Lecture 11:
Polymer structure and bonding

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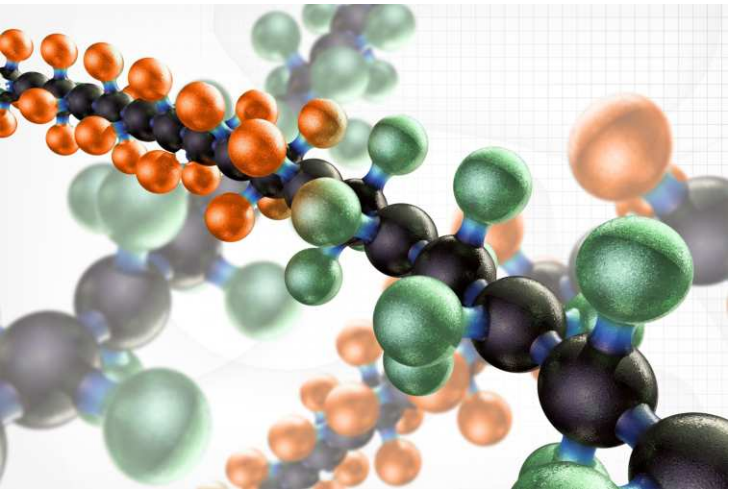
Polymers are very different from what we've studied so far – but equally important!

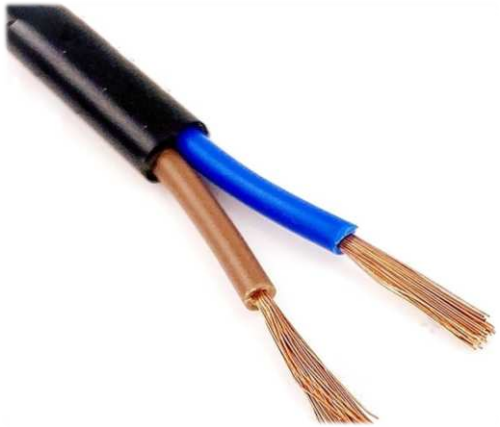




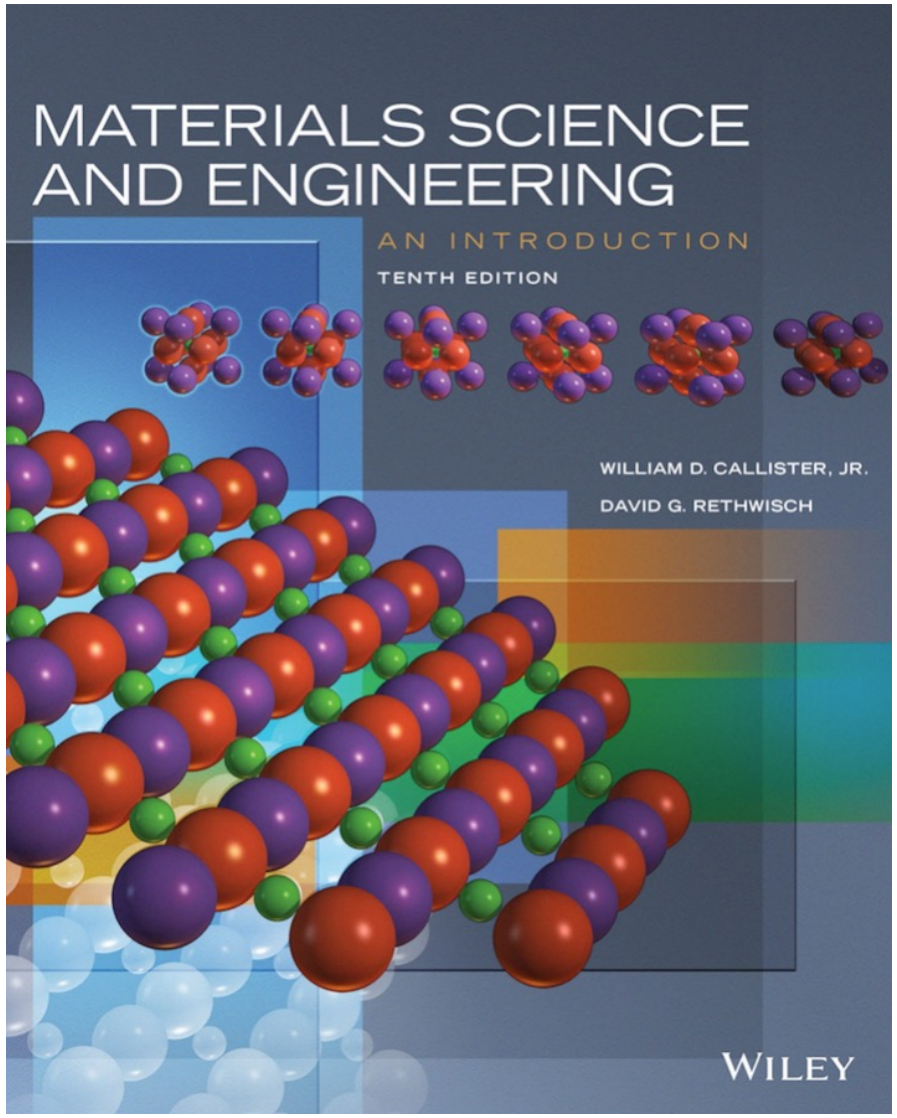








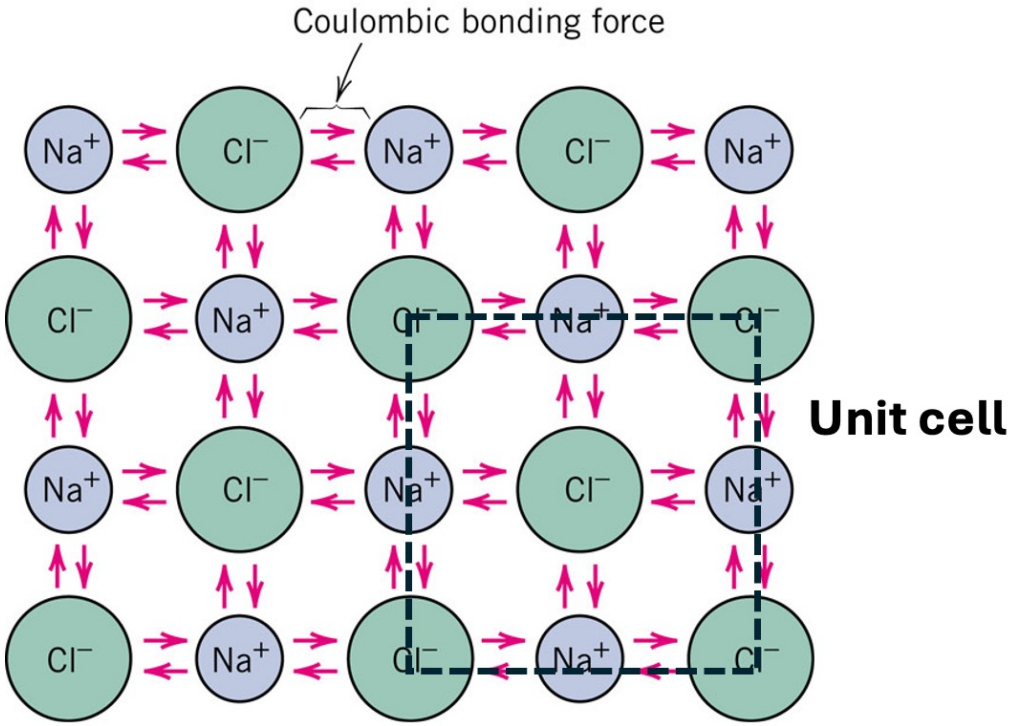
Reading for this subject

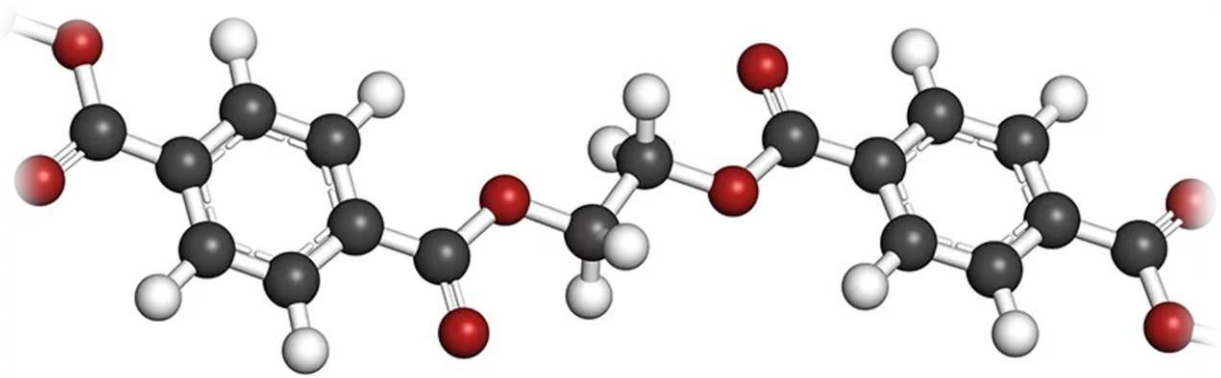


Chapter 14 Polymer Structures

This discussion will closely follow **Chapter 14** of Callister, **pages 480-506** of the 10th edition.

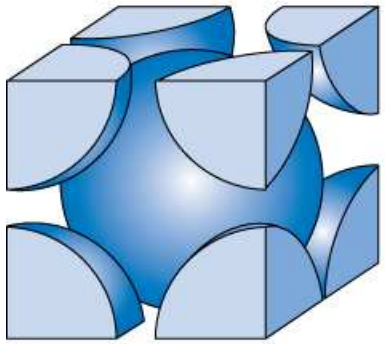
What makes polymers unique: Structure

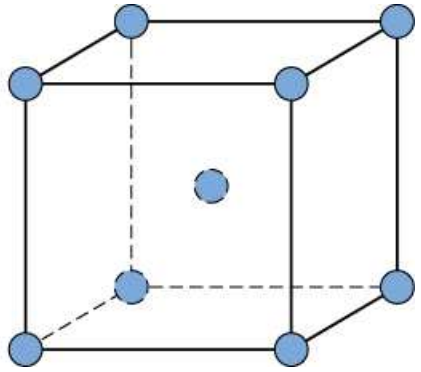


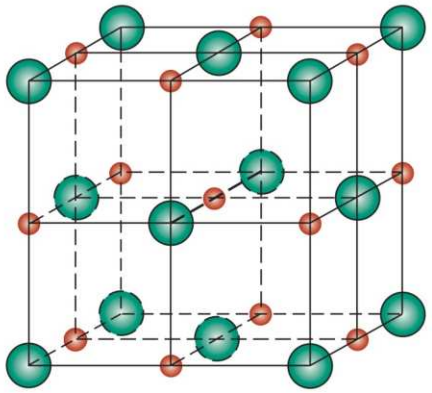


In contrast, **polymers generally consist of long 1D chains**

Metals and ceramics have 3D structures composed of unit cell building blocks

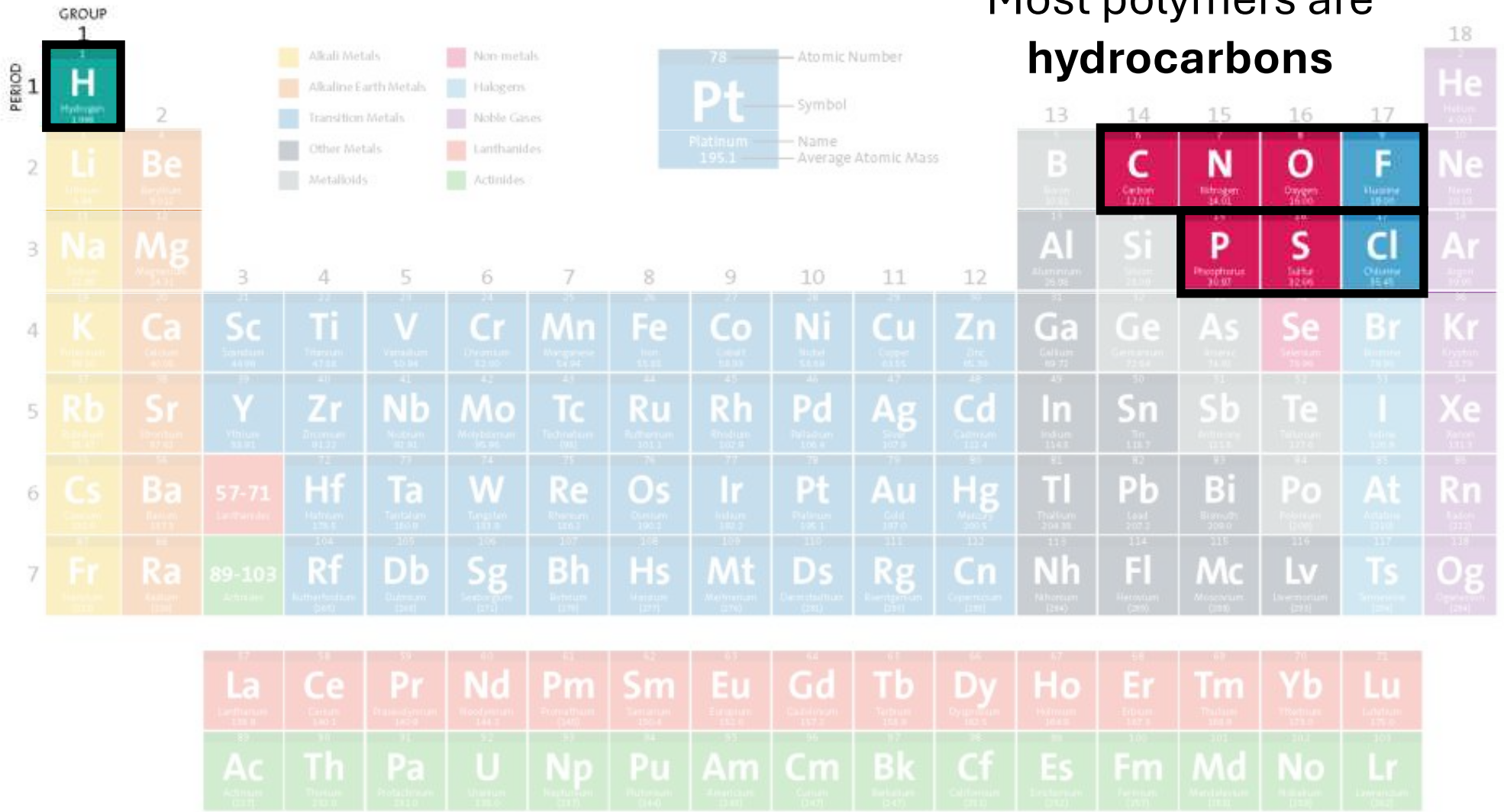




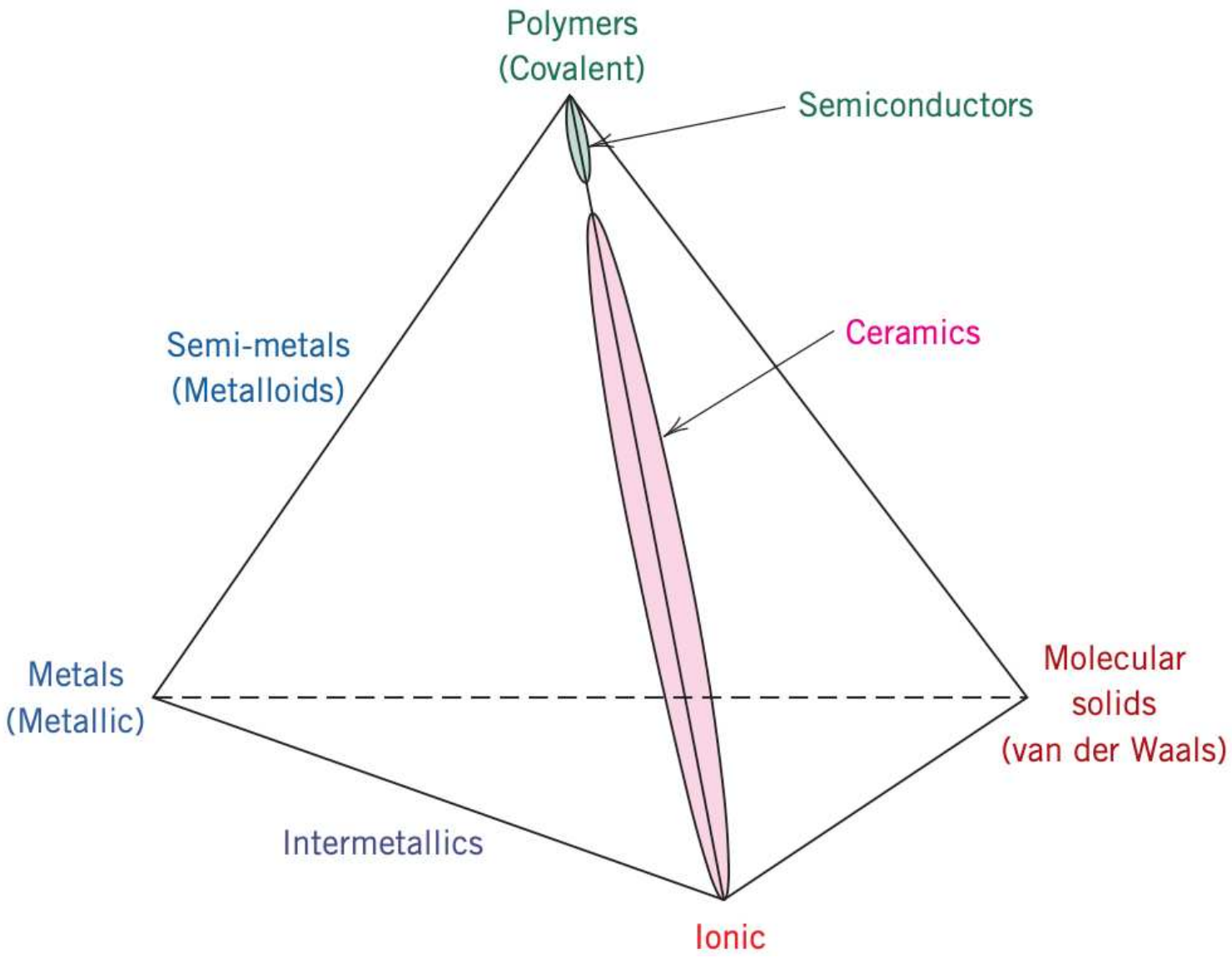


What makes polymers unique: Composition

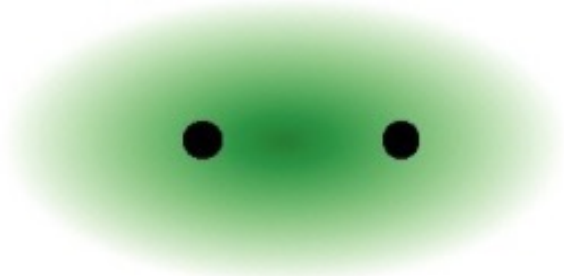
Most polymers are **hydrocarbons**



What makes polymers unique: Bonding



Covalent bonds form the backbone of all polymers



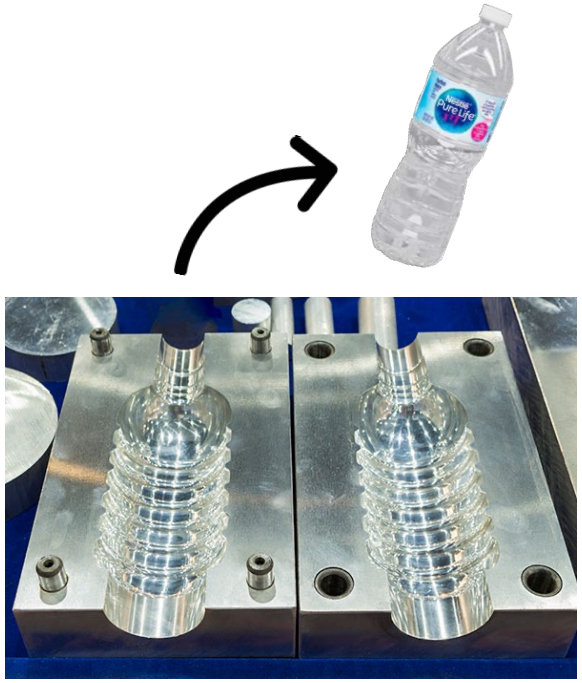
Electrons are shared

What makes polymers unique: Applications

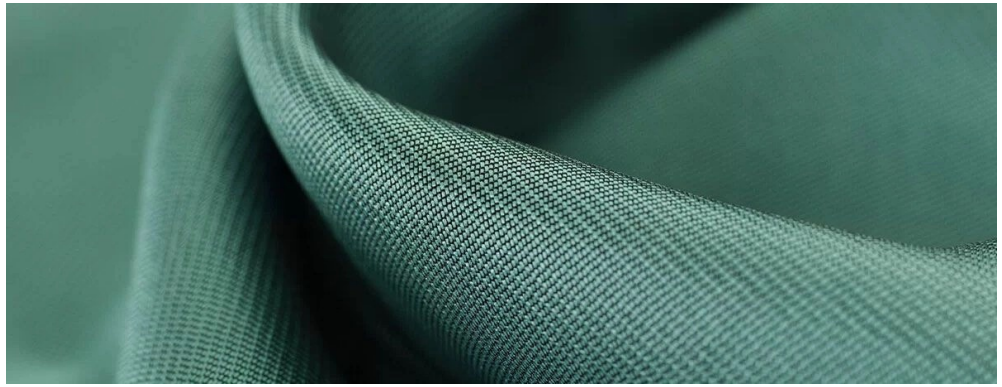
Properties:

- Lightweight but often strong
- Easily melted/formed at low *T*
- Relatively inexpensive

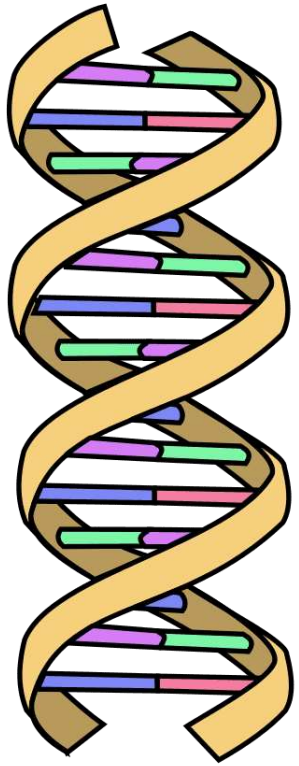






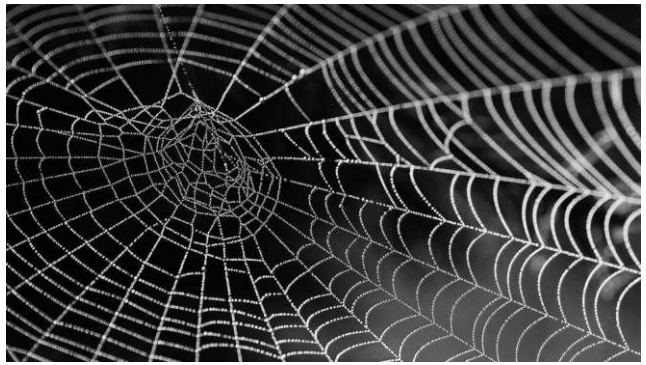


Many polymers also occur naturally



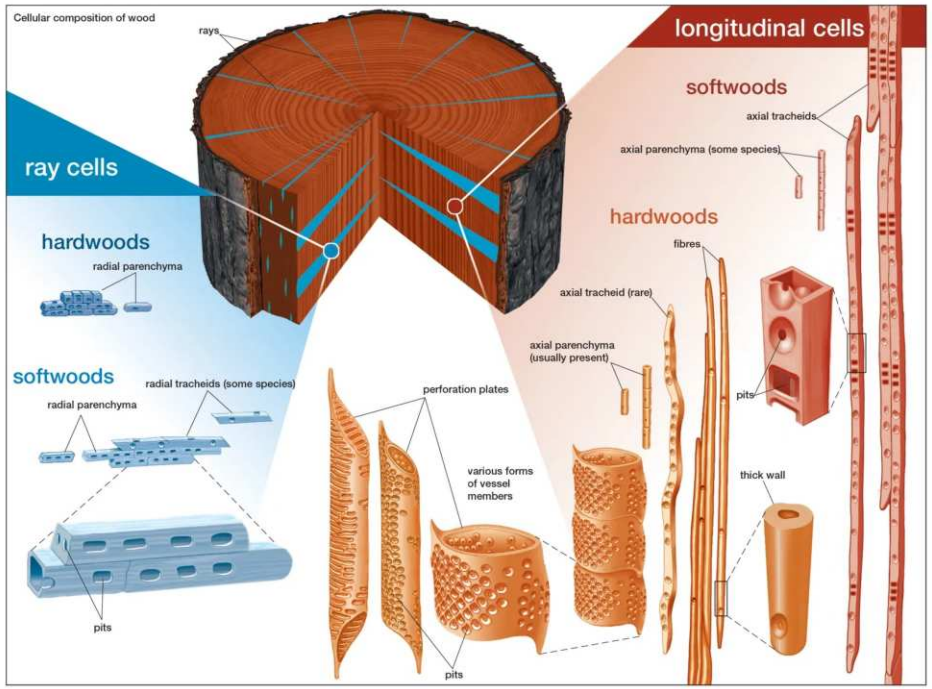
DNA

Spider silk

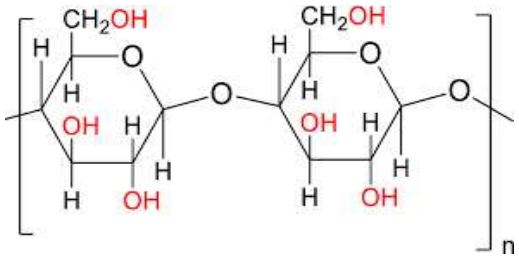




Wool



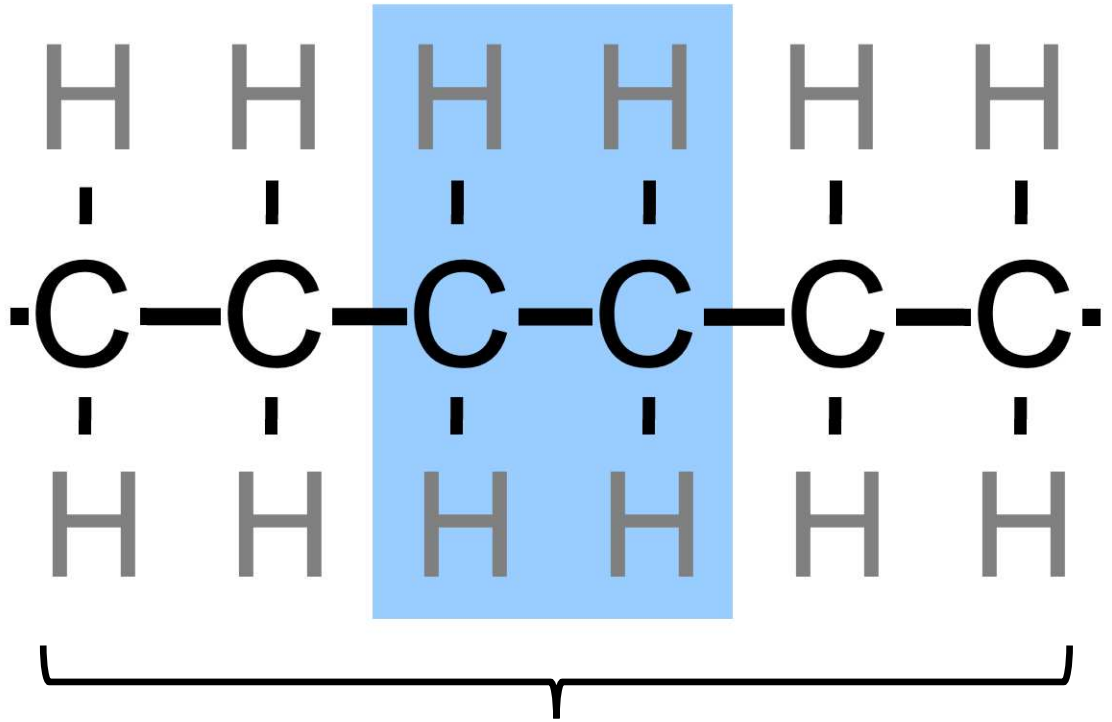
Cellulose



Poly = Many Mer = repeat unit

Ethylene (C_2H_4) is the repeat unit (*monomer*)

This is a **hydrocarbon;** the case for many polymers



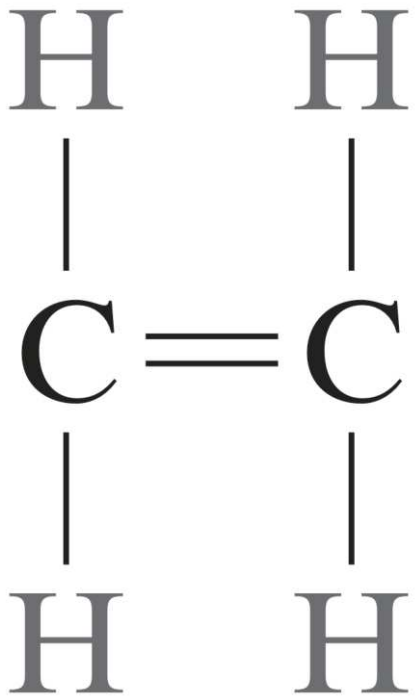


HDPE

The entire chain is called *poly*ethylene (PE)

Bond formation in polymers

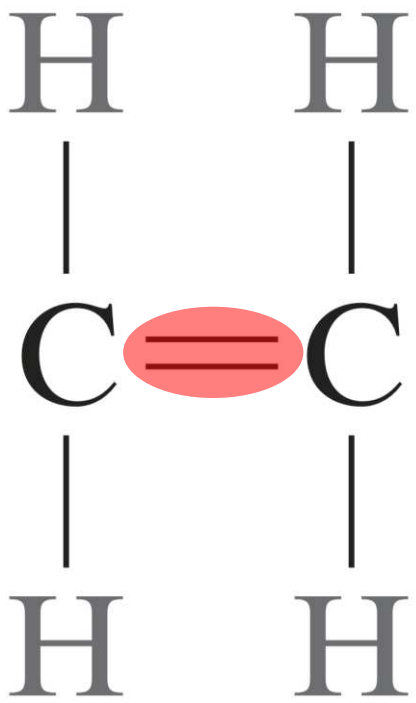
Ethylene (C_2H_4)



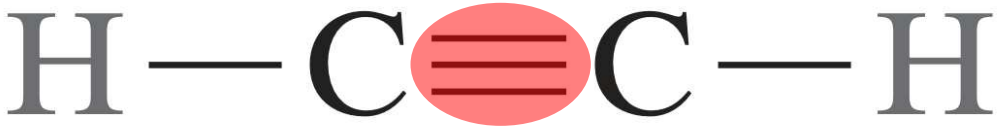
If ethylene is a stable molecule on its own, why does a polymer form?

Bond formation in polymers

Ethylene (C_2H_4)



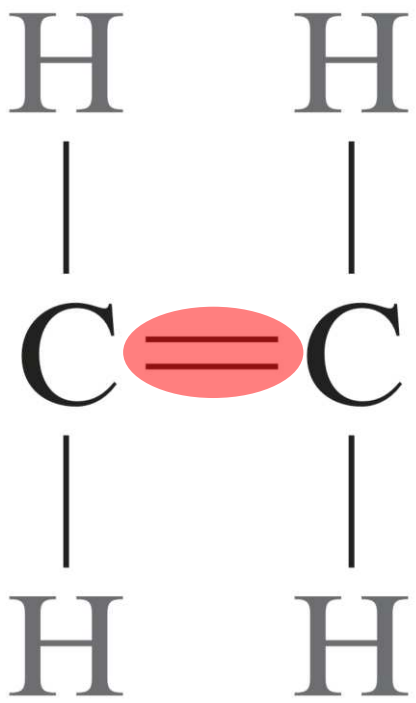
Molecules with double or triple bonds are termed ***unsaturated***.



Another example of an unsaturated molecule.

Bond formation in polymers

Ethylene (C_2H_4)

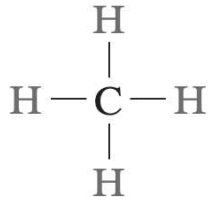
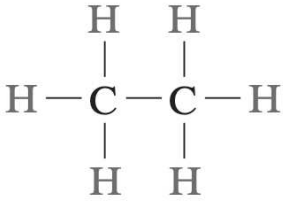
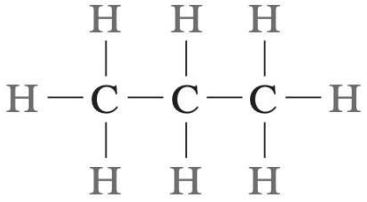


Molecules with double or triple bonds are termed ***unsaturated***.

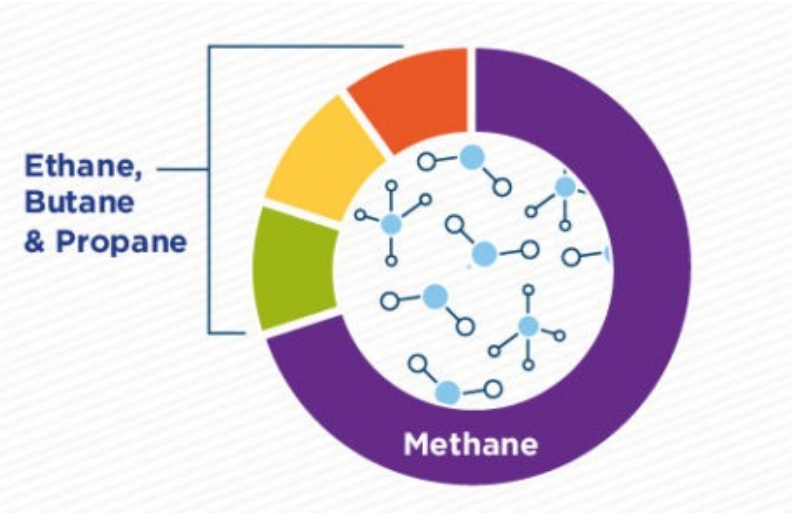
Nature would prefer to attach additional atoms onto this molecule, forming a ***saturated*** molecule with only single bonds.

Bond formation in polymers

Examples of **saturated hydrocarbons**: the paraffin family (C_nH_{2n+2})

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		–164
Ethane	C_2H_6		–88.6
Propane	C_3H_8		–42.1
Butane	C_4H_{10}		–0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0



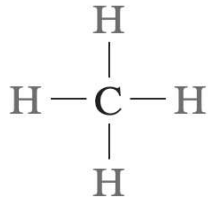
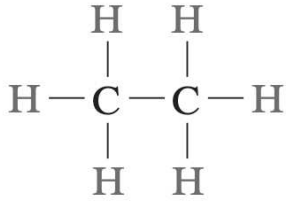
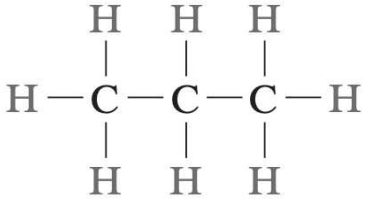


Combustion of **natural gas** provides heat + energy

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

Bond formation in polymers

Examples of **saturated hydrocarbons**: the paraffin family (C_nH_{2n+2})

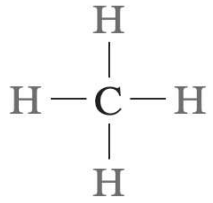
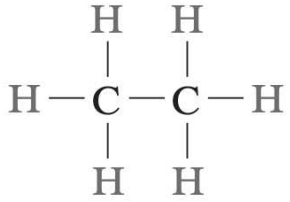
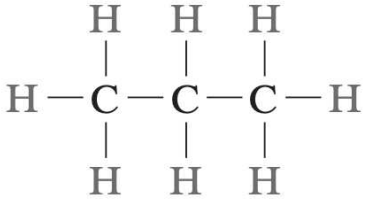
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		–164
Ethane	C_2H_6		–88.6
Propane	C_3H_8		–42.1
Butane	C_4H_{10}		–0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

Notice the relatively **low boiling points**, which increase with molecular weight.

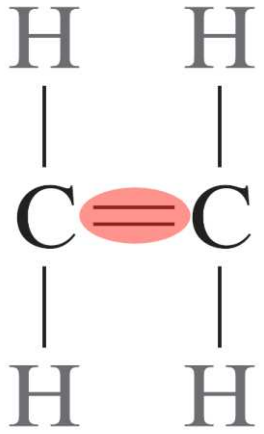
Covalent bonds within each molecule are strong, but there is only weak vdW bonding in between molecules.

Bond formation in polymers

Examples of **saturated hydrocarbons**: the paraffin family (C_nH_{2n+2})

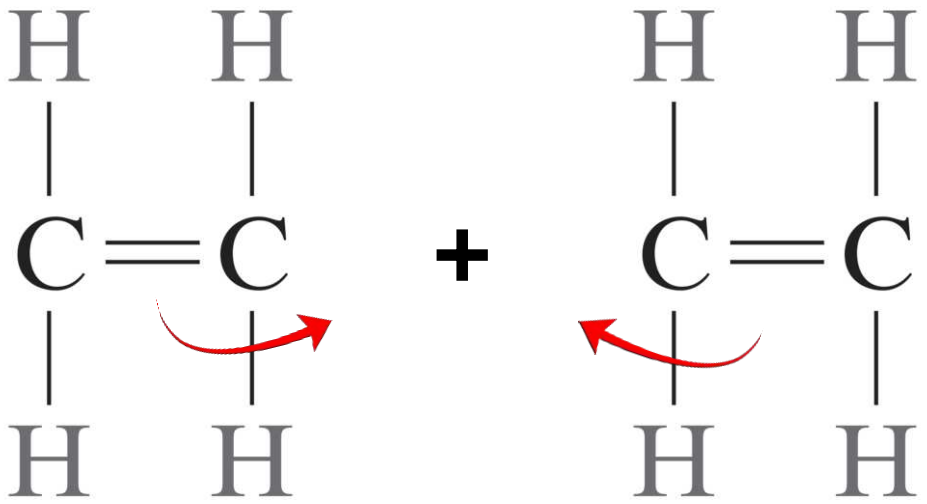
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		–164
Ethane	C_2H_6		–88.6
Propane	C_3H_8		–42.1
Butane	C_4H_{10}		–0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

These molecules do *not* want to form polymers, since they are already saturated.



But this can form a polymer… How?

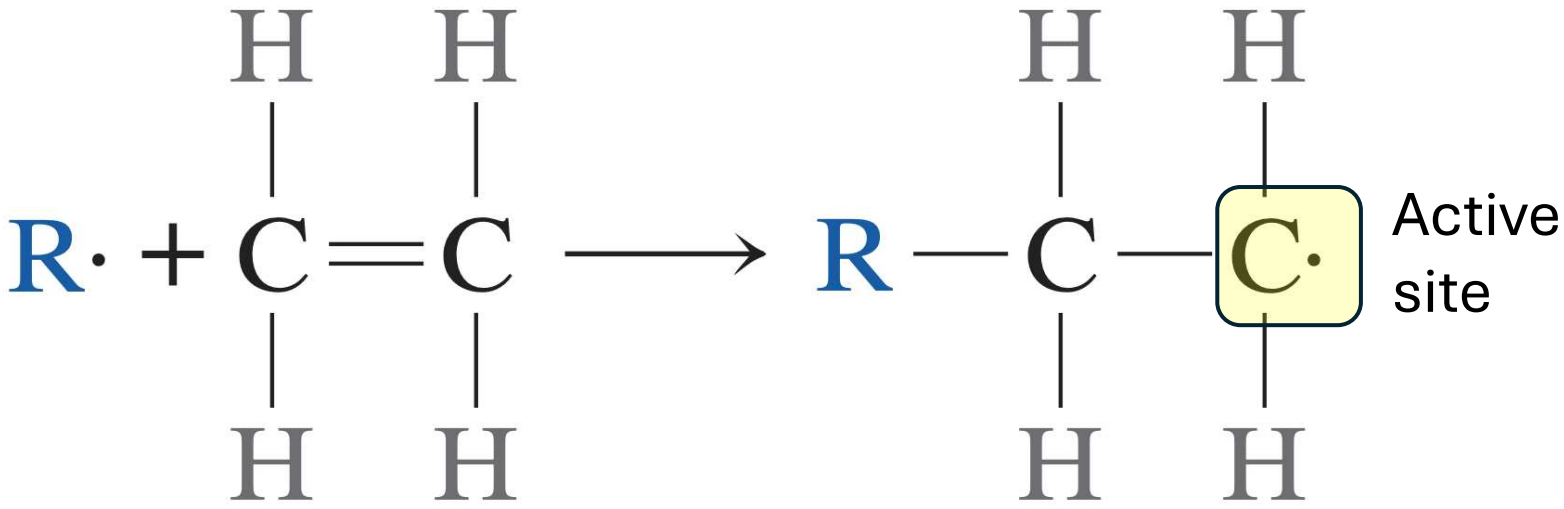
Bond formation in polymers



→ **Polyethylene(?)**

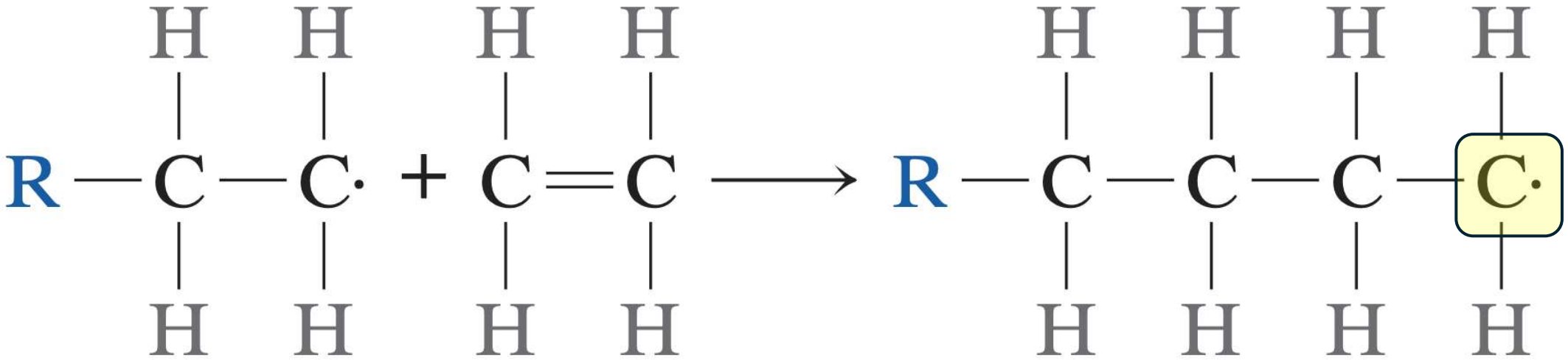
This will usually not happen on its own…

We can introduce an *initiator* (R) that bonds with ethylene and creates an *active site*

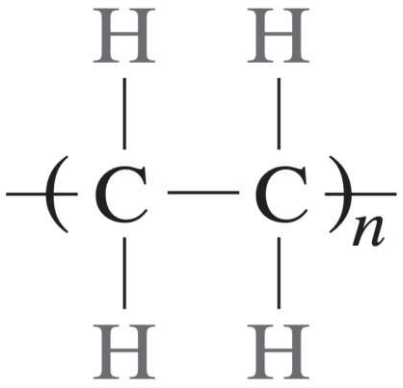


Bond formation in polymers

Once the initiator is attached and the active site is formed, we are **ready for bonding**



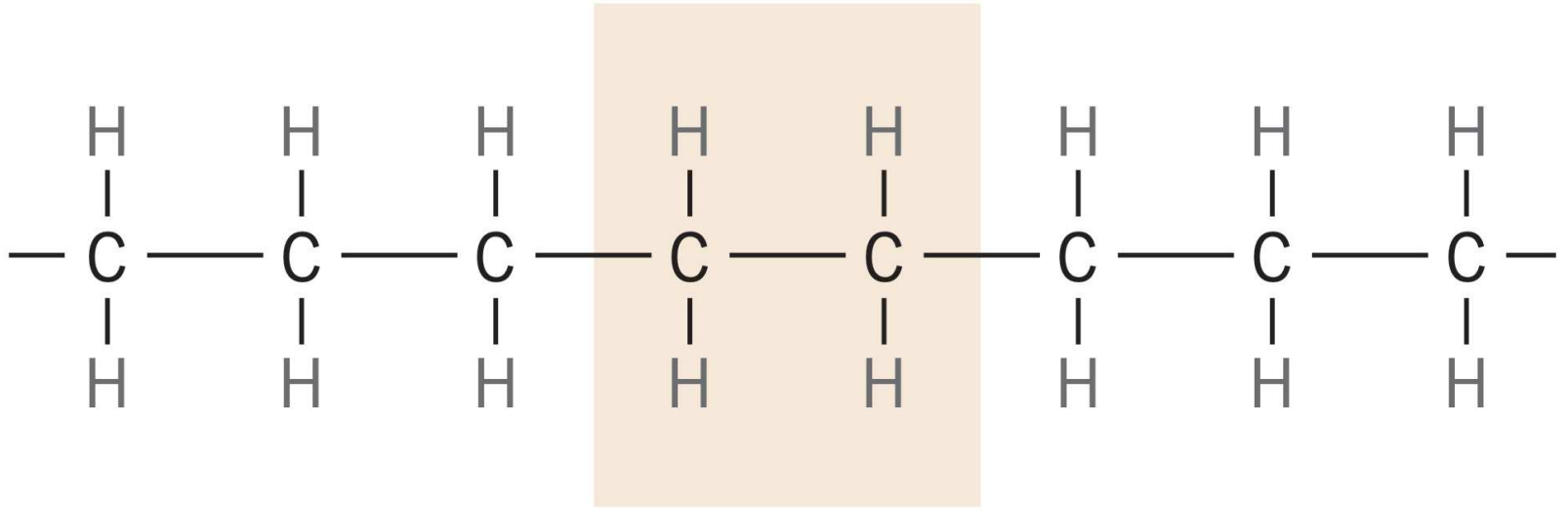
Repeated n times



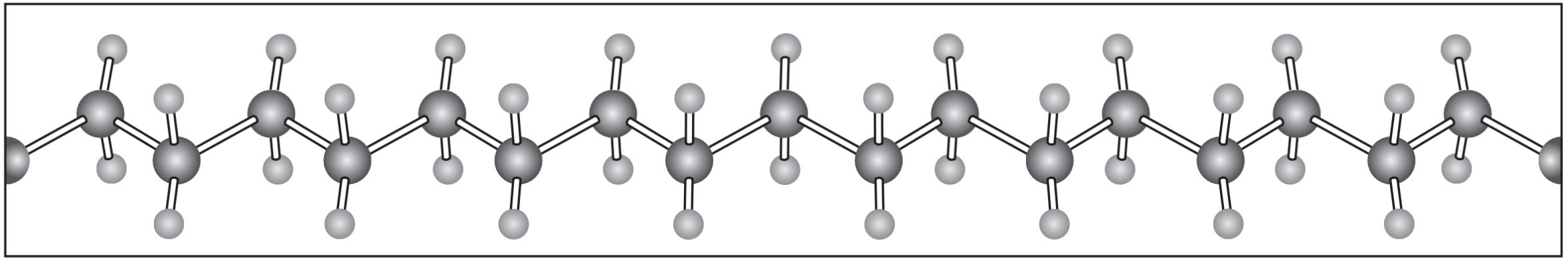
Because an active site remains on the product site, this process can be repeated over and over…

Questions on bond formation in polymers?

Structure of polymer chains



This picture is a bit misleading

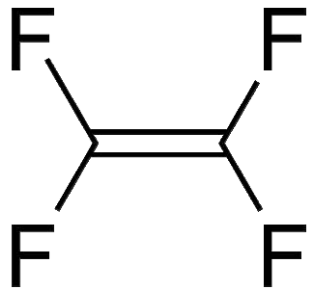


Zig-zag pattern, ~109° angles

Minimizes repulsion

C H

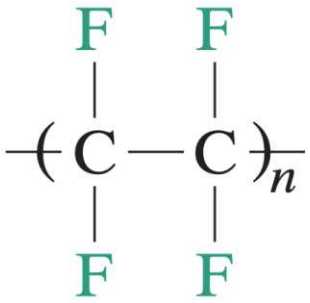
Some other examples of polymers



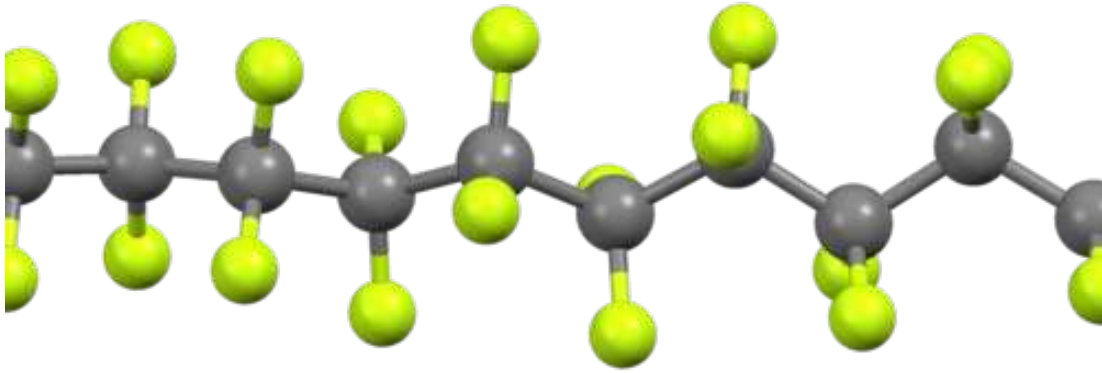
tetrafluoroethylene

$CF_2=CF_2$

Polymerization



Polytetrafluoroethylene (PTFE)





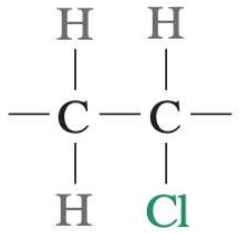


Teflon

- Very low friction (slippery, non-stick)
- Highly stable (C-F bond is strong)
- Electrically insulating

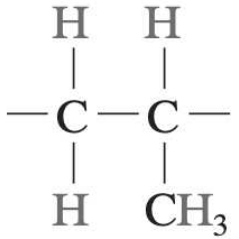
Some other examples of polymers

Poly(vinyl chloride) (PVC)



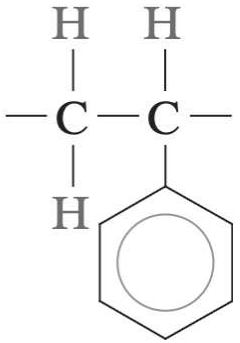


Polypropylene (PP)





Polystyrene (PS)





What gives rise to these distinct properties?

Properties of polymers: Molecular weight



Low *M*

One sample will contain many polymer chains with a wide range of molecular weights (M_i)

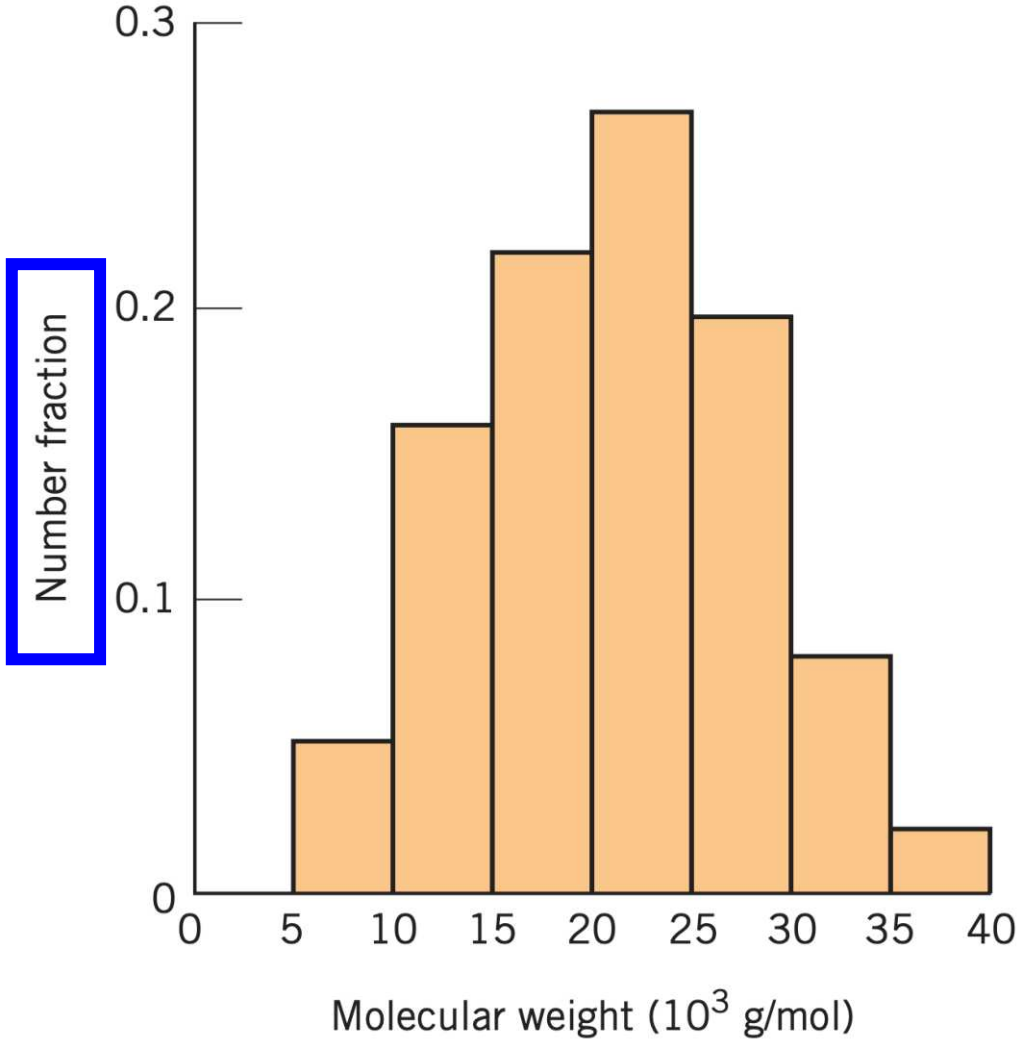


High *M*

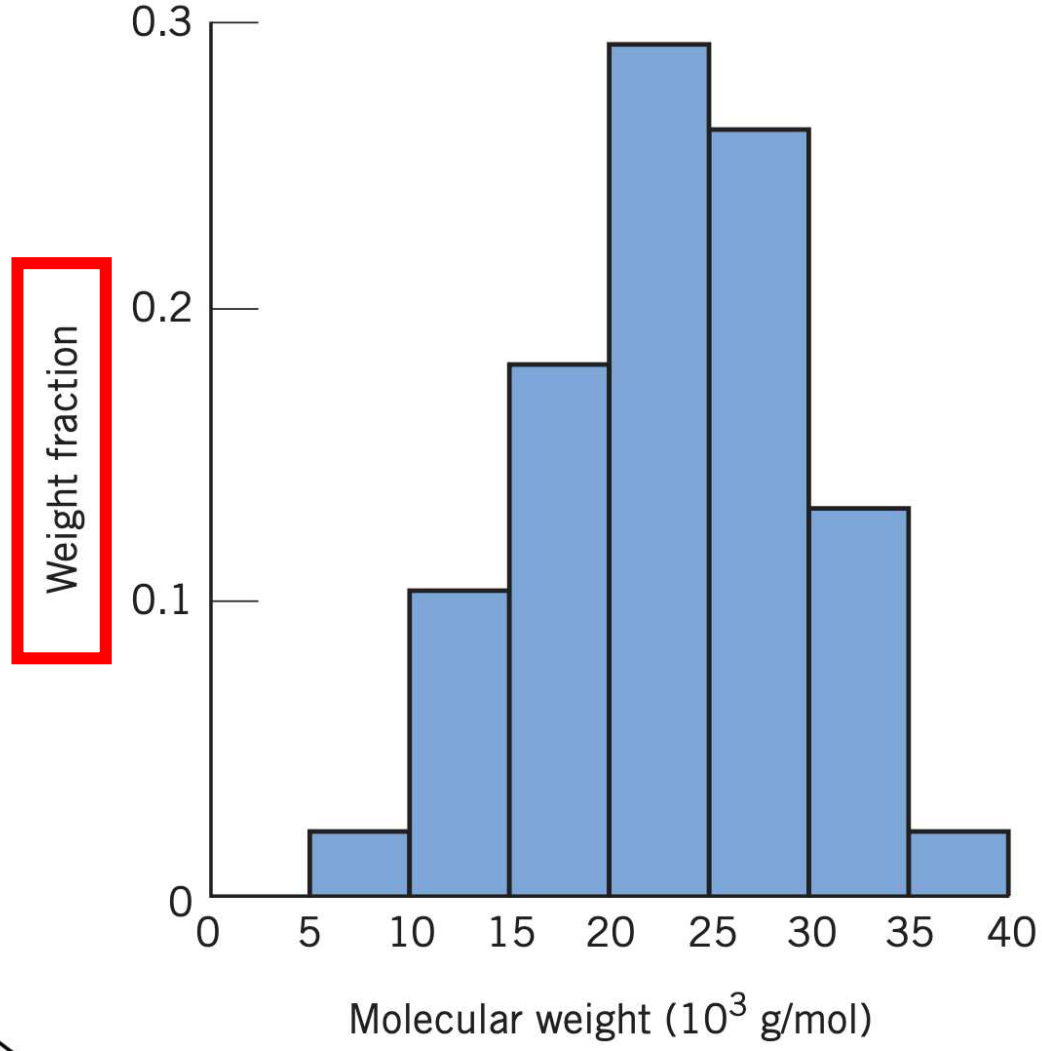
One descriptor of this distribution is the **"number-average" molecular weight:**

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

x_i is the fraction of chains with mass M_i



Properties of polymers: Molecular weight

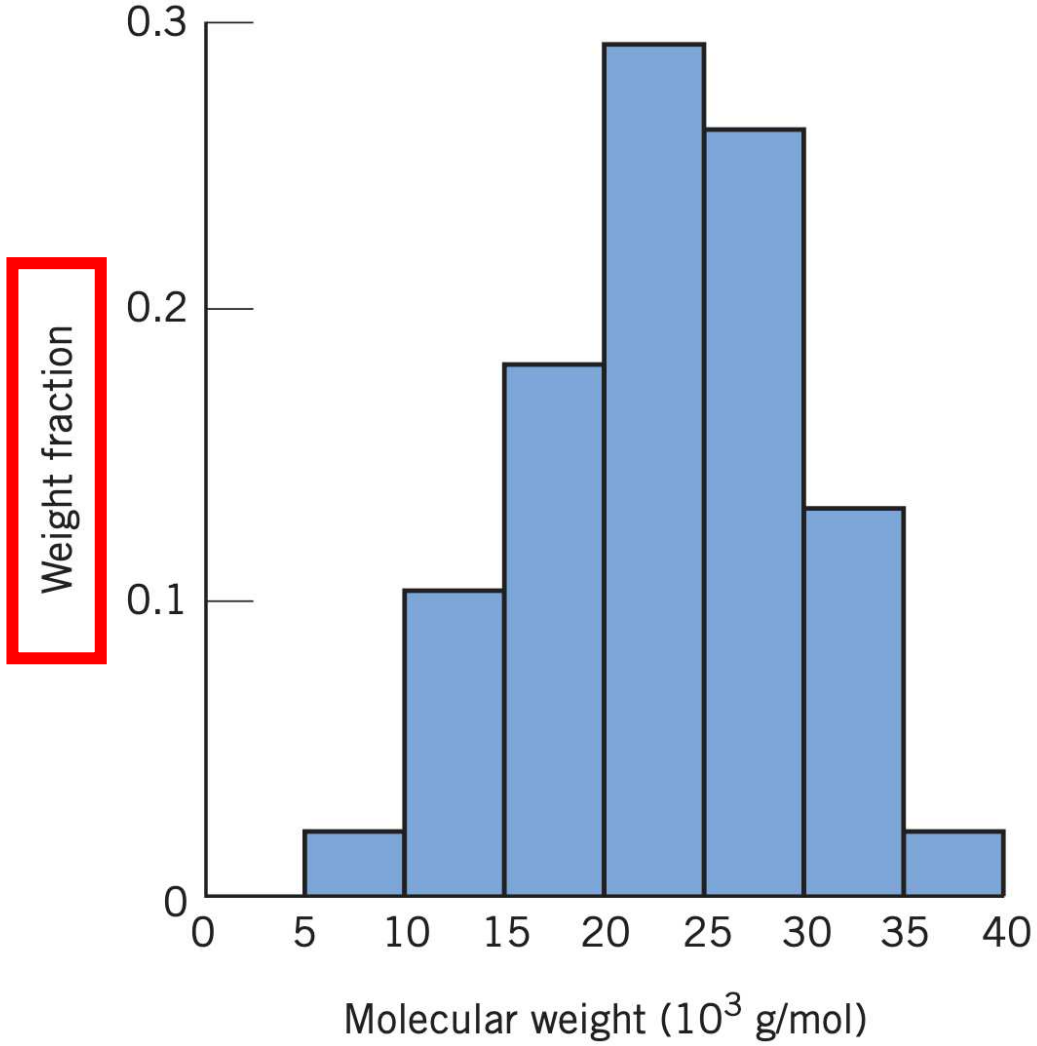


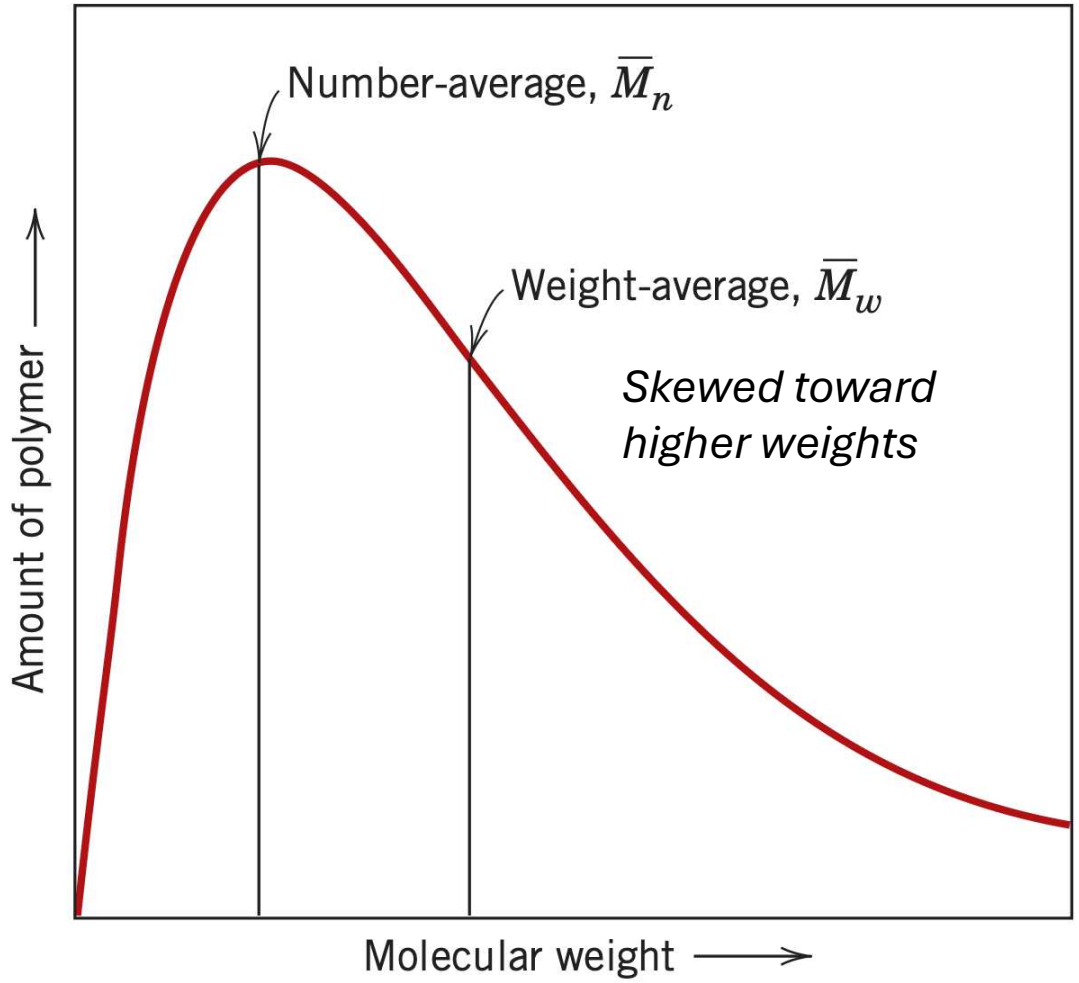
Another descriptor is the
"weight-average" molecular weight:

$$\bar{M}_w = \sum_i w_i M_i$$

w_i is the **weight** fraction of chains with mass M_i

Properties of polymers: Molecular weight





Both are specified to give shape of distribution

Example: Molecular weight

Number of Molecules	Mass of each Molecule
1	800,000
3	750,000
5	700,000
8	650,000
10	600,000
13	550,000
20	500,000
13	450,000
10	400,000
8	350,000
5	300,000
3	250,000
1	200,000

Units: g/mol

This is how data we get from experiment (*e.g.*, using size exclusion chromatography) might look…So **what is the average weight?**

First, let's compute the **number-average:**

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

x_i is the fraction of chains with mass M_i

Example: Molecular weight

Number of Molecules	Number Fraction (x_i)	Mass of each Molecule
1	1/100	800,000
3	3/100	750,000
5	5/100	700,000
8	8/100	650,000
10	10/100	600,000
13	13/100	550,000
20	20/100	500,000
13	13/100	450,000
10	10/100	400,000
8	8/100	350,000
5	5/100	300,000
3	3/100	250,000
1	1/100	200,000

number-average:

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

Total number:
100 molecules

$$\bar{M}_n = \left(\frac{1}{100}\right)(800{,}000) + \left(\frac{3}{100}\right)(750{,}000) + \cdots$$

$$\boldsymbol{\bar{M}_n = 500{,}000\ \text{g/mol}}$$

Example: Molecular weight

Number of Molecules	Mass of each Molecule	Weight of Group
1	800,000	1 ×800,000
3	750,000	3 ×750,000
5	700,000	5 ×700,000
8	650,000	8 ×650,000
10	600,000	10 ×600,000
13	550,000	13 ×550,000
20	500,000	20 ×500,000
13	450,000	13 ×450,000
10	400,000	10 ×400,000
8	350,000	8 ×350,000
5	300,000	5 ×300,000
3	250,000	3 ×250,000
1	200,000	1 ×200,000

Total weight:

50,000,000

weight-average:

$$\bar{M}_w = \sum_i w_i M_i$$

Example: Molecular weight

Number of Molecules	Mass of each Molecule	Weight of Group	Weight fraction (w_i)
1	800,000	1 ×800,000	×800,000 /50,000,000
3	750,000	3 ×750,000	×750,000 /50,000,000
5	700,000	5 ×700,000	×700,000 /50,000,000
8	650,000	8 ×650,000	×650,000 /50,000,000
10	600,000	10 ×600,000	×600,000 /50,000,000
13	550,000	13 ×550,000	×550,000 /50,000,000
20	500,000	20 ×500,000	×500,000 /50,000,000
13	450,000	13 ×450,000	×450,000 /50,000,000
10	400,000	10 ×400,000	×400,000 /50,000,000
8	350,000	8 ×350,000	×350,000 /50,000,000
5	300,000	5 ×300,000	×300,000 /50,000,000
3	250,000	3 ×250,000	×250,000 /50,000,000
1	200,000	1 ×200,000	×200,000 /50,000,000

Total weight:

50,000,000

Example: Molecular weight

Number of Molecules	Mass of each Molecule	Weight fraction (w_i)
1	800,000	1 ×800,000 /50,000,000
3	750,000	3 ×750,000 /50,000,000
5	700,000	5 ×700,000 /50,000,000
8	650,000	8 ×650,000 /50,000,000
10	600,000	10 ×600,000 /50,000,000
13	550,000	13 ×550,000 /50,000,000
20	500,000	20 ×500,000 /50,000,000
13	450,000	13 ×450,000 /50,000,000
10	400,000	10 ×400,000 /50,000,000
8	350,000	8 ×350,000 /50,000,000
5	300,000	5 ×300,000 /50,000,000
3	250,000	3 ×250,000 /50,000,000
1	200,000	1 ×200,000 /50,000,000

Multiply each pair of terms and sum them

Skewed toward higher weights

$$\bar{M}_w = \sum_i w_i M_i = (800{,}000^2)(50{,}000{,}000) + \cdots = \mathbf{531{,}600}\ \text{g/mol}$$

These are quite different! $\bar{M}_n = \mathbf{500{,}000\ g/mol}$

Questions on molecular weight?

Larger molecule weight → tougher and more viscous, usually higher melting point

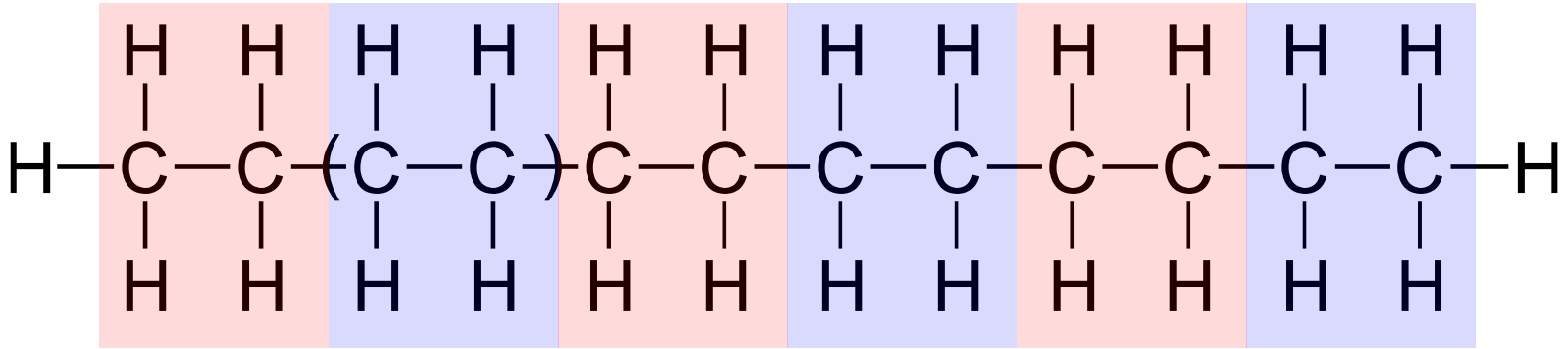
One more descriptor: the degree of polymerization

The Degree of Polymerization (DP) is the **average number of repeat units (monomers) per chain**

$$DP = \frac{\bar{M}_n}{\bar{m}}$$

$\bar{M}_n$ → Number-average molecular weight

$\bar{m}$ → Mass of the repeat unit



***DP* = 6**

Usually, polymers with larger DP will have higher melting and boiling points

Back to our example

Number of Molecules	Mass of each Molecule
1	800,000
3	750,000
5	700,000
8	650,000
10	600,000
13	550,000
20	500,000
13	450,000
10	400,000
8	350,000
5	300,000
3	250,000
1	200,000

Number-average:

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

$$\bar{M}_n = \left(\frac{1}{100}\right)(800{,}000) + \left(\frac{3}{100}\right)(750{,}000) + \cdots$$

$$\boldsymbol{\bar{M}_n = 500{,}000\ \text{g/mol}}$$

What is the degree of polymerization?

Assume each repeat unit has a mass of $\bar{m} = 50$ g/mol

(in practice, we could get this from molecular formula)

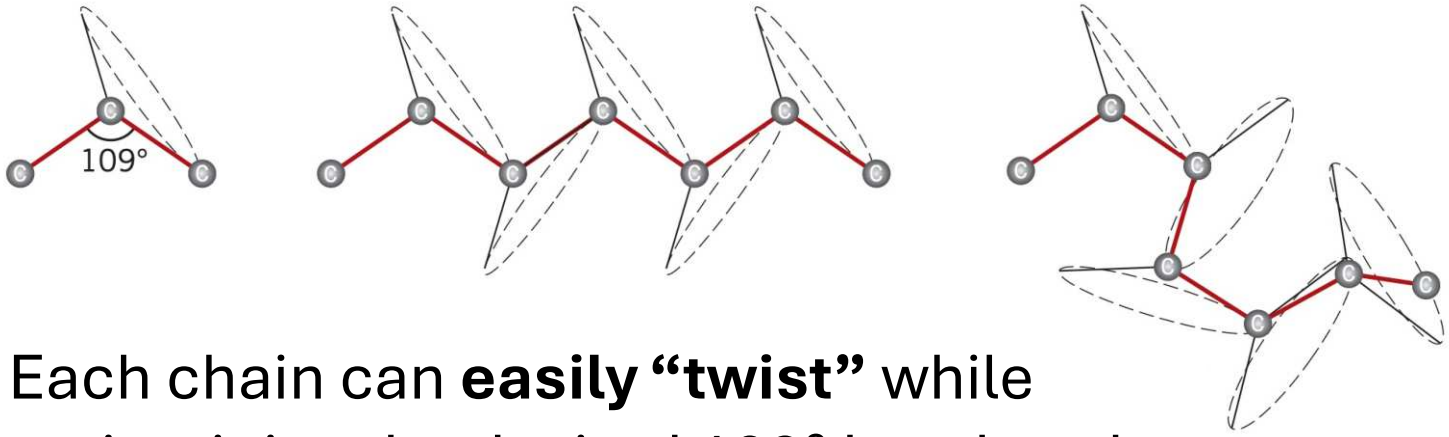
$$DP = \frac{\bar{M}_n}{\bar{m}} = \frac{500{,}000\ \text{g}}{50\ \text{g}} = 10{,}000$$

There are (on average) 10,000 repeat units in each chain

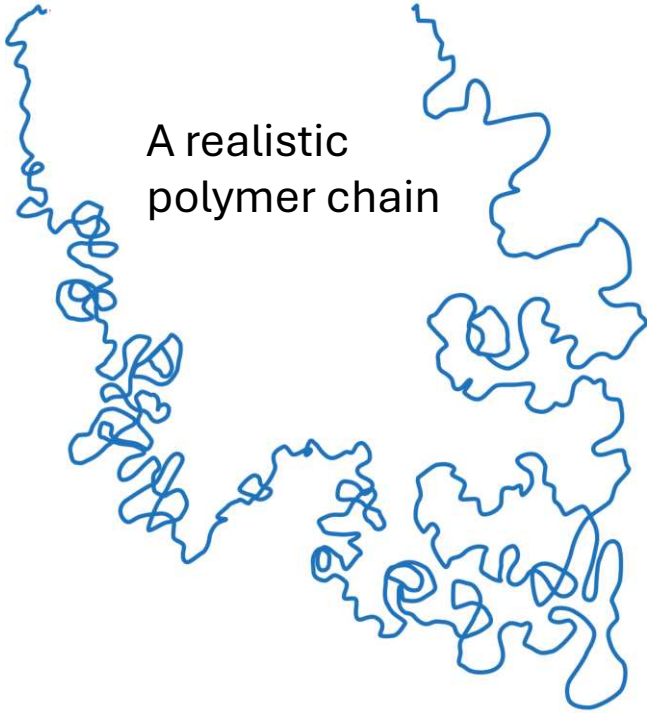
Questions on degree of polymerization?

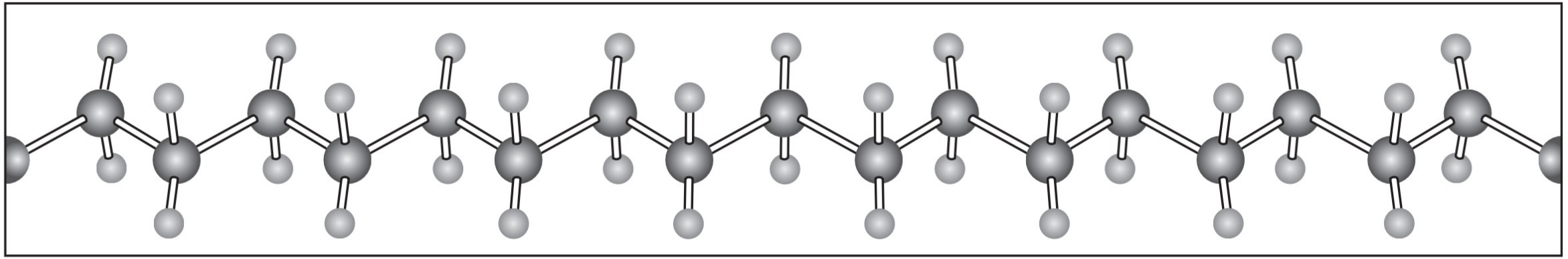
Know how to compute this!

Polymer structures: single chain



Each chain can **easily "twist"** while maintaining the desired 109° bond angle

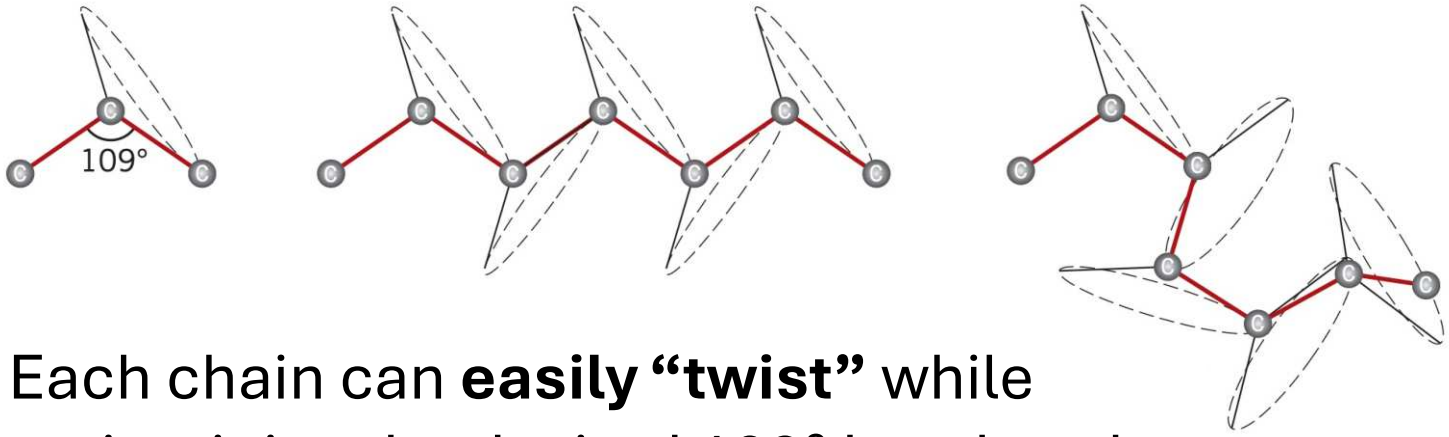


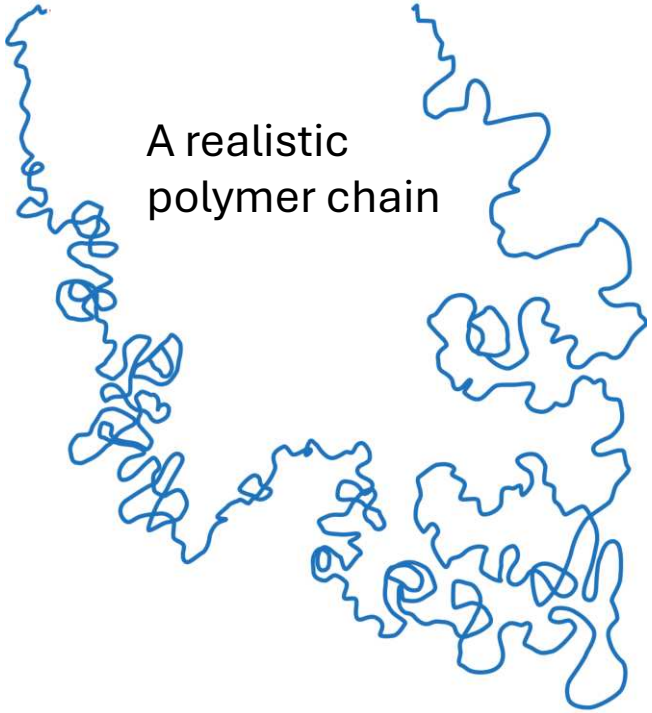


Zig-zag pattern, ~109° angles

Minimizes repulsion

Polymer structures: single chain

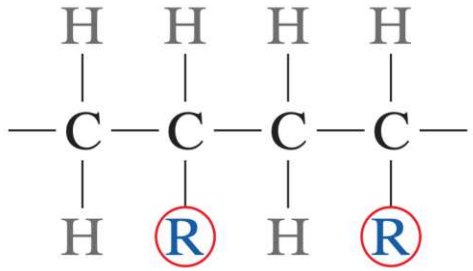




Each chain can **easily "twist"** while maintaining the desired 109° bond angle

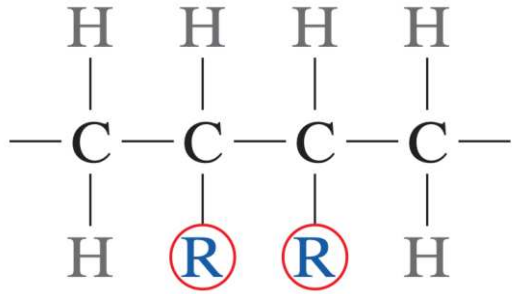
The polymer shape is also known as the **conformation**. It will vary from chain to chain.

But we can also have different **configurations** of atoms/groups in the chain – many different configurations are possible for one composition



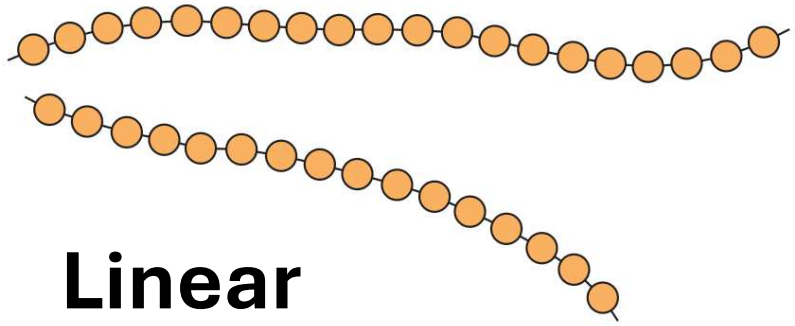
R = some other atom or group

Isomerism



Polymer structures: many chains

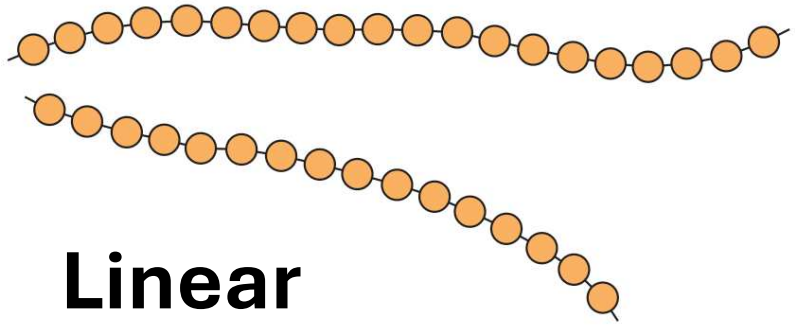
No connections



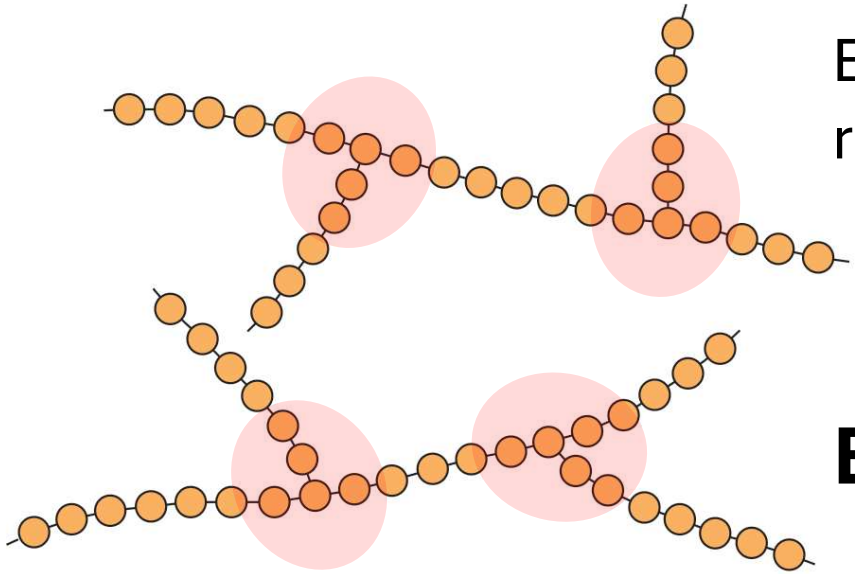
Linear

We often care about how the chains are connected, if at all

Polymer structures: many chains



Linear

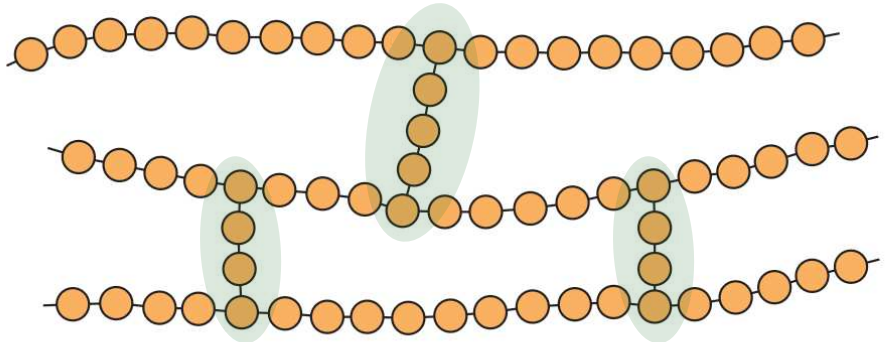


Each branch remains separate



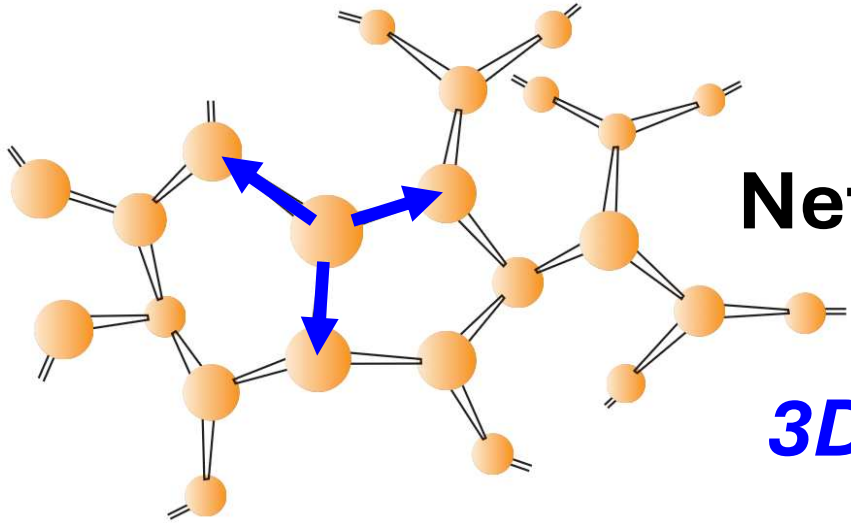
Branched

Branches connect!



Crosslinked

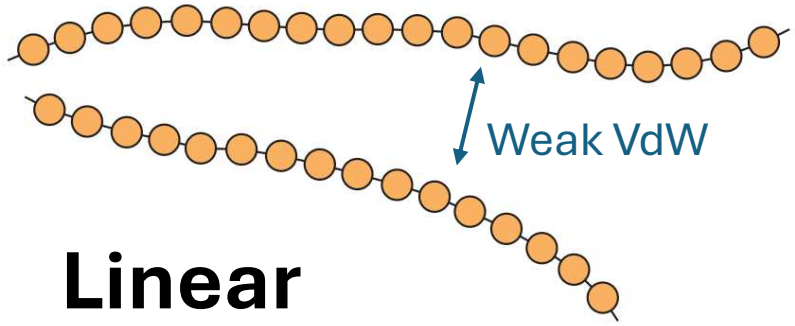




Network

***3D** linking*

Polymer structures: many chains



Linear



Thermoplastics are often linear: these are polymers that soften/melt quite easily under heat

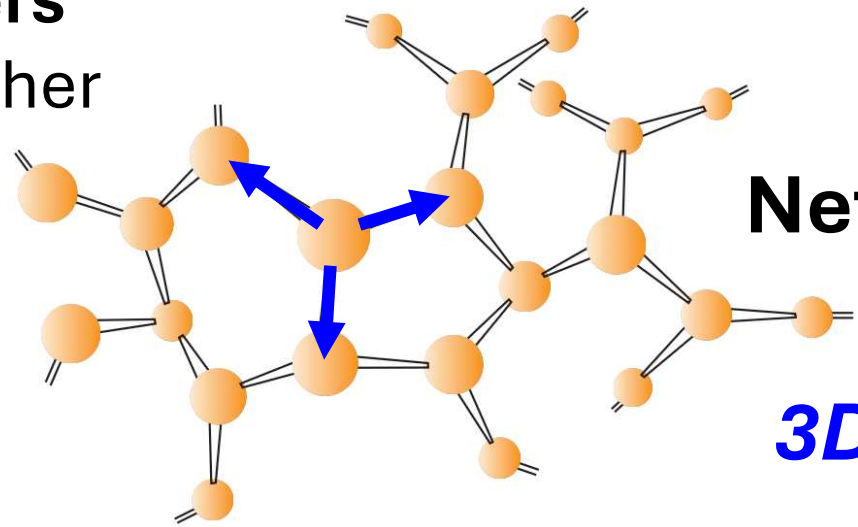


Vulcanized rubber

Thermosetting polymers are network: much tougher



Epoxy

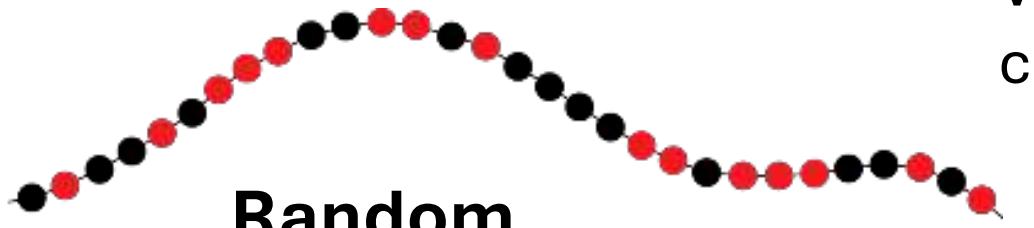


Network

***3D** linking*

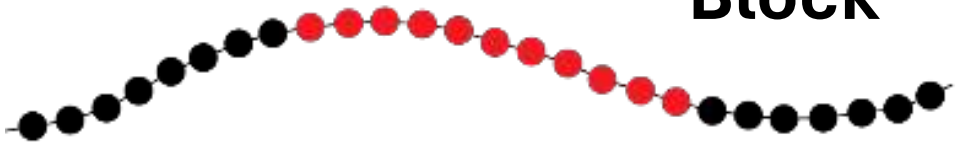
Copolymers: stitching different repeat units together

Varying relative amounts and ordering can be useful to **tune properties**



Random

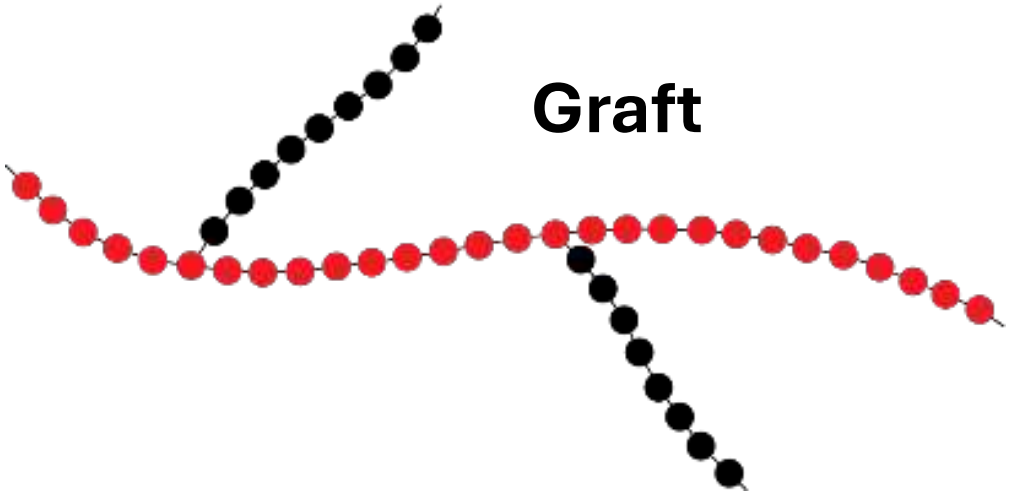
Block





Alternating

Graft



A ● **B** ● Different repeat units

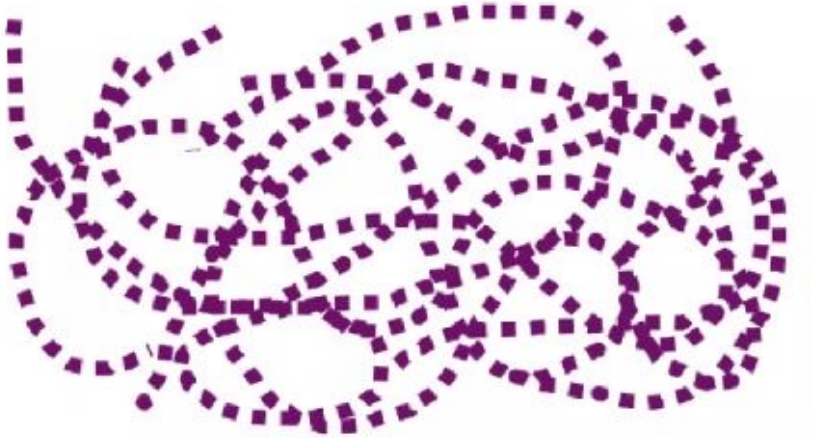
Questions on polymer architectures?

Know how to relate architecture to properties

Linear polymers are much weaker, and melt more easily,
than cross-linked and network polymers

Polymer crystallinity

Polymer Chains

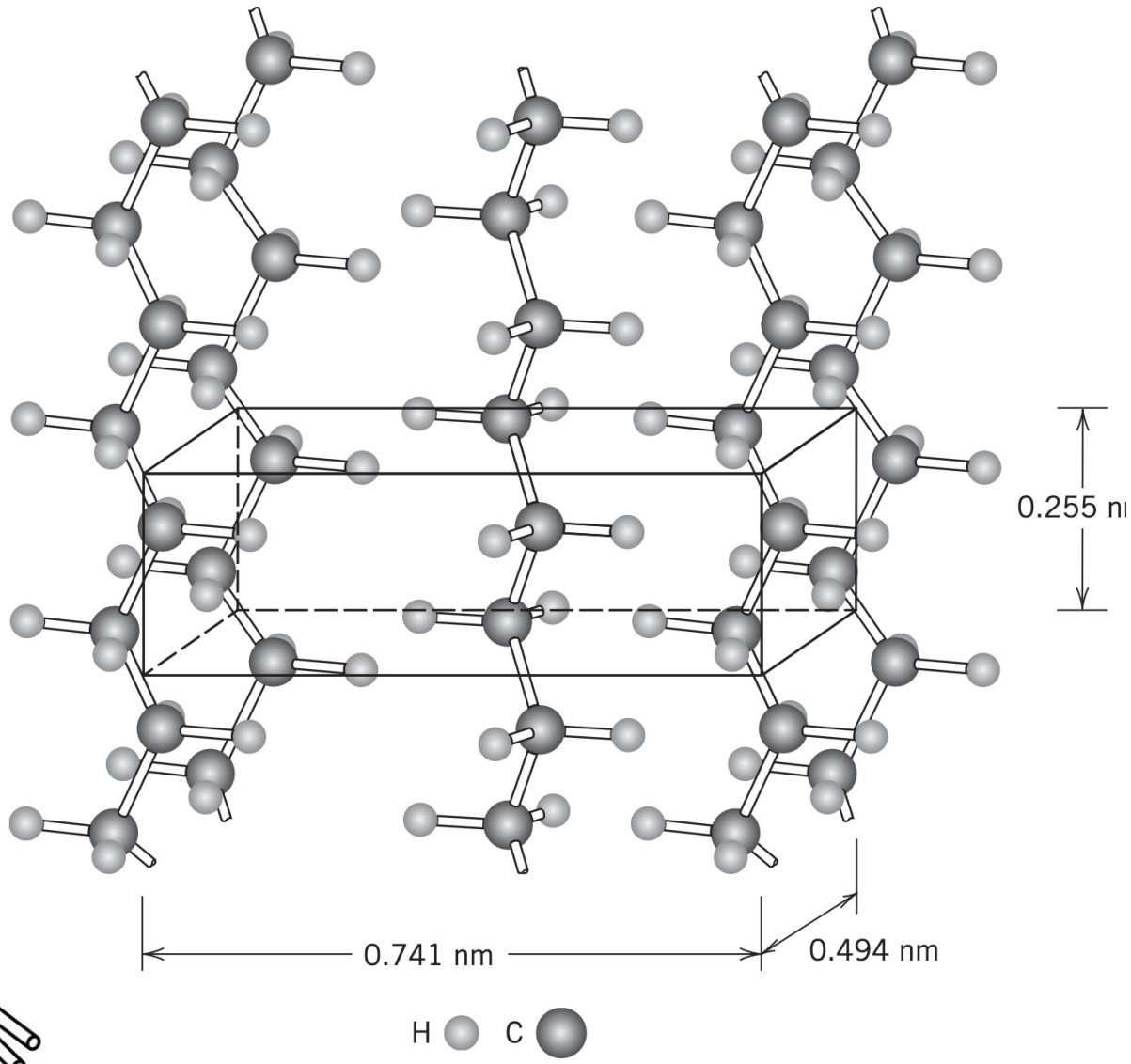


Spaghetti



This is not always the case!

Polymer crystallinity



- A crystal forms when the polymer chains arrange in an ordered fashion relative to one another
- This is done to minimize the energy of weak interactions (van der Waals) between the chains

Because these interactions are weak, and because the chains are often long and complicated, polymers are usually only **partially crystalline**

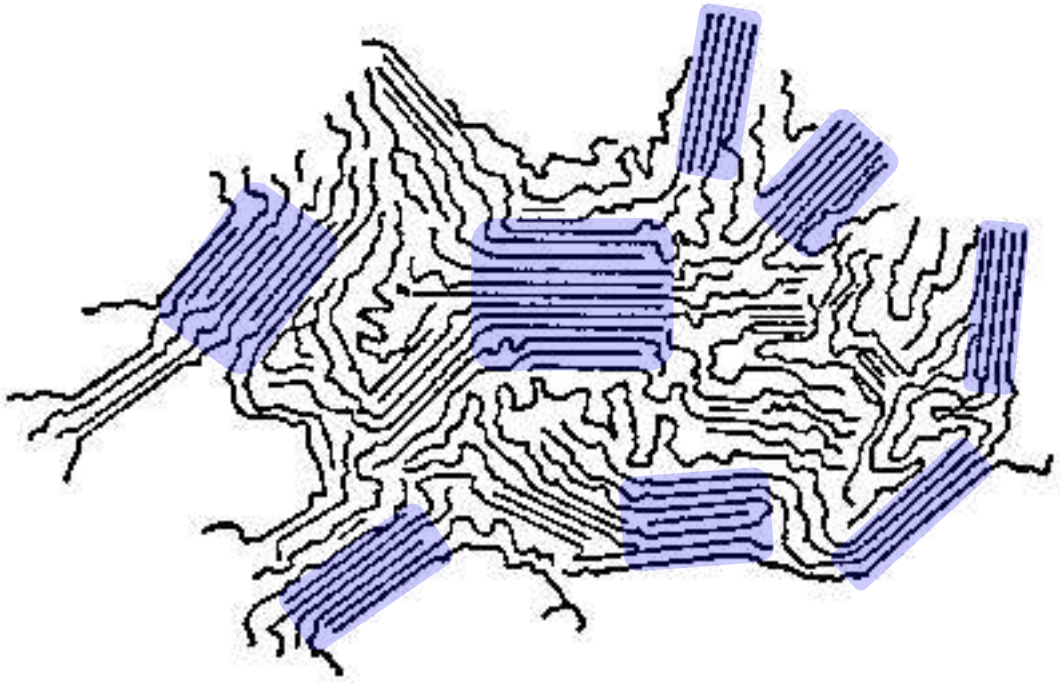
Polymer crystallinity

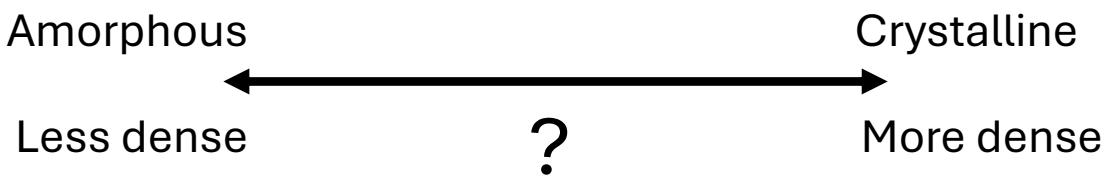
You might think of this as a two-phase mixture, where each phase has its own unique **density (ρ)**

The **% crystallinity** is then defined as:

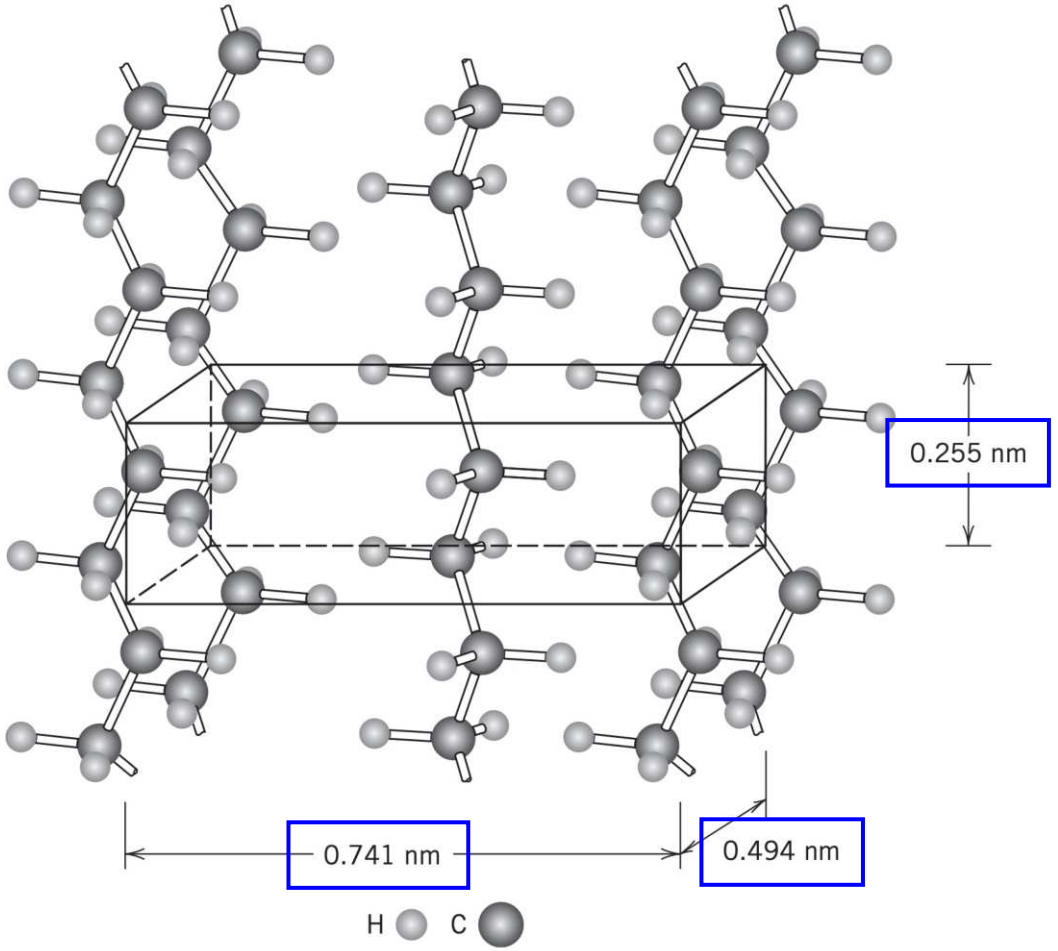
$$\% \text{ cryst} = \frac{\rho_{\text{cryst}}\left(\rho_{\text{tot}} - \rho_{\text{amorph}}\right)}{\rho_{\text{tot}}\left(\rho_{\text{cryst}} - \rho_{\text{amorph}}\right)} \times 100$$

This may span a wide range (0-95%) depending on composition, molecular weight, and cooling rates





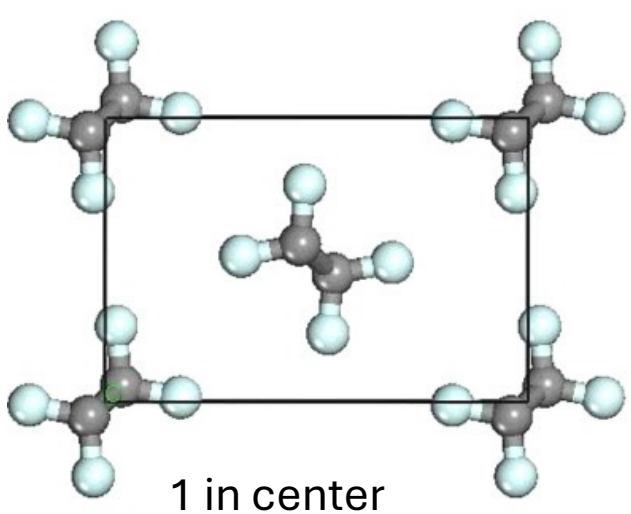
Example calculation



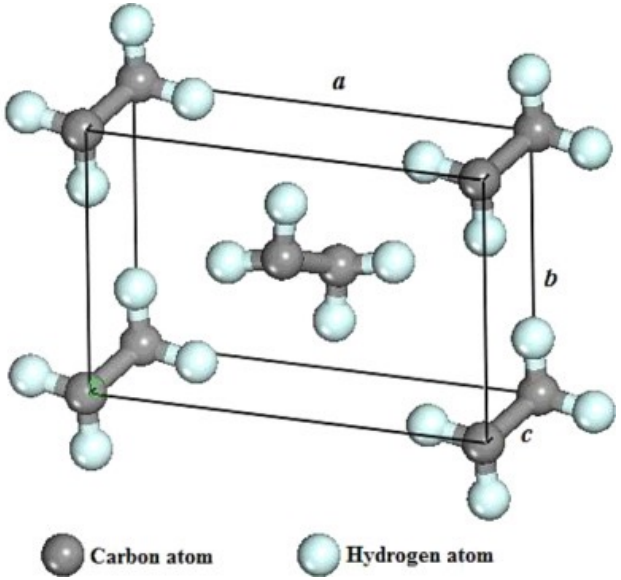
What is the density of 100% crystalline polyethylene?

$$\rho = \frac{n_{\text{units}} m_{\text{units}}}{V_{\text{C}} N_{\text{avogadro}}}$$

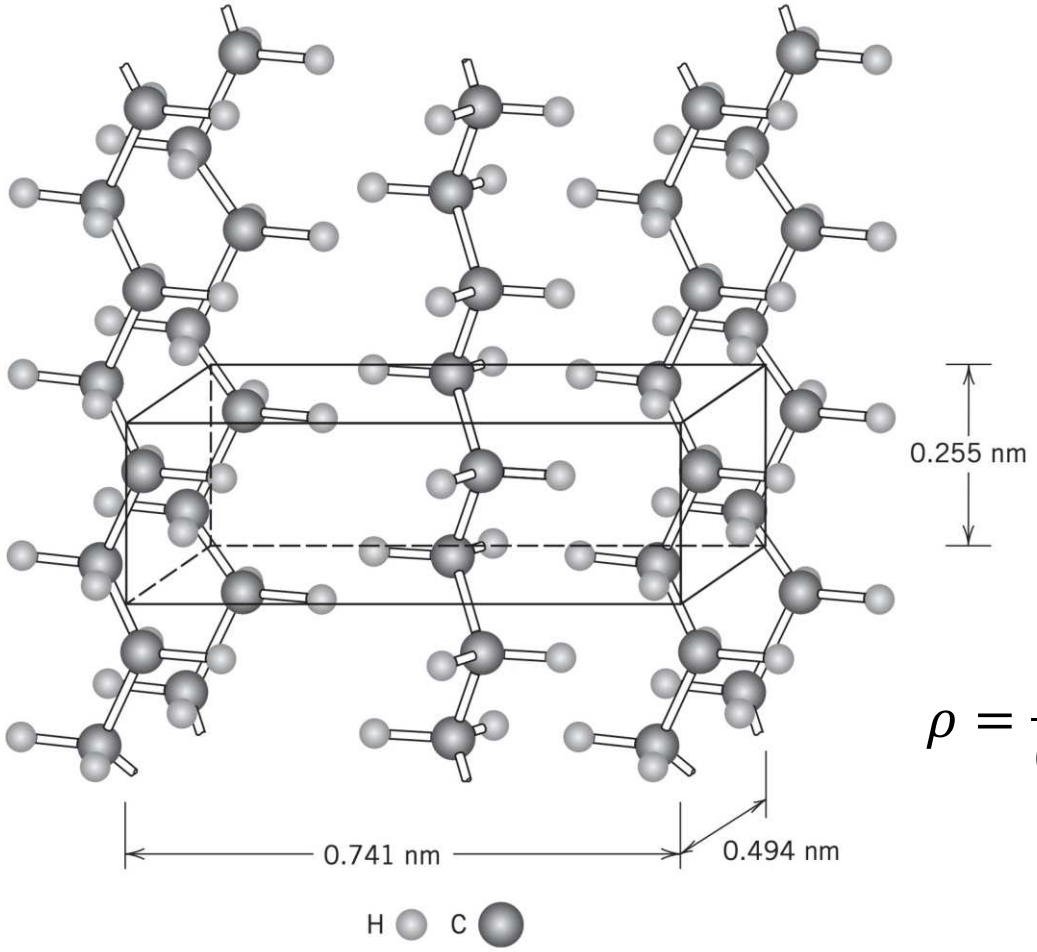
There are **2 repeat units** (C_2H_4) per unit cell



1 in center
¼ at each corner



Example calculation



There are **2 repeat units** (C_2H_4) per unit cell

What is the density of 100% crystalline polyethylene?

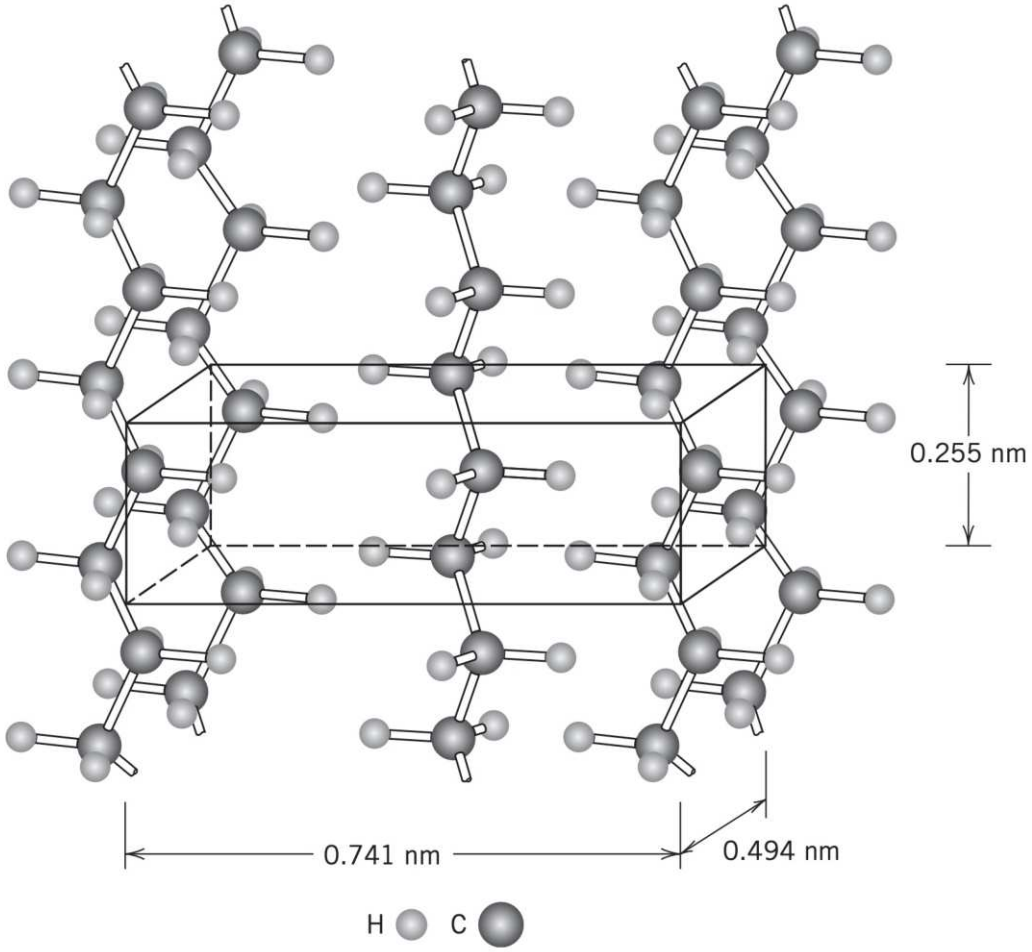
$$\rho = \frac{n_{\text{units}} m_{\text{units}}}{V_C N_{\text{avogadro}}}$$

$$\rho = \frac{2\,[(2)(12.01\ \text{g/mol}) + 4(1.08\ \text{g/mol})]}{(0.741\ \text{nm})(0.494\ \text{nm})(0.255\ \text{nm})\ 6.022\times10^{23}\ \text{units/mol}}$$

$$\boldsymbol{\rho = 0.998\ \text{g/cm}^3}$$

For the crystalline phase

Example calculation



Now suppose we melt this specimen, then rapidly quench it into a fully amorphous state, whose density we measure to be:

$$\rho_{\mathbf{amorph}} = \mathbf{0.870\ g/cm^3}$$

After we anneal it for an hour, its density changes to:

$$\rho_{\mathbf{tot}} = \mathbf{0.925\ g/cm^3}$$

What is its % crystallinity?

Example calculation

$$\rho_{\text{cryst}} = 0.998\ \text{g/cm}^3$$

$$\%\ \text{cryst} = \frac{\rho_{\text{cryst}}\left(\rho_{\text{tot}} - \rho_{\text{amorph}}\right)}{\rho_{\text{tot}}\left(\rho_{\text{cryst}} - \rho_{\text{amorph}}\right)} \times 100$$

$$\%\ \text{cryst} = \frac{0.998(0.925 - 0.870)}{0.925(0.998 - 0.870)} \times 100$$

$$\%\ \textbf{cryst} = 46.4\%$$

Now suppose we melt this specimen, then rapidly quench it into a fully amorphous state, whose density we measure to be:

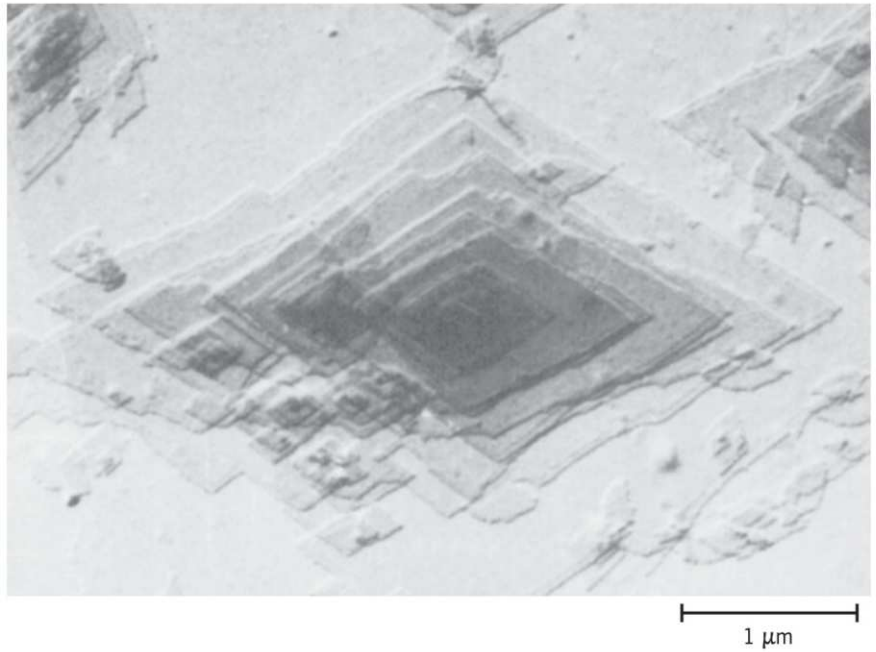
$$\rho_{\text{amorph}} = 0.870\ \text{g/cm}^3$$

After we anneal it for an hour, its density changes to:

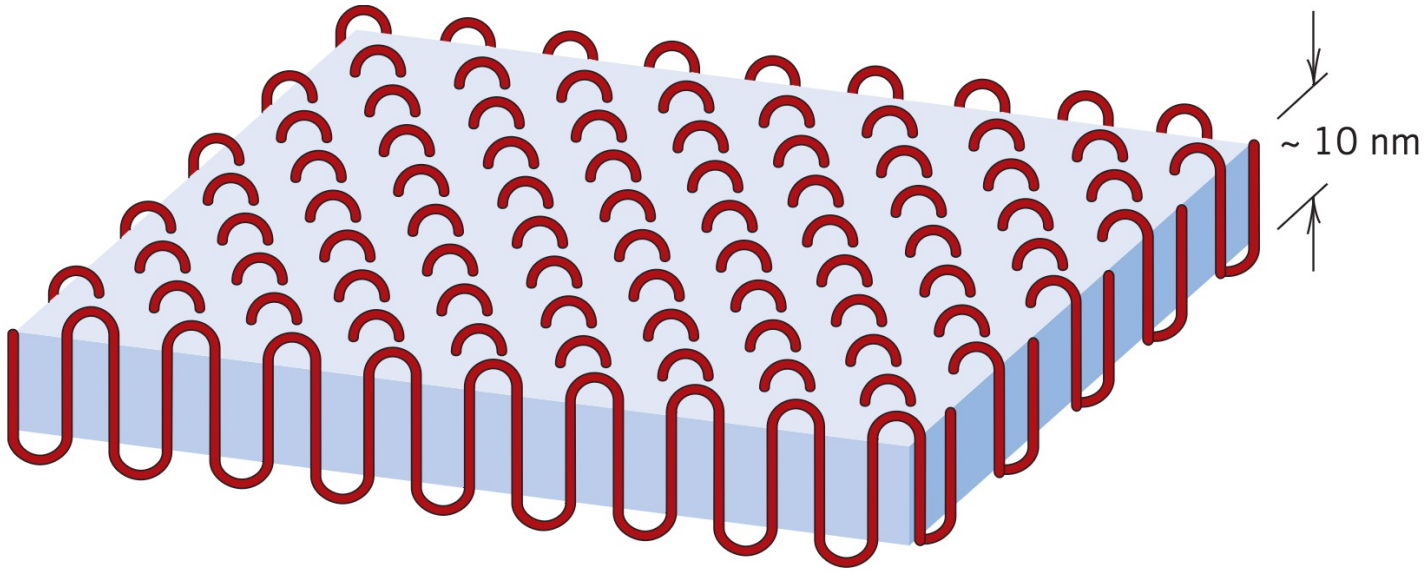
$$\rho_{\text{tot}} = 0.925\ \text{g/cm}^3$$

What is its % crystallinity?

Polymer crystallinity

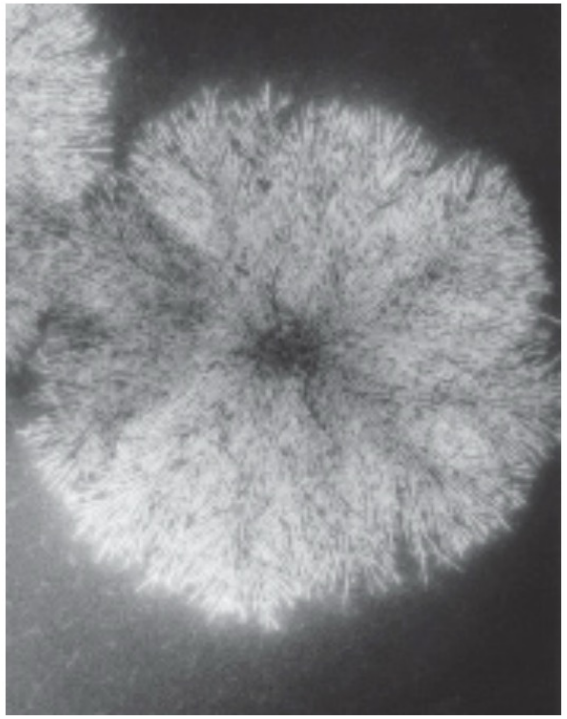


The crystalline regions often form as **platelets**, which consist of polymer chains that fold back and forth on themselves like below.



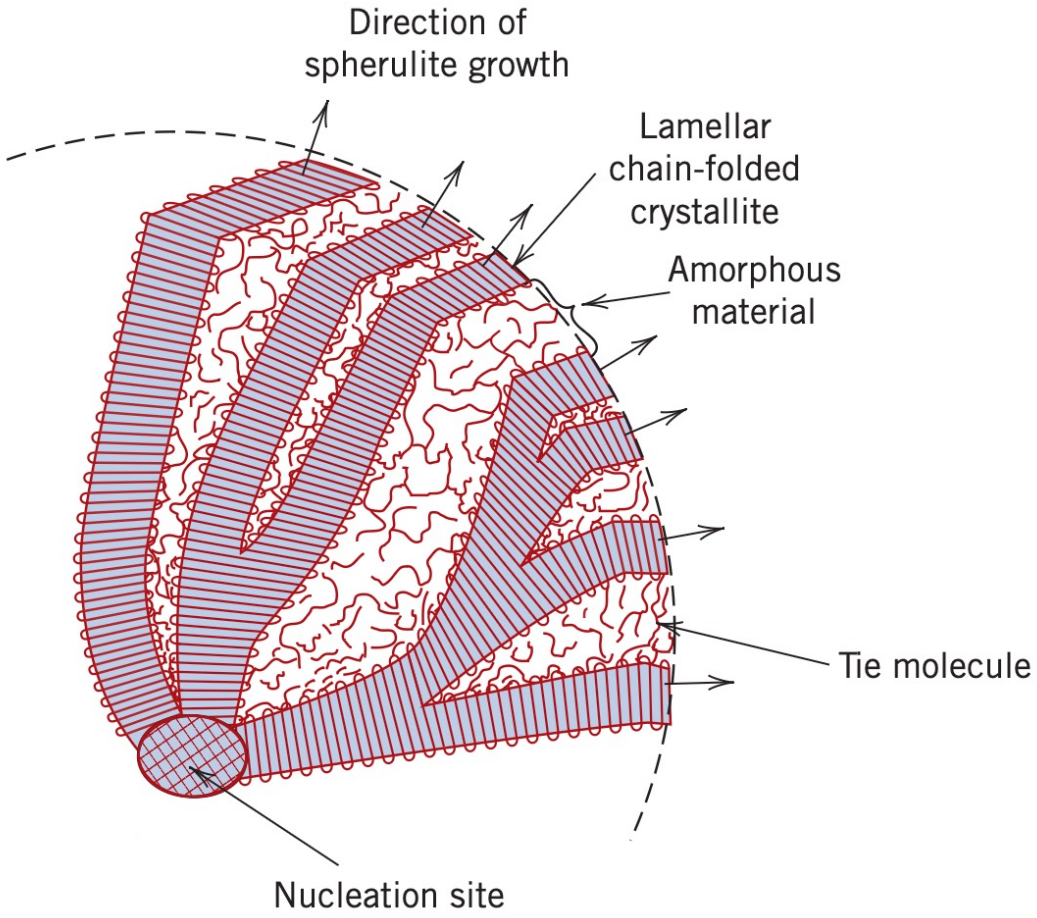
But this is not the only way semicrystalline polymers might look

Polymer crystallinity



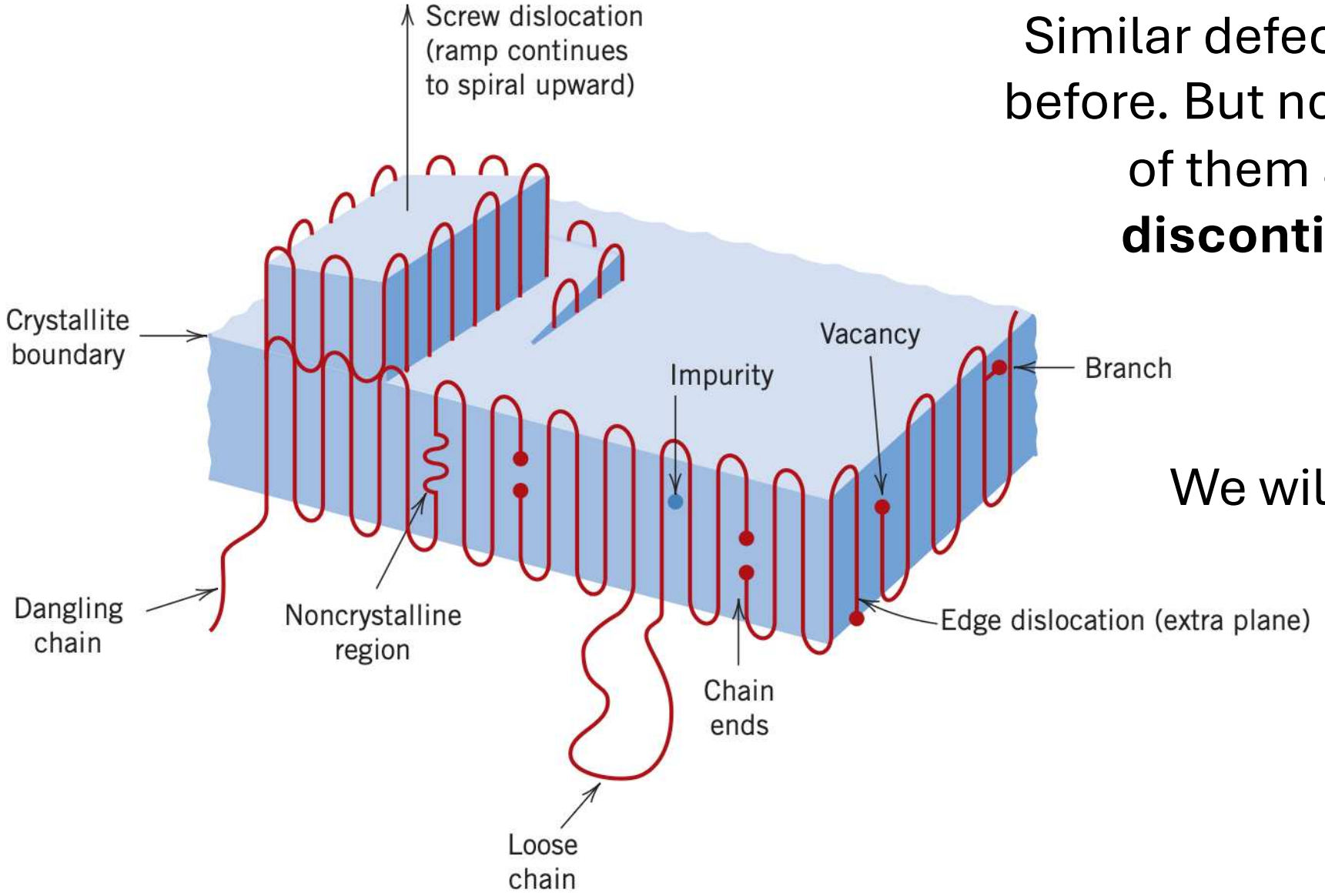
The **spherulite** structure occurs when chain-folded crystallites extend outward radially, forming a sphere-like structure.

Crystalline branches embedded in an amorphous matrix



This sort of microstructure is commonly observed in **natural rubber**

What about defects?



Similar defect to what we've seen before. But now it is easier to think of them as **irregularities and discontinuities in the chain.**

We will mostly ignore these

Summary of things to know

- Polymers are based on 1D chains of strong, covalent bonds
- They are low-density, tough, and have low melting points
- These polymer chains vary in length, and we describe this using:
  - Molecular weight
  - Degree of polymerization
- Inter-chain bonding may be strong (cross-linking) or weak (linear)
  - Know how this affects the properties!
- The chains may arrange regularly (crystalline) or randomly (amorphous)
  - Know how to compute the degree of crystallinity from density