Polymers

Recap of Basic Concepts

Poly........mer

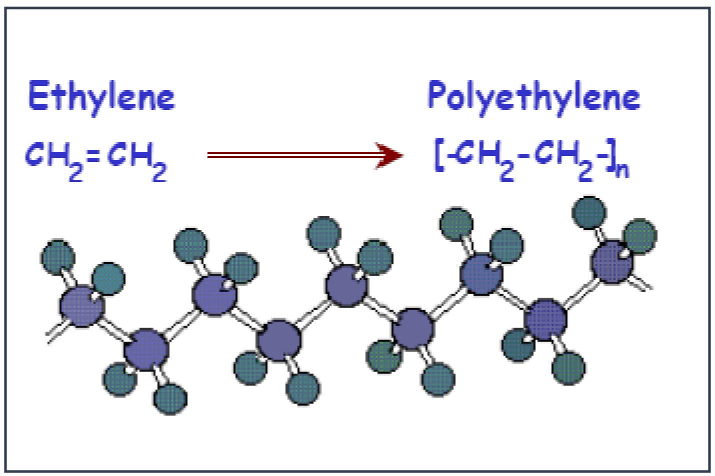
many *units*

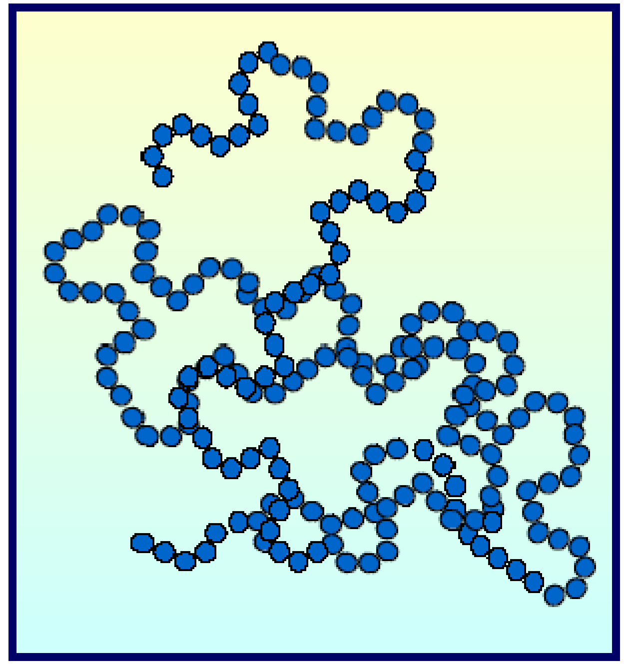
—M—M—M—M—M—M—

or

$-(M)_n-$

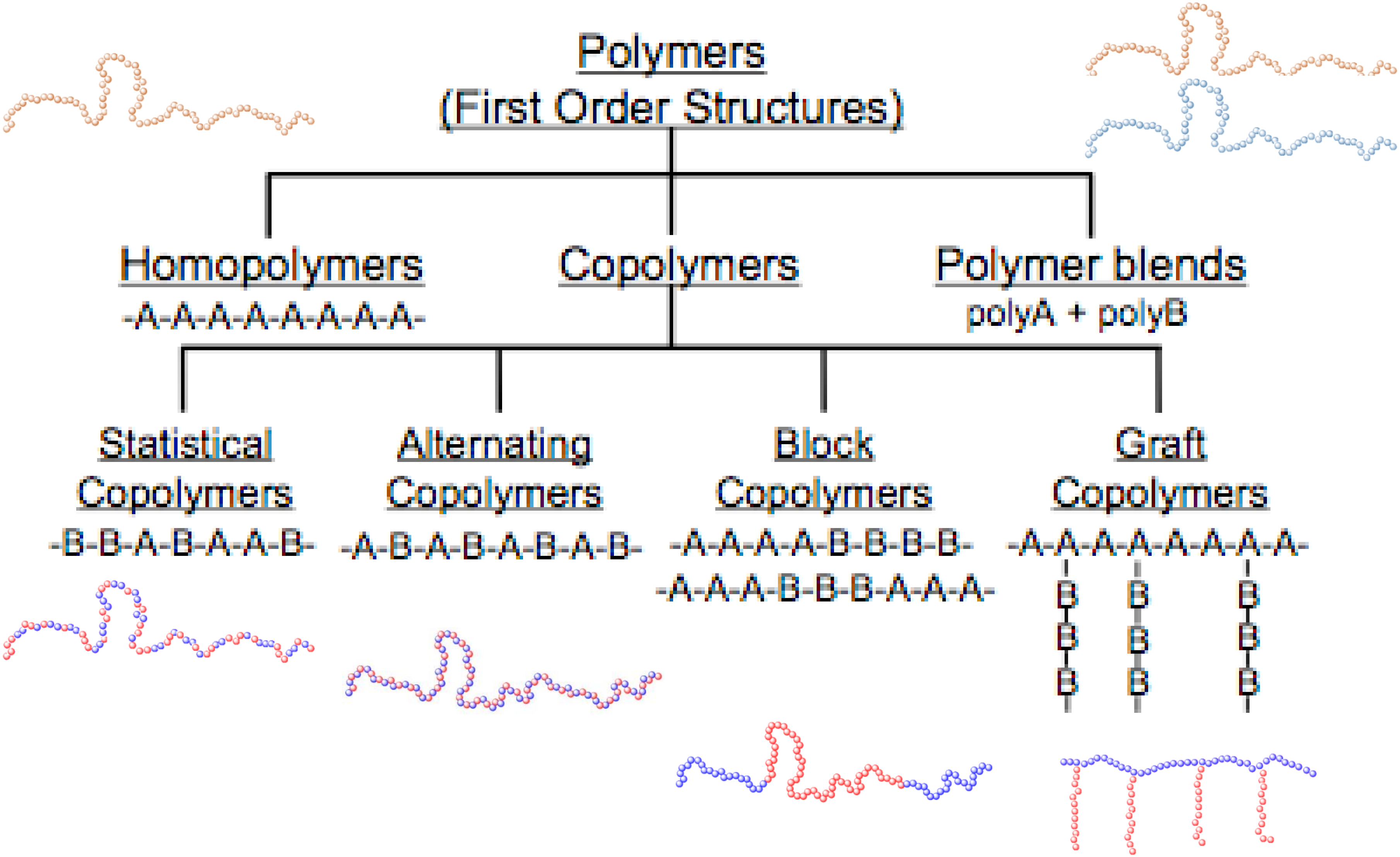
- Long chain molecules that consists of many covalently linked repeating units
- Extraordinary range of properties



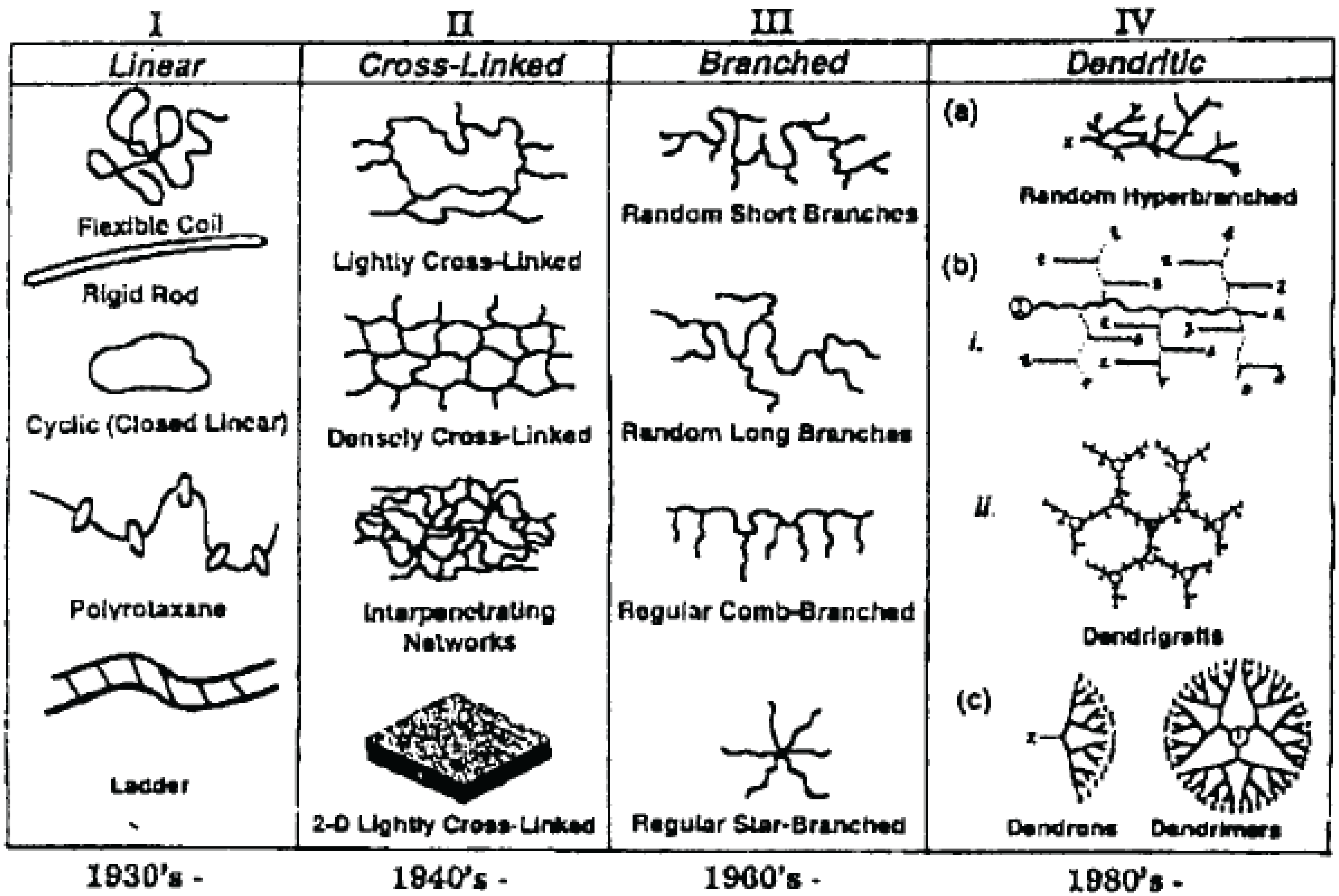


- Consider this chain of beads as Polyethylene where each bead represents an ethylene unit
- There are 200 beads in this chain – What is the molecular weight of this polymer?

Polymers – Various Architectures



Polymers – Various Architectures



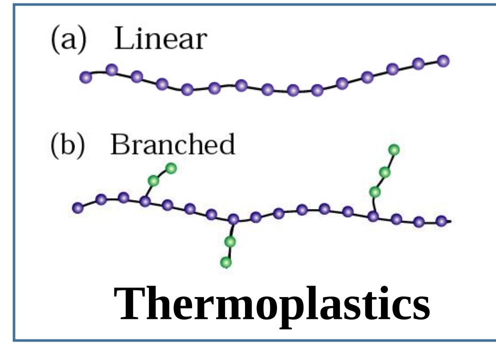
Source: R. Esfand, D.A. Tomalia, A.E. Beezer, J.C. Mitchell, M. Hardy, C. Orford, Polymer Preprints, 41 (2), 1324 (2000)

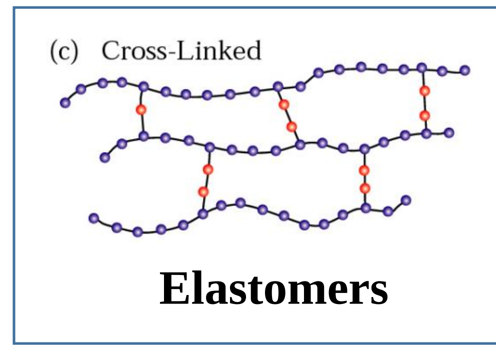
Types and Broad Categories of Synthetic Polymers

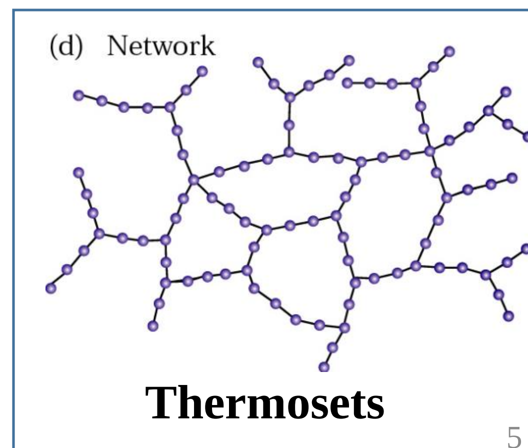
Based on flow and deformation behavior

Polymers

- **Not cross-linked** ("thermoplastic")
  Product will flow when heated
  Product has many molecules that flow past each other.
  - **Amorphous**
  - **Semi-crystalline**
- **Cross-linked**
  Product will not flow when heated;
  Entire product is one large molecule
  - **"Thermosets"**
    Often glassy, high density of crosslinks
  - **"Elastomers"**
    Rubbery, stretchable







Types and Broad Categories of Synthetic Polymers

Based on transition temperature

Polymers

(at any given temperature)

Polymer below Tg of chains

(Glassy)

Amorphous/ semi-crystalline

Ex (RT): PS/ PET

Polymer above Tg of chains

(Rubbery)

Amorphous/ semi-crystalline

Ex (RT): Polyisoprene/ HDPE

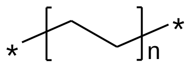
Polymer near Tg of chains

(Leathery)

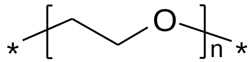
Amorphous/ semi-crystalline

Ex (RT): Polynorbornene/ plasticized PVC

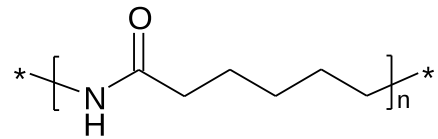
Polymers – Some Examples



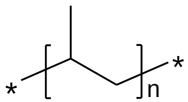
Polyethylene
Poly(methylene)



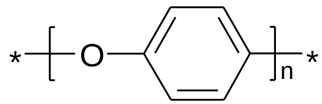
Poly(oxyethylene)



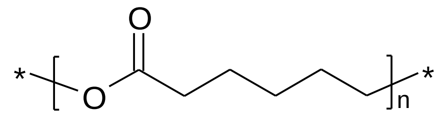
Poly[imino(1-oxohexamethylene)]



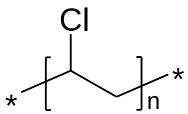
Poly(propylene)



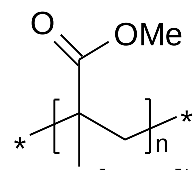
Poly(oxy-1,4-phenylene)



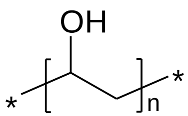
Poly[oxy(1-oxohexamethylene)]



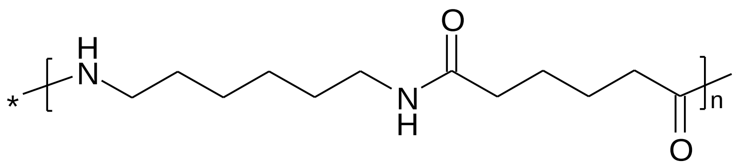
Poly(1-chloroethylene)



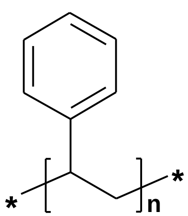
Poly[(1-methoxycarbonyl)-1-methylethylene]



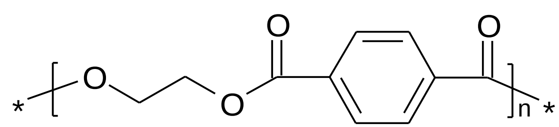
Poly(1-hydroxyethylene)



Poly(iminohexamethyleneiminoadipoyl)



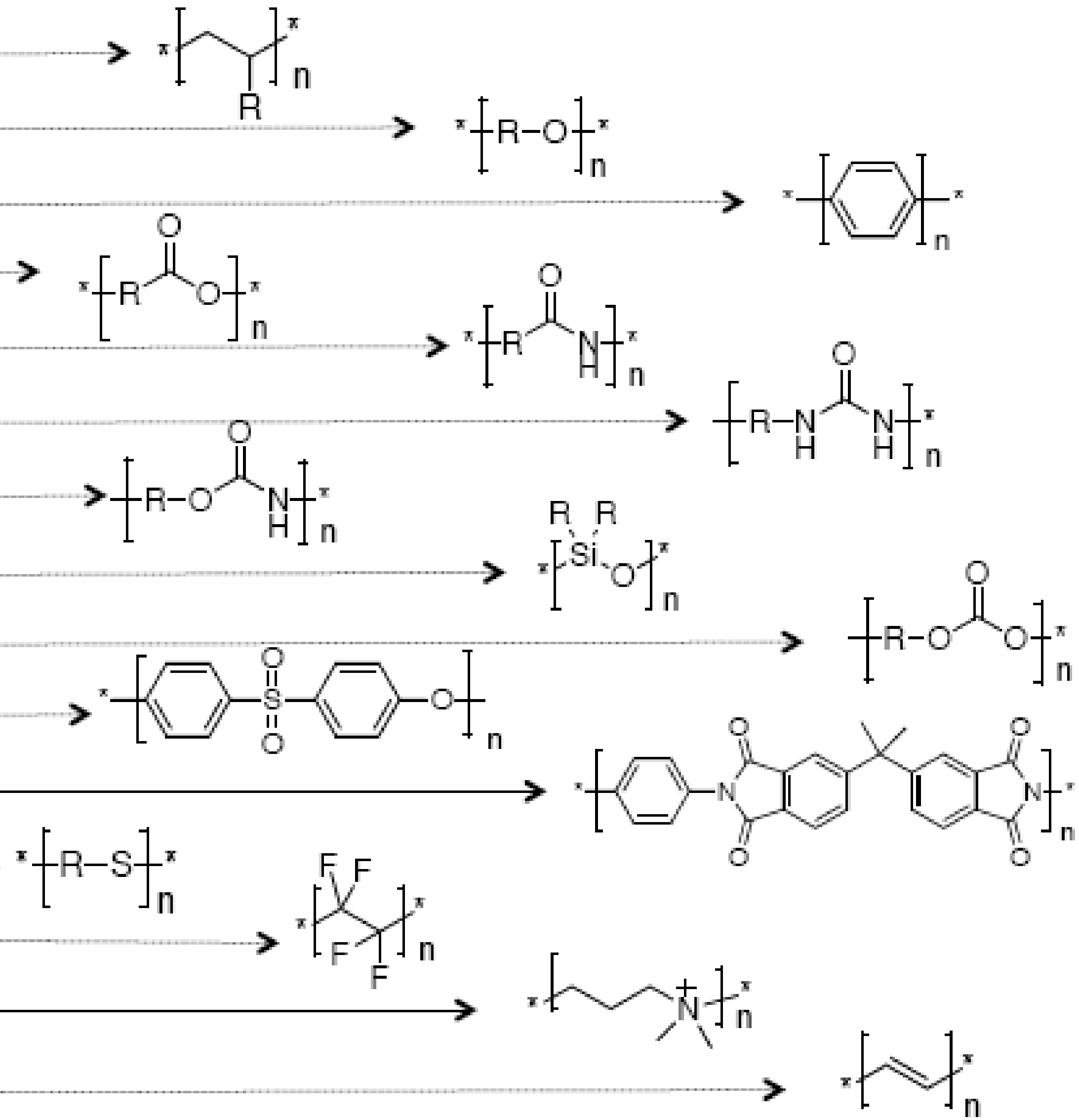
Poly(1-phenylethylene)



Poly(oxyethyleneoxyterephthaloyl)

Polymer Functionality

Vinyl Polymers
Polyethers
Polyarylenes
Polyesters
Polyamides
Polyureas
Polyurethanes
Polysiloxanes
Polycarbonates
Polysulfones
Polyimides
Polysulfides
Fluoropolymers
Polyionomers
Polyacetylenes

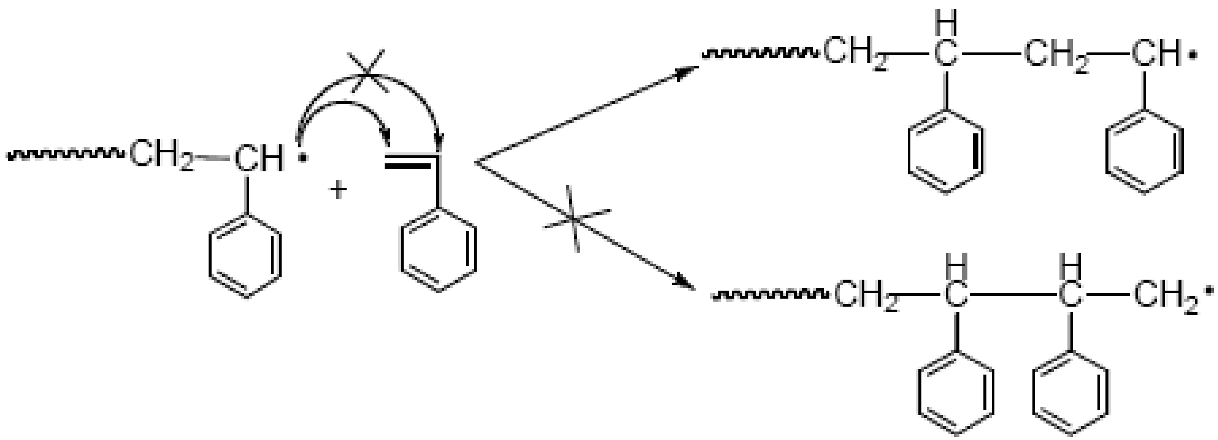


Polymer IUPAC Nomenclature - Copolymers

Copolymers are named by the arrangement of the comonomers

Type of Connection	Name
Unspecified	Poly(A-*co*-B)
Obeys statistical laws	Poly(A-*stat*-B)
Random	Poly(A-*ran*-B)
Alternating	Poly(A-*alt*-B)
Block	Poly(A-*block*-B)
Graft	Poly(A-*graft*-B)

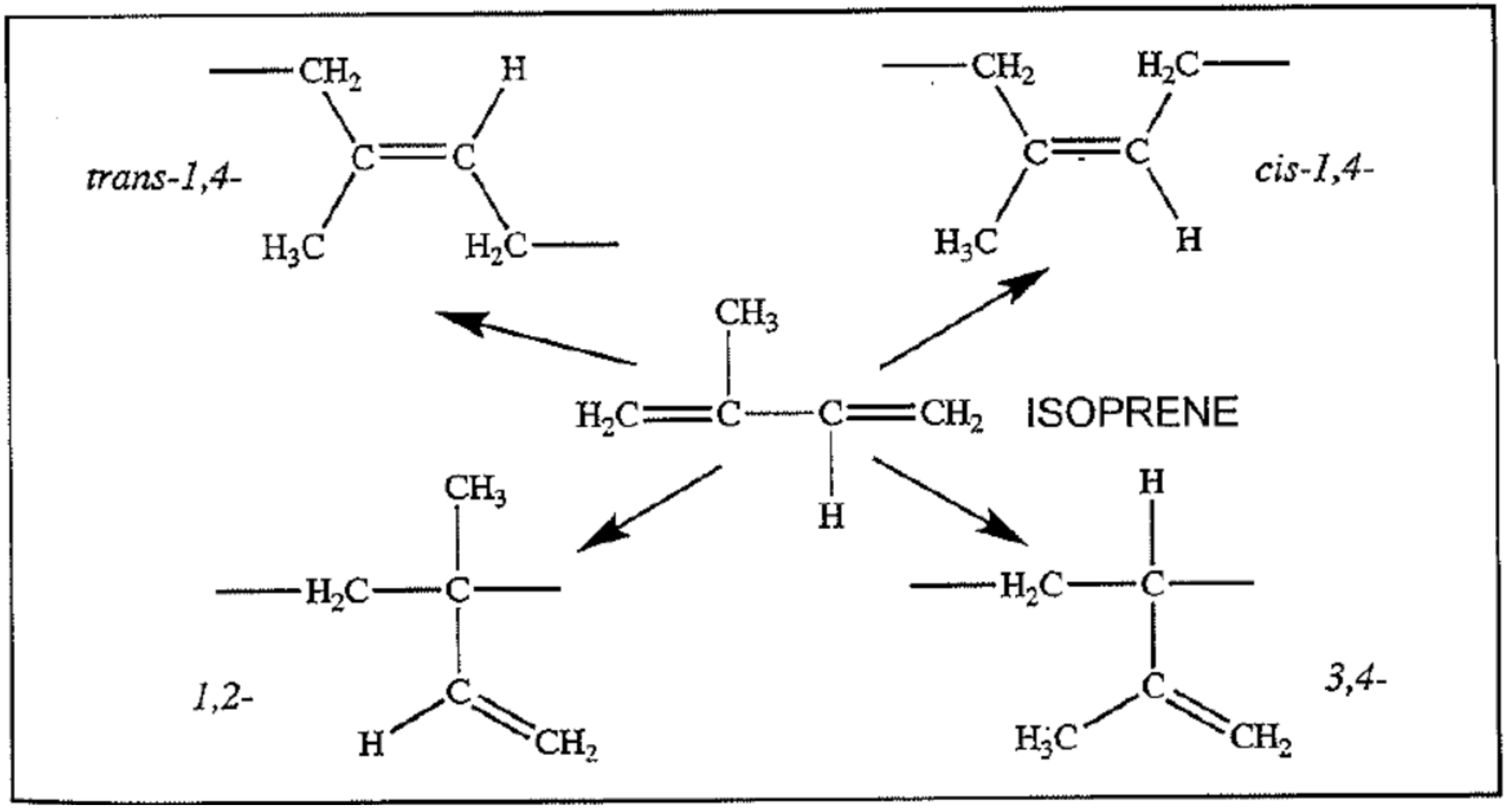
Sequence Isomerism



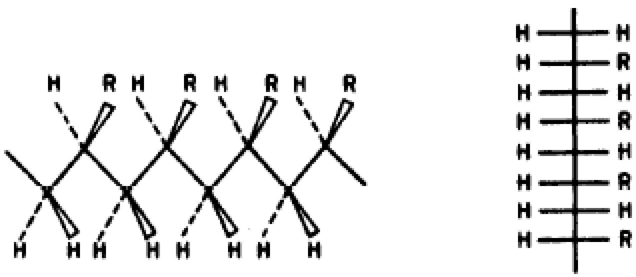
head-to-tail

head-to-head

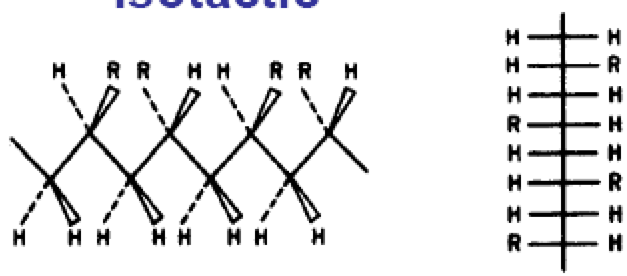
Structural Isomerism



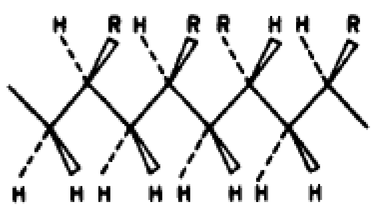
Stereoisomerism

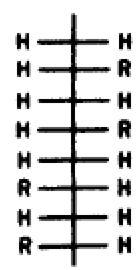


Isotactic



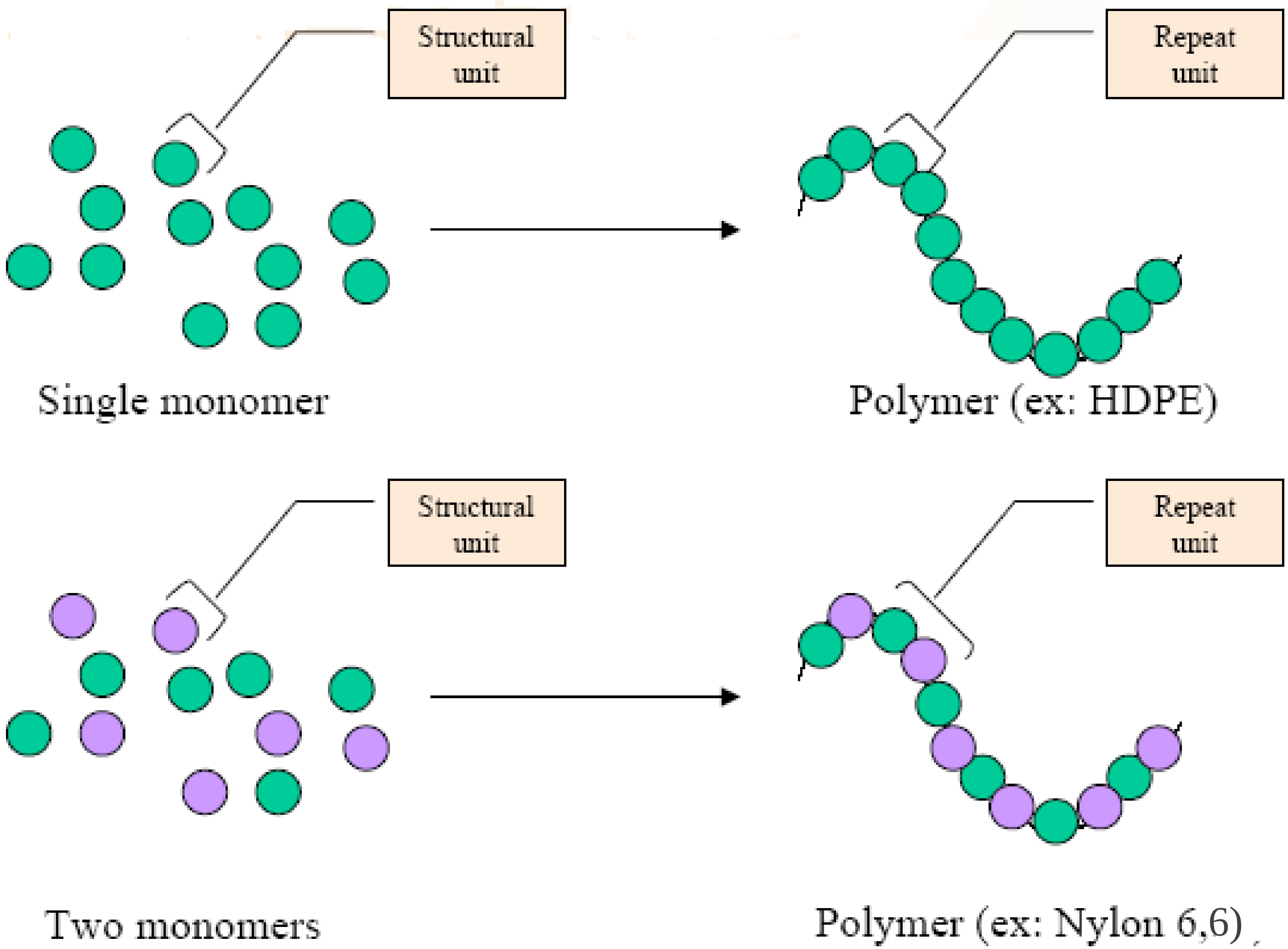
Syndiotactic





Atactic

Degree of Polymerization (DP)



Degree of polymerization (DP) = Number of SU

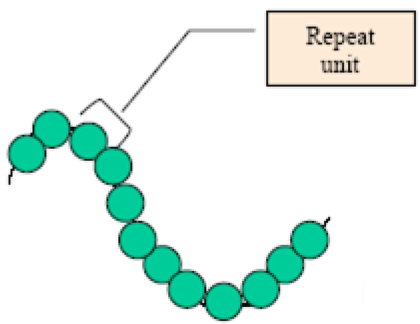
Chain vs. Step Growth Polymerization

Chain Length and Molecular Weight - Molar Mass of Polymer

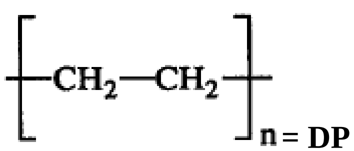
Molecular weight (or strictly, Molar Mass) – Mass of 1 mole of polymer and usually quoted in units of g/mol

Molecular weight of a chain = [Degree of Polymerization (DP)] x [Molecular weight of average RU]

Chain Growth Polymers

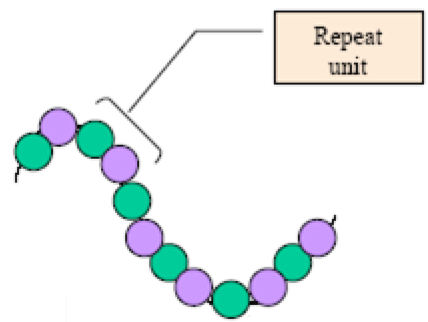


Mol Wt = DP x M_0

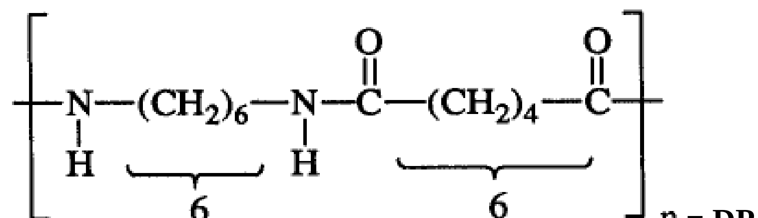


Polyethylene

Step Growth Polymers



Mol Wt = DP x (M_0/2)



Nylon 6,6

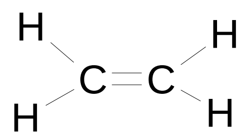
Where M_0 = Molecular weight of average RU

Polymers – Molecular Weight

All synthetic and most of natural polymers have molecular weight distribution – **WHY?**

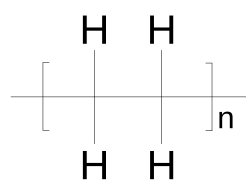
Example

Ethylene



M = 28 g/mol

n = 1000



M = 28 000 g/mol

n = 5000 M = **??????** g/mol

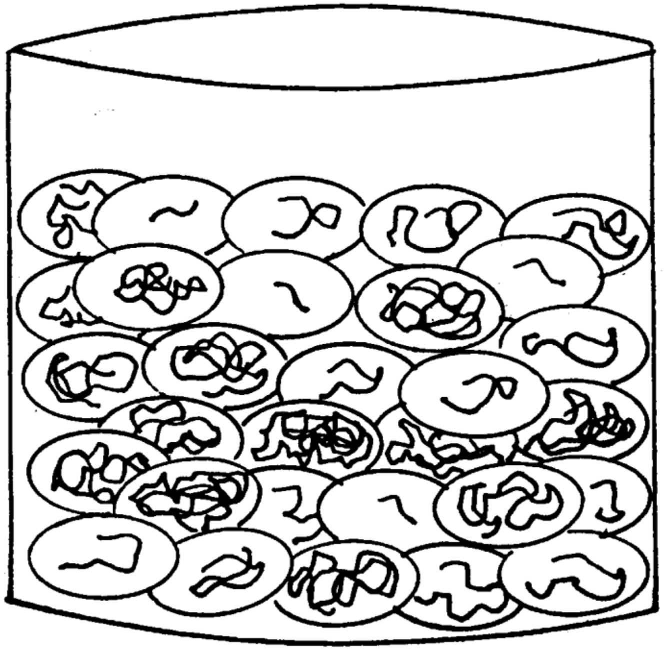
n = 100,000 M = **??????** g/mol

Molecular weights are presented as average values

Number Average Molecular Weight

Number average molecular weight, $\overline{M}_n$

- Each capsule contains a polymer molecule
- All capsules are of same size independent of the size of polymer molecule
- All polymer molecules have same chance to be picked up to determine molecular weight



Colligative properties

- Vapour-phase and membrane osmometry
- Depression in freezing point
- Elevation in boiling point
- End group analysis
- MALDI

Number Average Molecular Weight

Common arithmatic average value

<u>Example</u>	1 mol	P_1	M = 1 x 10^5 g/mol
	1 mol	P_2	M = 2 x 10^5 g/mol
	1 mol	P_3	M = 3 x 10^5 g/mol

$$\overline{M}_n = \frac{1x(1x10^5) + 1x(2x10^5) + 1x(3x10^5)}{3} = \frac{6x10^5}{3} = 2x10^5\, g/mol$$

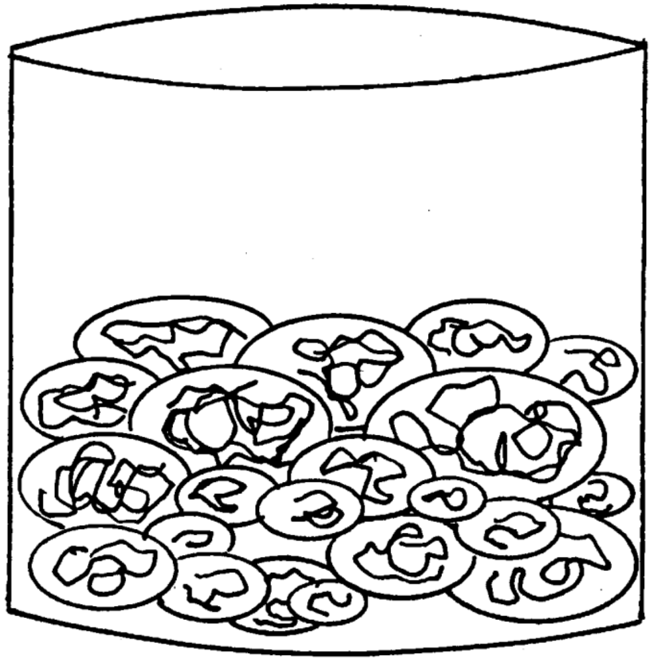
$\overline{M}_n$ = total weight of samples / number of molecules

$$\overline{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i}$$

Weight Average Molecular Weight

Weight average molecular weight, $\overline{M}_w$

- Capsules having longer polymer chains are bigger than those having small polymer chains
- Bigger polymer molecules have high chance to be picked up to determine molecular weight



- Light scattering
- Ultracentrifugation
- MALDI

Weight Average Molecular Weight

- Individual polymer chains are considered
- $\overline{M}_w$ is more dependent on high molecular weight polymer chains than $\overline{M}_n$, which just looks at number of polymer chains

<u>Example</u>	1 mol	P_1	$M = 1 \times 10^5$ g/mol
	1 mol	P_2	$M = 2 \times 10^5$ g/mol
	1 mol	P_3	$M = 3 \times 10^5$ g/mol

$$\overline{M}_w = \frac{1x\left(1x10^5\right)^2 + 1x\left(2x10^5\right)^2 + 1x\left(3x10^5\right)^2}{1x(1x10^5) + 1x(2x10^5) + 1x(3x10^5)} = \frac{14x10^{10}}{6x10^5} = 2.33x10^5\, g/mol$$

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i}$$

Z-Average Molecular Weight

Z-average molecular weight, $\overline{M}_z$

- Even more statistical weight to high molecular weight chains
- Ultracentrifugation

Example	1 mol	P_1	$M = 1 \times 10^5$ g/mol
	1 mol	P_2	$M = 2 \times 10^5$ g/mol
	1 mol	P_3	$M = 3 \times 10^5$ g/mol

$$\overline{M}_z = \frac{1x(1x10^5)^3 + 1x(2x10^5)^3 + 1x(3x10^5)^3}{1x(1x10^5)^2 + 1x(2x10^5)^2 + 1x(3x10^5)^2} = \frac{36x10^{15}}{14x10^{10}} = 2.57x10^5\, g/mol$$

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} M_i^3 N_i}{\sum_{i=1}^{\infty} M_i^2 N_i}$$

<u>Polydispersityindex (PDI) *or* Molecular weight distribution (MWD)</u>

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

- Globular proteins — PDI = 1
- Random polymerization — PDI ~ 2
- Living anionic polymerization — PDI < 1.1