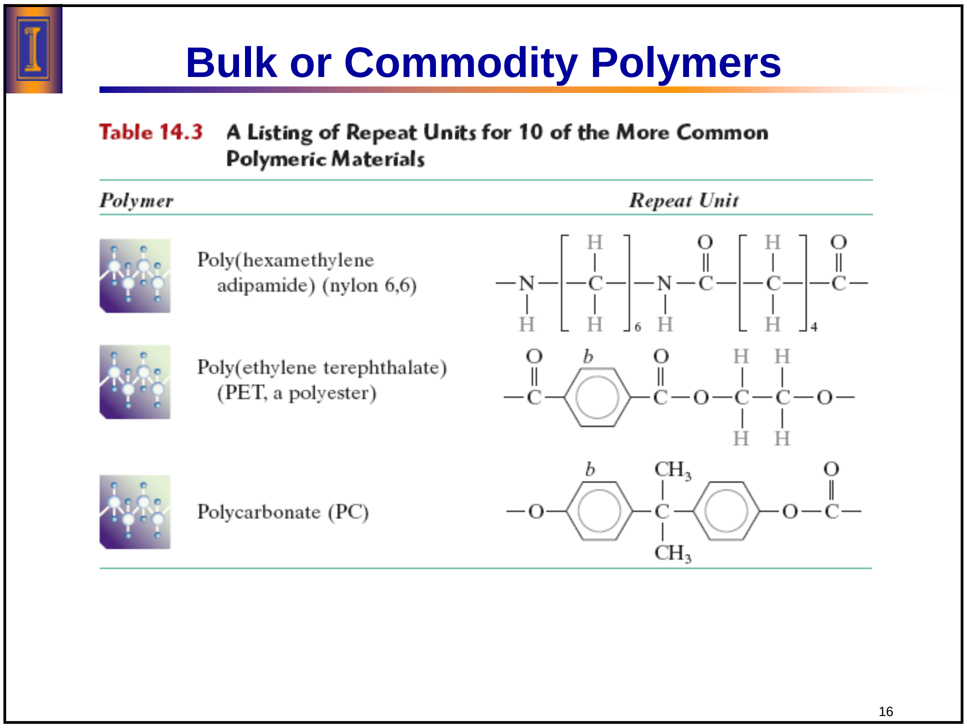
| *Polymer* | *Repeat Unit* |
|---|---|
| Polyethylene (PE) | $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$ |
| Poly(vinyl chloride) (PVC) | $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$ |
| Polytetrafluoroethylene (PTFE) | $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$ |
| Polypropylene (PP) | $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$ |



## Bulk or Commodity Polymers

**Table 14.3** A Listing of Repeat Units for 10 of the More Common Polymeric Materials

| *Polymer* | *Repeat Unit* |
|---|---|
| Polystyrene (PS) | |
| Poly(methyl methacrylate) (PMMA) | |
| Phenol-formaldehyde (Bakelite) | |



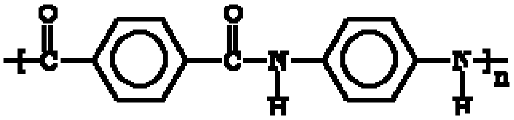
## Bulk or Commodity Polymers

**Table 14.3** A Listing of Repeat Units for 10 of the More Common Polymeric Materials

| *Polymer* | *Repeat Unit* |
|---|---|
| Poly(hexamethylene adipamide) (nylon 6,6) | |
| Poly(ethylene terephthalate) (PET, a polyester) | |
| Polycarbonate (PC) | |

## Advanced Polymers

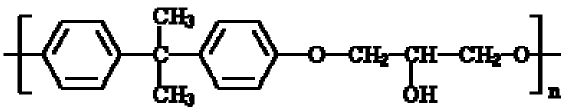
- *Kevlar* **is an aramid polymer:**



- **Chains are stiff and straight.**
- **Highly crystalline polymer, difficult to process.**
- **Melting temperature 500° C**
- **Tensile strength 3.6 *GPa,* about 4x steel!**

## Advanced Polymers

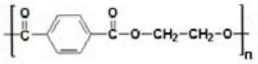
- *Epoxy resin* **is made from the 2-part kits.**



- **It’s the basis of composites like fiberglass, carbon fiber composites etc.**
- **Apart from an excellent glue, it is an important molding compound for rapid prototyping.**
- **Tensile strength 60 MPa**
- **Stiffness 2.6 GPa**

# Recycled Polymers

1
PETE



poly(ethylene terephthalate) (PET)

Invented by J.R. Whinfield and J.T. Dickson, 1940.
Uses: clothing, plastic films, plastic bottles

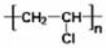
2
HDPE

$-[CH_2-CH_2]_n-$

high-density polyethylene (HDPE)

Invented by Robert L. Banks and J. Paul Hogan, 1951.
Uses: plastics of all kinds, high-strength fibers

3
V



$-[CH_2-CH(Cl)]_n-$

poly(vinyl chloride)

Invented by Waldo Semon, 1926.
Uses: water pipes, LP records, vinyl car tops

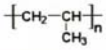
4
LDPE

$-[CH_2-CH_2]_n-$

low-density polyethylene (LDPE)

Invented by Eric Fawcett and Reginald Gibson, 1935.
Uses: plastic films, bags

5
PP

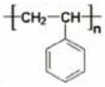


$-[CH_2-CH(CH_3)]_n-$

polypropylene (PP)

Invented by Robert L. Banks and J. Paul Hogan, 1951.
Uses: fibers for rope, indoor-outdoor carpeting, plastics

6
PS



polystyrene (PS)

Invented by Eduard Simon, 1839.
Uses: rigid plastics of all kinds, polystyrene foams
Hermann Staudinger 1922 (Nobel 1953)

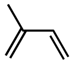
7
OTHER

anything else, including items made from more than one kind of polymer

# Natural Polymers

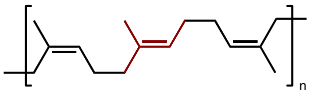
**Monomer**

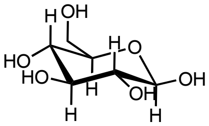
**Polymer**



Isoprene

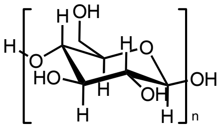
Polyisoprene:
Natural rubber

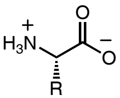




ß-D-glucose

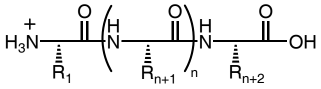
Poly(ß-D-glycoside):
cellulose

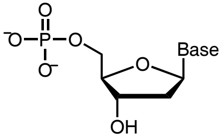




Amino Acid

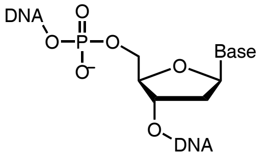
Polyamino acid:
protein





Nucleotide
Base = C, G, T, A

oligonucleic acid
DNA



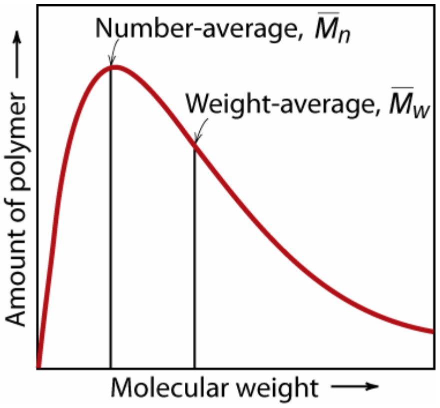
# MOLECULAR WEIGHT

- Molecular weight, $M_i$: Mass of a mole of chains.

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\overline{M}_n = \Sigma x_i M_i$$
$$\overline{M}_w = \Sigma w_i M_i$$

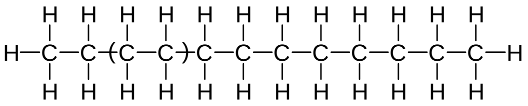
$\overline{M}_w$ is more sensitive to higher molecular masses



Adapted from Fig. 14.4, *Callister 7e.*

# Degree of Polymerization, *n*

$n$ = number of repeat units per chain



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\!\left(\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}\right)\!{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H}$$

$n_i = 6$

$$n_n = \sum x_i n_i = \frac{\overline{M}_n}{\overline{m}} \qquad n_w = \sum w_i n_i = \frac{\overline{M}_w}{\overline{m}}$$

where $\overline{m}$ = average molecular weight of repeat unit

$$\overline{m} = \Sigma \underbrace{f_i}_{\text{Chain fraction}} \underbrace{m_i}_{\text{mol. wt of repeat unit i}}$$

## Polymers: Molecular Weight

- Ratio of $M_w$ to $M_n$ is known as the polydispersity index (PI):

a measure of the breadth of the molecular weight

PI = 1 indicates $M_w = M_n$, i.e. all molecules have equal length (monodisperse)

PI = 1 is possible for natural proteins

Typical synthetic polymers have $1.5 < PI < 5$

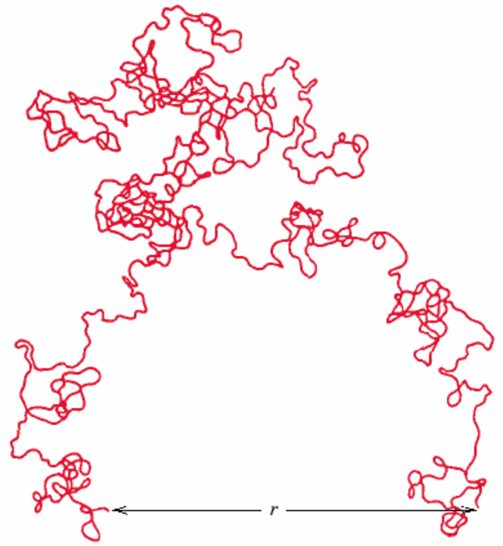
At best, PI = 1.1 can be attained with special techniques.

---

## Polymers: Molecular Weight

- Biomedical applications: $25,000<M_n<100,000$ and $50,000<M_w<300,000$
- Increasing molecular weight increases physical properties (e.g., tensile strength).
- Increasing MW, however, decreases processibility

# End to End Distance, *r*



Adapted from Fig. 14.6, *Callister 7e.*

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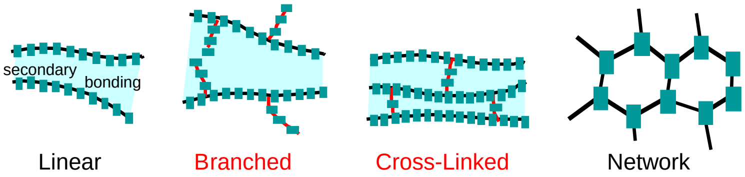
# Molecular Structures

- Covalent chain configurations and strength:



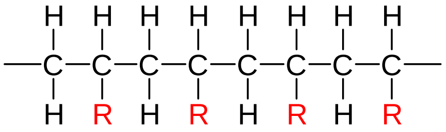
Direction of increasing strength

Adapted from Fig. 14.7, *Callister 7e.*

# Tacticity

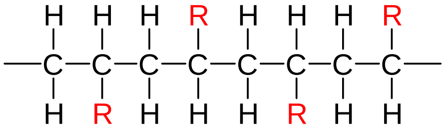
Tacticity – stereoregularity of chain

**isotactic** – all R groups on same side of chain



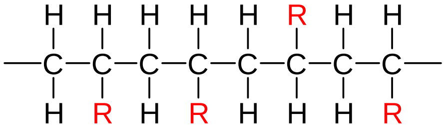
$$\begin{array}{ccccccccccccccccc} & H & & H & & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & R & & H & & R & & H & & R & & H & & R & \end{array}$$

**syndiotactic** – R groups alternate sides



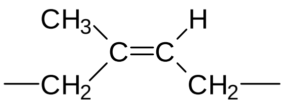
$$\begin{array}{ccccccccccccccccc} & H & & H & & H & & R & & H & & H & & H & & R & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & R & & H & & H & & H & & R & & H & & H & \end{array}$$

**atactic** – R groups random



$$\begin{array}{ccccccccccccccccc} & H & & H & & H & & H & & H & & R & & H & & H & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & R & & H & & R & & H & & H & & H & & R & \end{array}$$

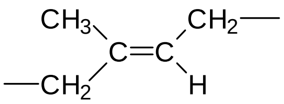
# cis/trans Isomerism



cis

cis-isoprene
(natural rubber)

bulky groups on same side of chain



trans

trans-isoprene
(gutta percha)

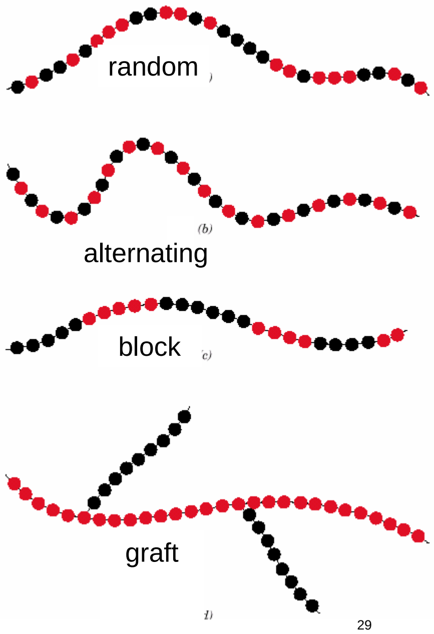
bulky groups on opposite sides of chain

# Copolymers

two or more monomers polymerized together

- random – A and B randomly vary in chain
- alternating – A and B alternate in polymer chain
- block – large blocks of A alternate with large blocks of B
- graft – chains of B grafted on to A backbone

A – ●  B – ●



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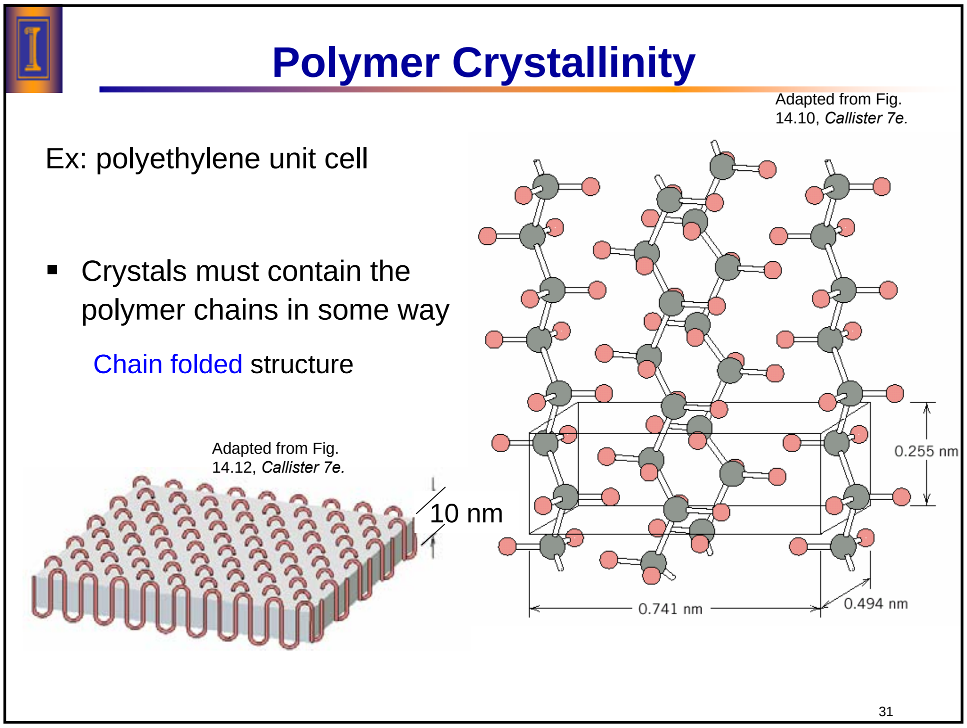

## Polymer Crystallinity

Ex: polyethylene unit cell

- Crystals must contain the polymer chains in some way

Chain folded structure

Adapted from Fig. 14.12, *Callister 7e*.

Adapted from Fig. 14.10, *Callister 7e.*

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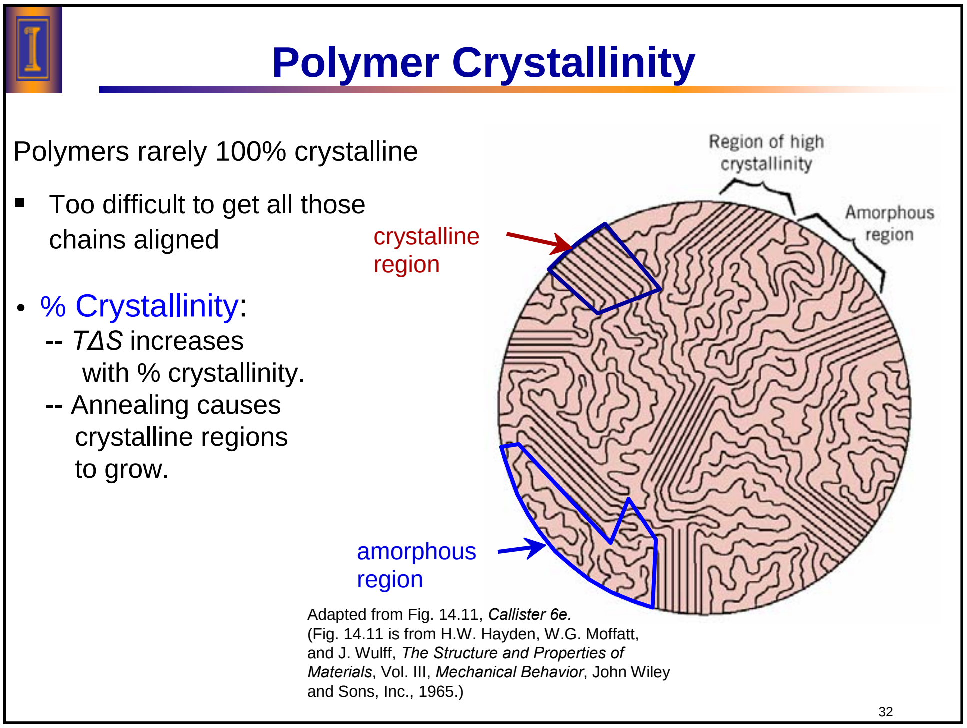


## Polymer Crystallinity

Polymers rarely 100% crystalline

- Too difficult to get all those chains aligned

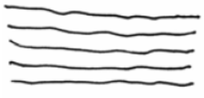
- % Crystallinity:
  - -- $T\Delta S$ increases with % crystallinity.
  - -- Annealing causes crystalline regions to grow.

Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 is 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.)

# Polymer Crystallinity

- **LDPE = Low density polyethylene**
  - branched chains
  - low density
  - amorphous structure

- **HDPE - high density polyethylene**
  - linear chains
  - high density
  - crystalline structure
  - higher MP
  - stronger than LDPE



**Polyethylene (PE)**

**five density grades: ultrahigh, high, low, linear low and very low density**

**UHMWPE and HDPE more crystalline**

**UHMWPE has better mechanical properties, stability and lower cost**

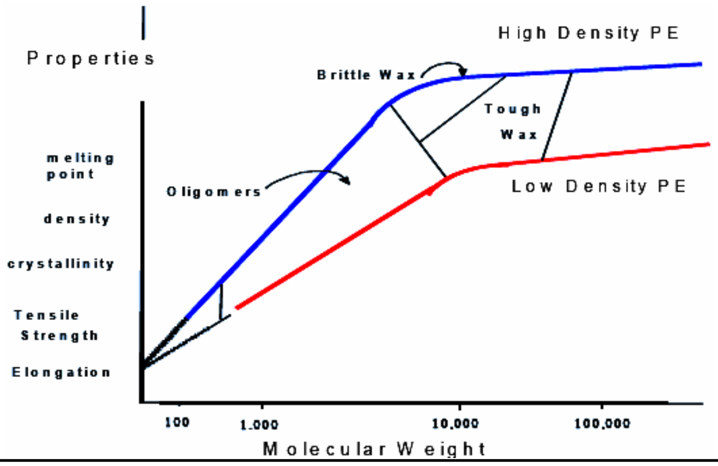
**UHMWPE can be sterilized**

# Polyethylene vs. MW

**5 density grades: ultrahigh, high, low, linear low and very low density**

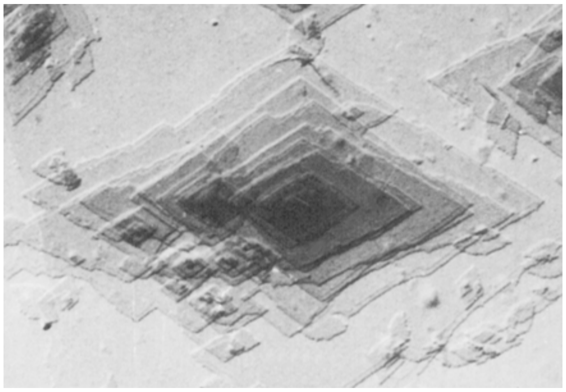
**UHMWPE and HDPE more crystalline**

**UHMWPE has best mechanical properties and stability.**



## Polymer Crystal Forms

- Single crystals – only if slow careful growth

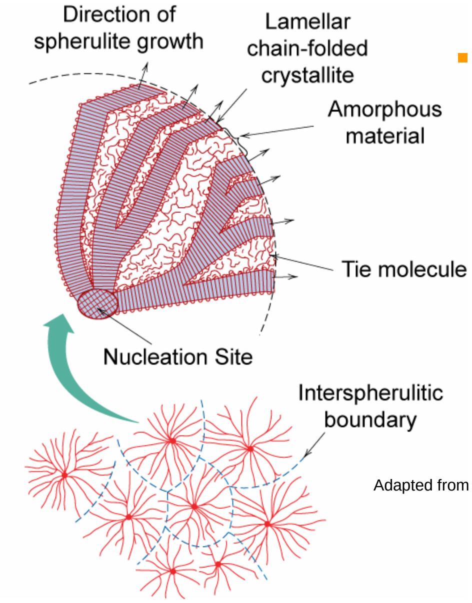


Adapted from Fig. 14.11, *Callister 7e.*

## Polymer Crystal Forms

- Spherulites – fast growth –

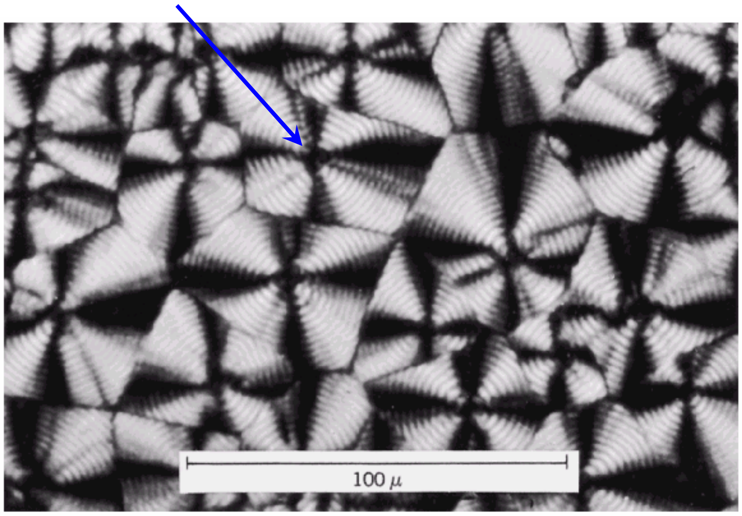
Nuc



Adapted from Fig. 14.13, *Callister 7e.*

## Spherulites – crossed polarizers

Maltese cross



Adapted from Fig. 14.14, *Callister 7e*.

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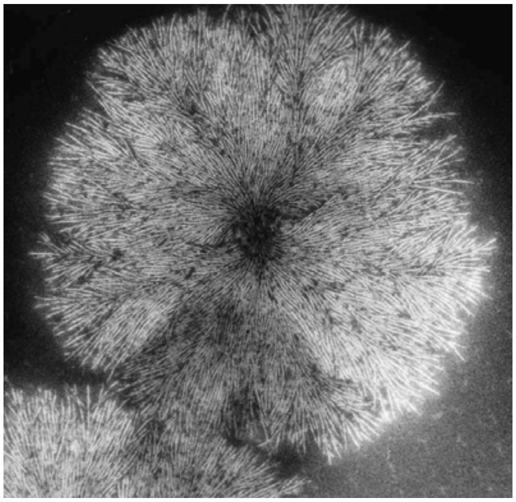
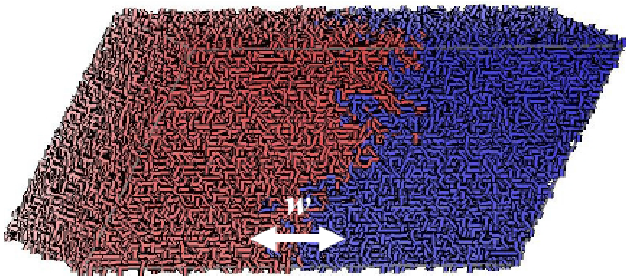
## Spherulites – TEM

lamellar crystallites 10 nm thick extend radially



# Polymer Blends:  Microstructure



w ~ 1 to 3 nm

In general, polymers are NOT soluble in each other:
even polyethylene vs. deuterated polyethylene!

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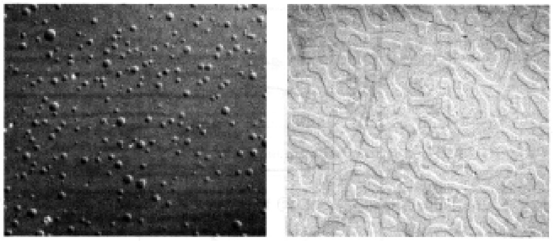
# Polymer Blends:  Microstructure

- Very characteristic microstructures can be observed in polymer blends which have separated by the two means



Nucleation and growth    Spinodal decomposition