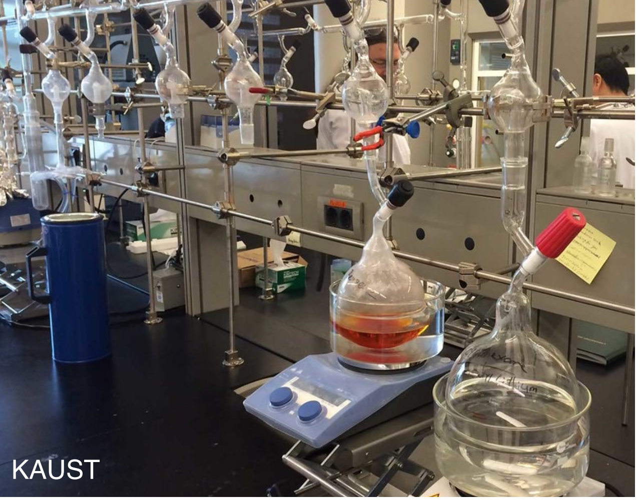
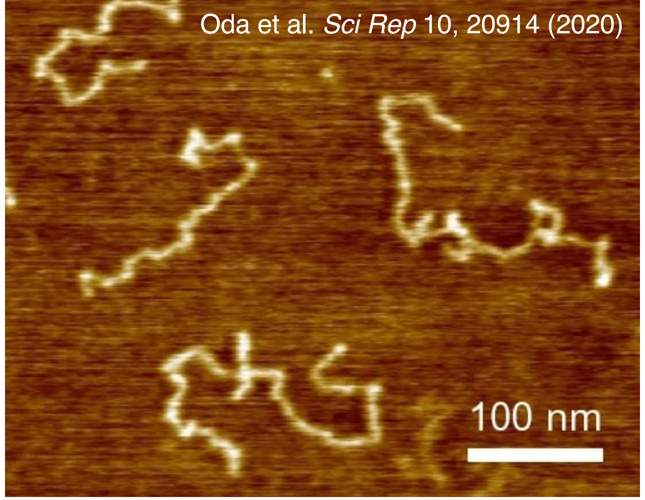




Materials Engineering I (MSE 214)

Lecture 2: Making Polymers (I)

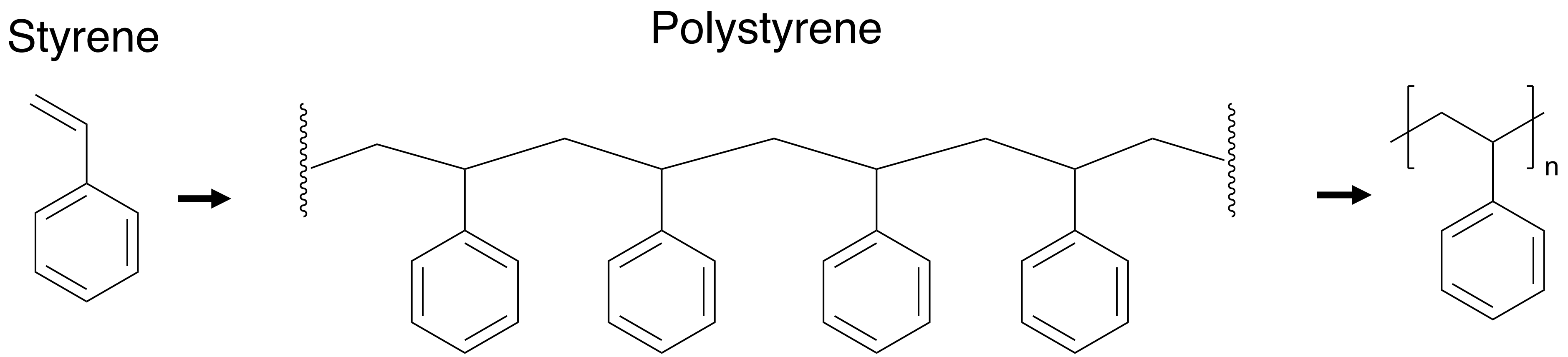
Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

EPFL

Week 1 Recap

Polymers are large molecules that are composed of many repeating subunits



Vertices: C ; 1 line = 1 bond ; H fills up rest
Everything other than C,H needs to be written explicitly

Week 1 Recap

Multiple ways of classifying polymers — Depends on the information you want to convey

1. Composition: Number of monomer types

2. Architecture: Monomer arrangement

3. Polymerization Mechanisms

4. Chemical Reaction

5. Physical Properties

.
.
.

→

Polymers are complex materials

No universal classification!

The classifications are often interdependent on each other

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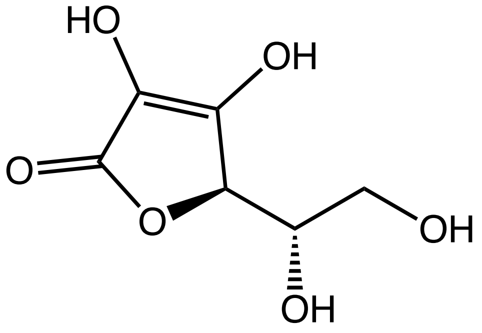
What Makes Synthetic Polymers Different from Other Materials?

Alumina (Ceramic)

Molecular formula: Al_2O_3
(101.96 g/mol)

Every molecule has the same molecular weight

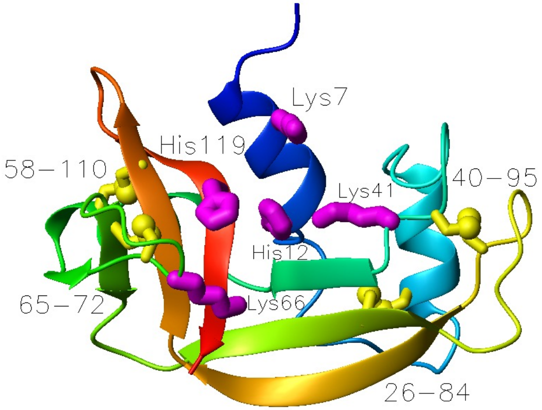
Vitamin C (Small Molecule)



Molecular formula: $C_6H_8O_6$
(176.12 g/mol)

Every molecule has the same molecular weight

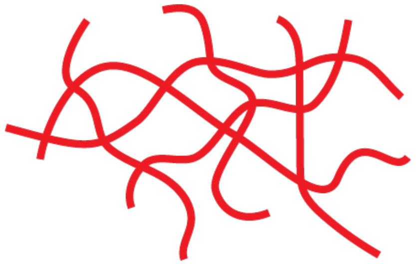
Ribonuclease A (Protein)

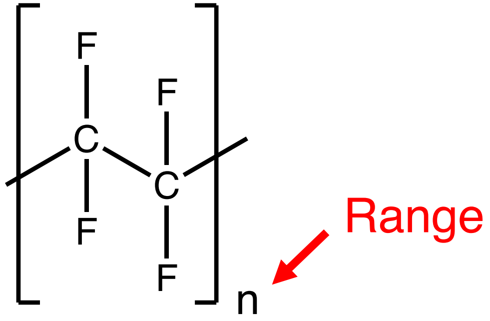


124 Amino Acids
(13.7 kg/mol)

Every protein chain has the same molecular weight

Synthetic Polymer





Mixtures of molecular weights

Synthetic polymers are mixtures

Synthetic Polymers are Mixtures

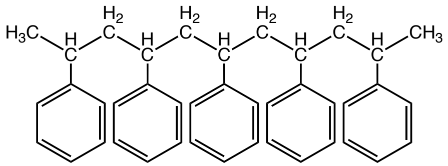
- Think back to the polymerization game: Do you think we can make the same polymer each time?

→ Statistical variations in the polymerization process

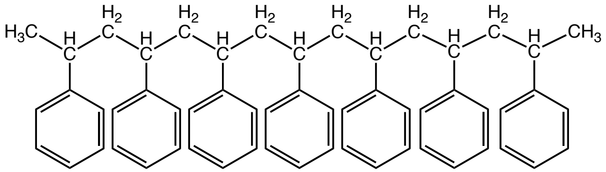
Mixtures of polymers of different molecular weights

- Average molecular weight and the molecular weight distribution needed to characterize the polymer

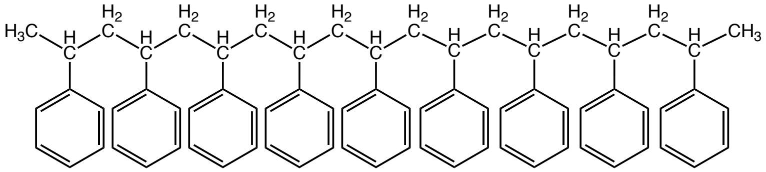
Consider this polystyrene sample of 3 different sizes



$(C_8H_8)_5 + C_2H_6$



$(C_8H_8)_7 + C_2H_6$



$(C_8H_8)_9 + C_2H_6$

A single molecular weight not sufficient
Average molecular weight needed

How do we determine an average?

Let's use cities as an example:

Zürich: 700000
Morges: 14600
Lutry: 9000
Zermatt: 5800

Average population of the four cities:

$$\frac{700000 + 14600 + 9000 + 5800}{4} = 182350$$

Does this seem accurate? That the average city size is 180k?

The cities are treated as similar
→ Bias towards smaller cities

Does the average **person** live in a city with a population of 182350?

If you picked a person from random out of the four cities, it is more likely that they live in Zürich

Need to use weighted average!

$$\left(\frac{700000}{729400}\times 700000\right) + \left(\frac{14600}{729400}\times 14600\right) + \left(\frac{9000}{729400}\times 9000\right) + \left(\frac{5800}{729400}\times 5800\right) = 672234$$

The average person lives in a city of 672k

The cities are not treated as similar
→ Bias towards larger cities

Number Average and Weight Average Molecular Weight (M_n, M_w)

Number Average Molecular Weight (M_n)

$$M_n = \frac{\sum N_x M_x}{\sum N_x}$$

N_x is the number of moles of polymer whose weight is M_x

M_n is biased towards the low molecular weight fraction

Weight Average Molecular Weight (M_w)

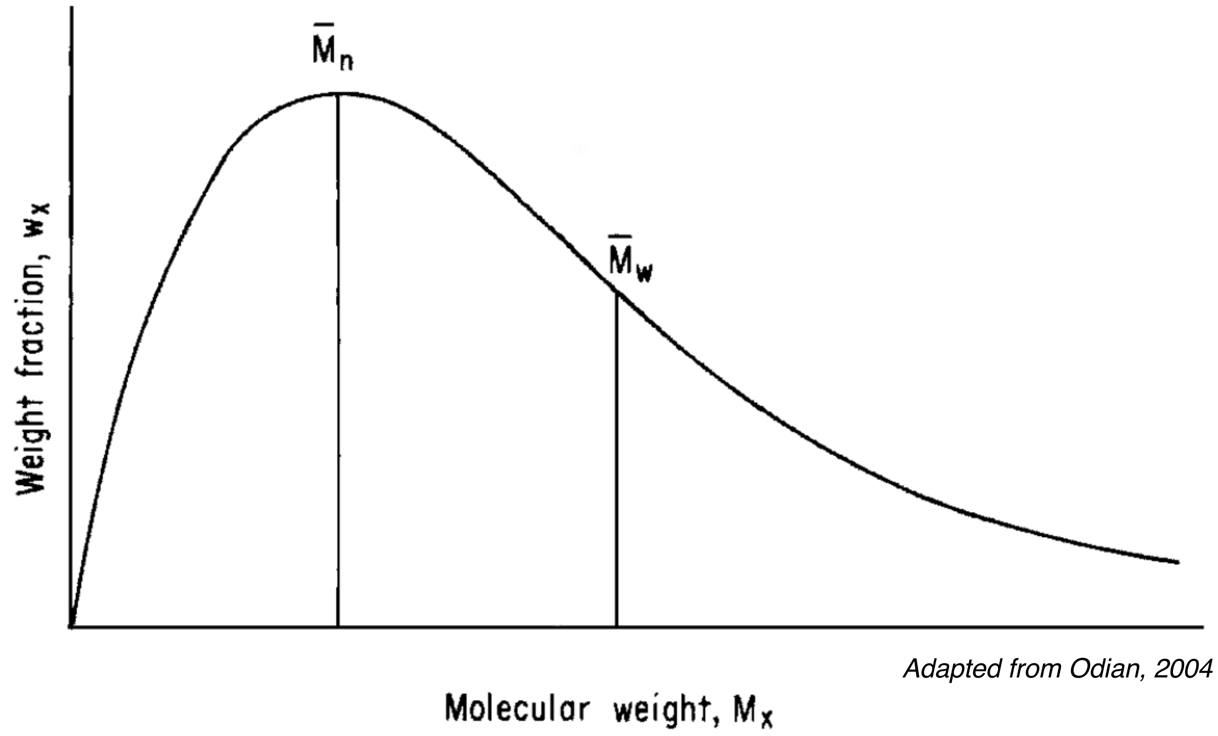
$$M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

N_x is the number of moles of polymer whose weight is M_x

M_w is biased towards the high molecular weight fraction

Different characterization methods will give different types of molecular weights!

Distribution and Dispersity (Đ)



Adapted from Odian, 2004

M_n is biased towards the low molecular weight fraction

M_w is biased towards the high molecular weight fraction

<u>Dispersity* (Đ)</u>

$$Đ = \frac{M_w}{M_n}$$

Đ is a parameter that measures the width of the molecular weight distribution of a polymer samples

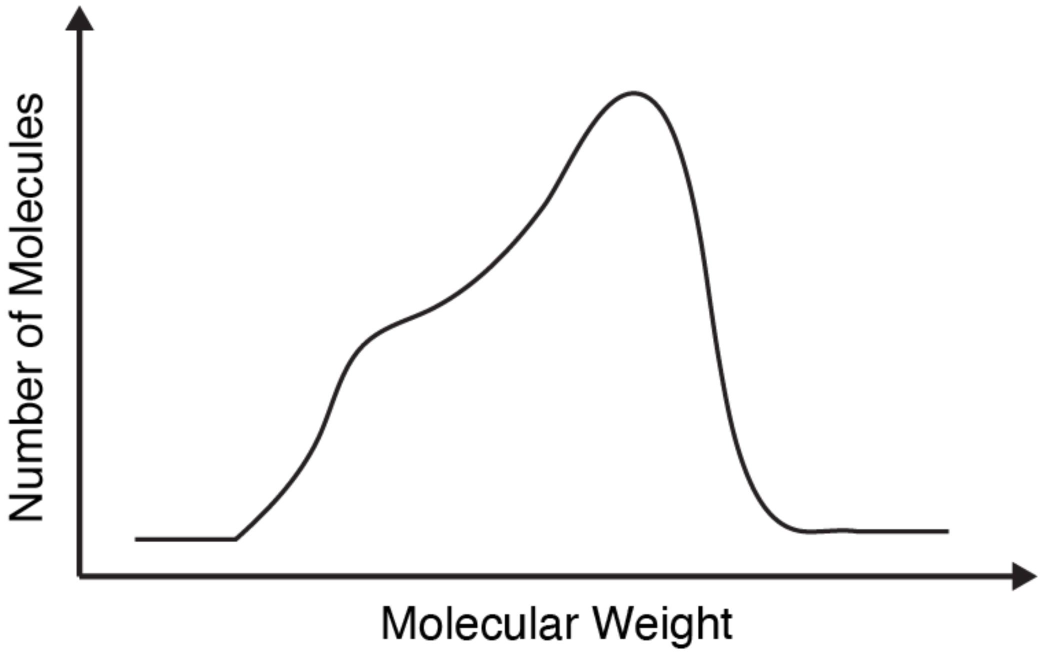
High dispersity = broad distribution
Low dispersity = narrow distribution

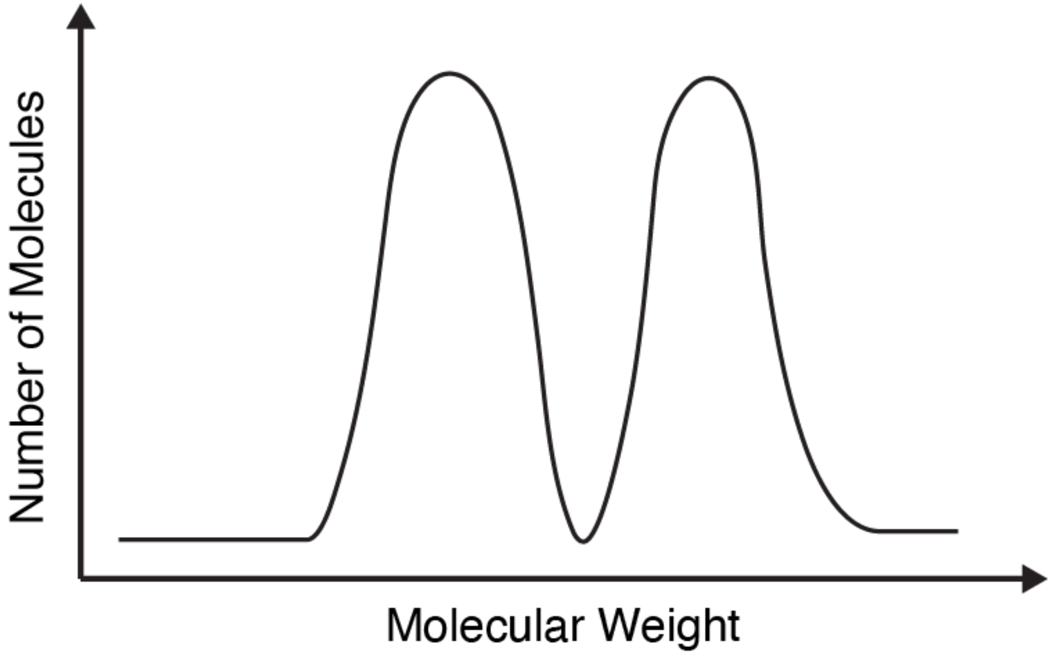
Đ cannot be smaller than 1

*Sometimes written as Polydispersity Index (PDI). This term has since been deprecated but can be found in older literature.

Distribution and Dispersity (Đ)

Average molecular weight alone is insufficient to characterize polymers.
Visualizing the complete distribution is important!



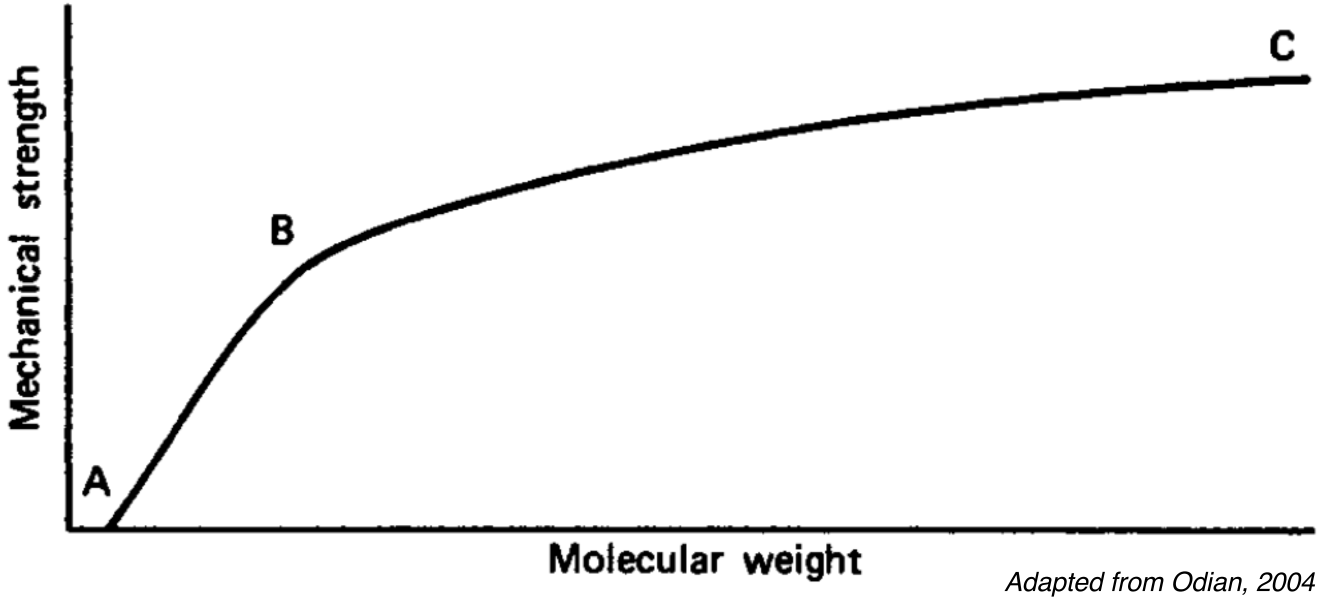


Just knowing M_n or M_w here alone would be misleading!

Why should we care about molecular weight?

The properties of a polymer are a function of its molecular weight (and other things)

E.g. Mechanical Properties



Adapted from Odian, 2004

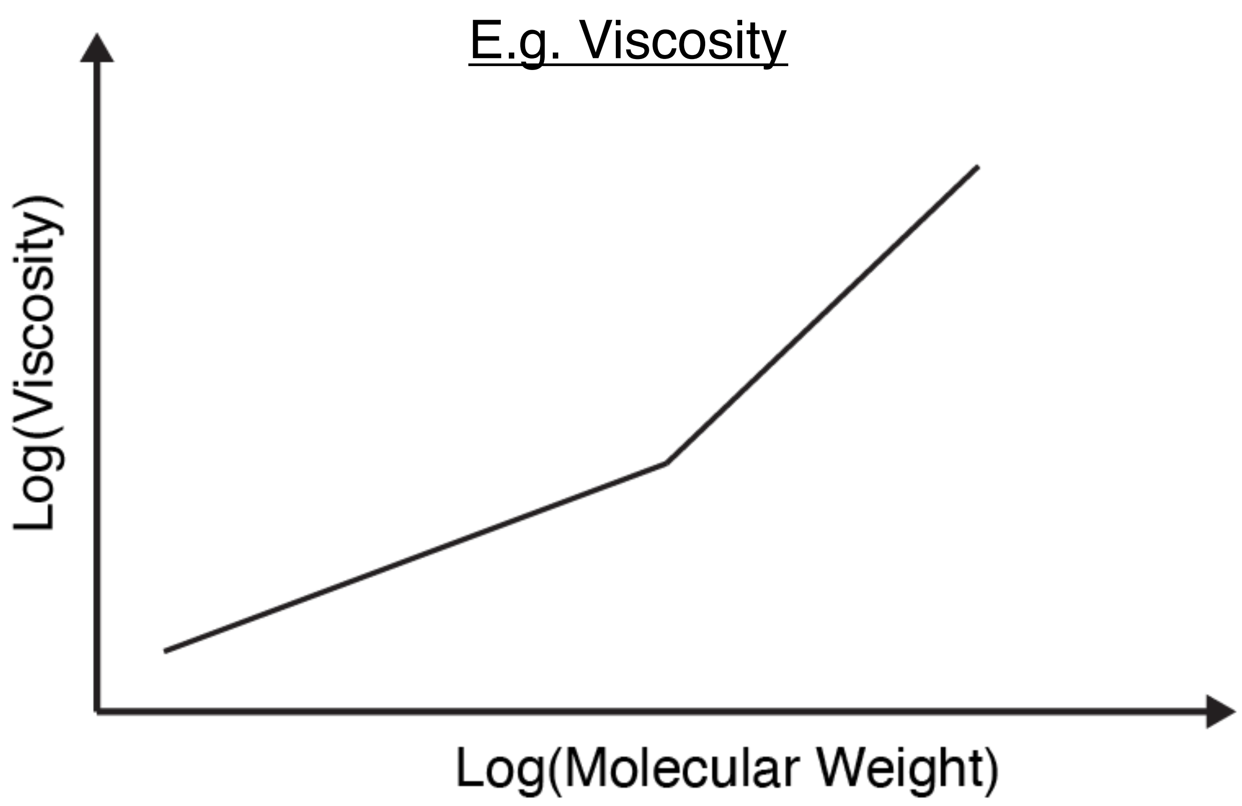
A. Minimal molecular weight for polymer to have appreciable strength

B. Above **A**, strength increases rapidly until a critical point **B** is reached.

C. Strength increases slowly past **B** until it reaches a limiting value **C**.

Why should we care about molecular weight?

The properties of a polymer are a function of its molecular weight (and other things)



Viscosity ∝ Molecular Weight

Viscosity impacts processability!

The ideal molecular weight is often not the manufactured molecular weight since compromises have to be made between properties and processability

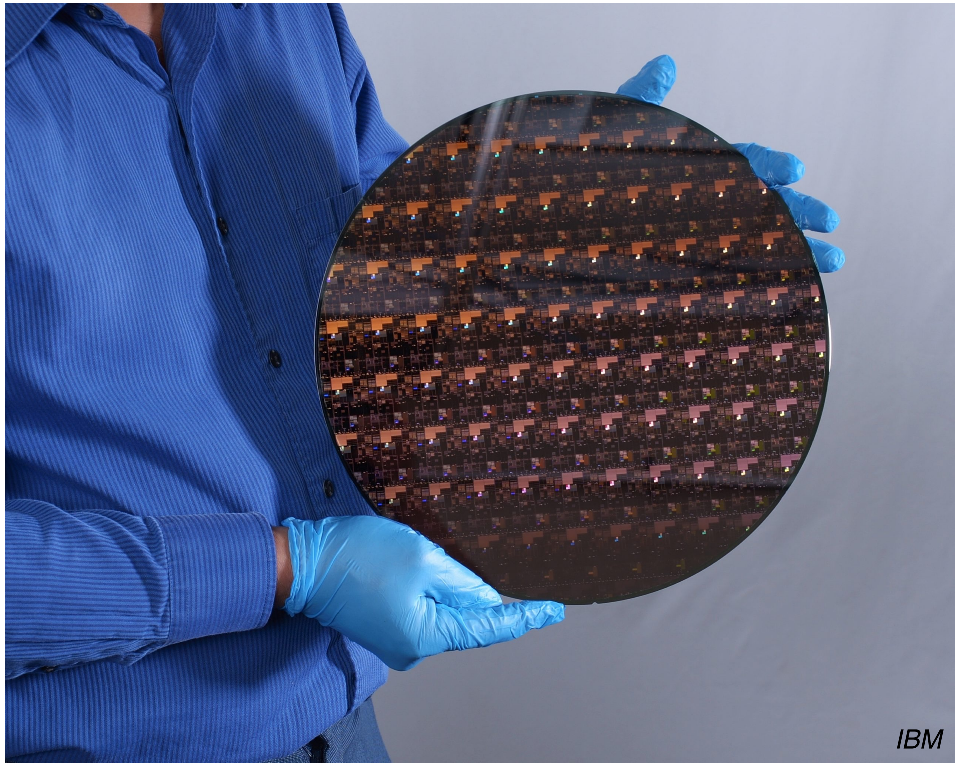
Week 2 Learning Objectives

- **Recognize some basic functional groups and their use in polymer synthesis**
- **Step-growth Polymerization**
  - Terms: Polyaddition, polycondensation, conversion, Carothers equation
- **Understand the molecular mechanisms of controlling molecular weight during step-growth polymerization**
- **Chain-growth Polymerization**
  - Terms: Chain polymerization, condensative chain polymerization, conversion, initiation, propagation, termination

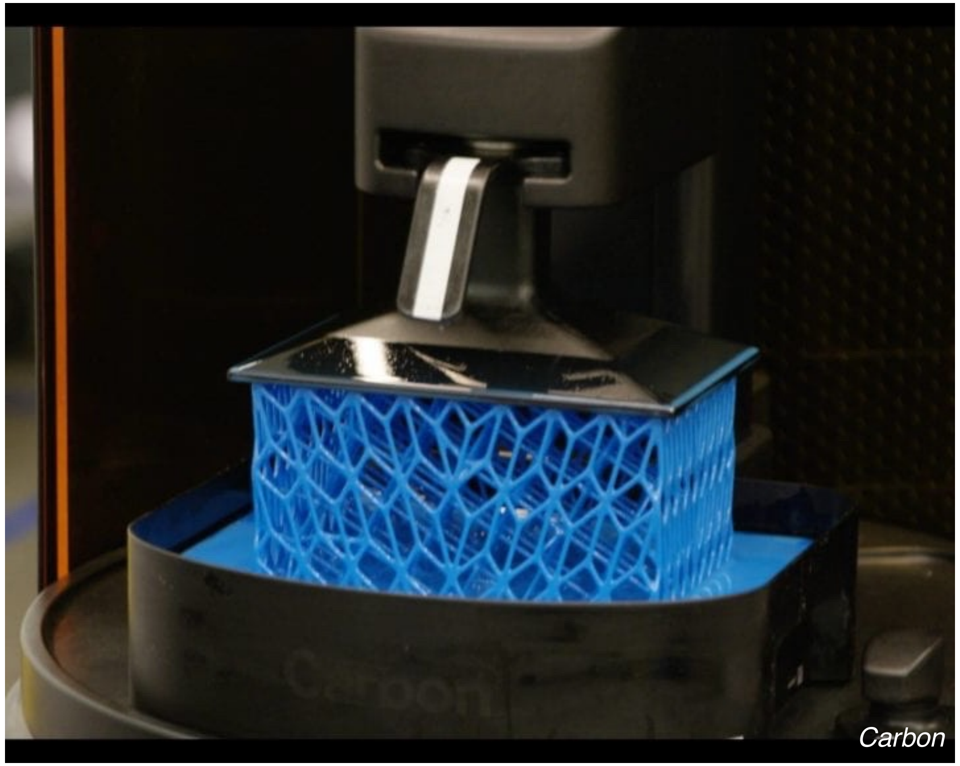
WHY SHOULD WE CARE ABOUT POLYMER SYNTHESIS?

Polymer Synthesis in Microengineering and Advanced Manufacturing

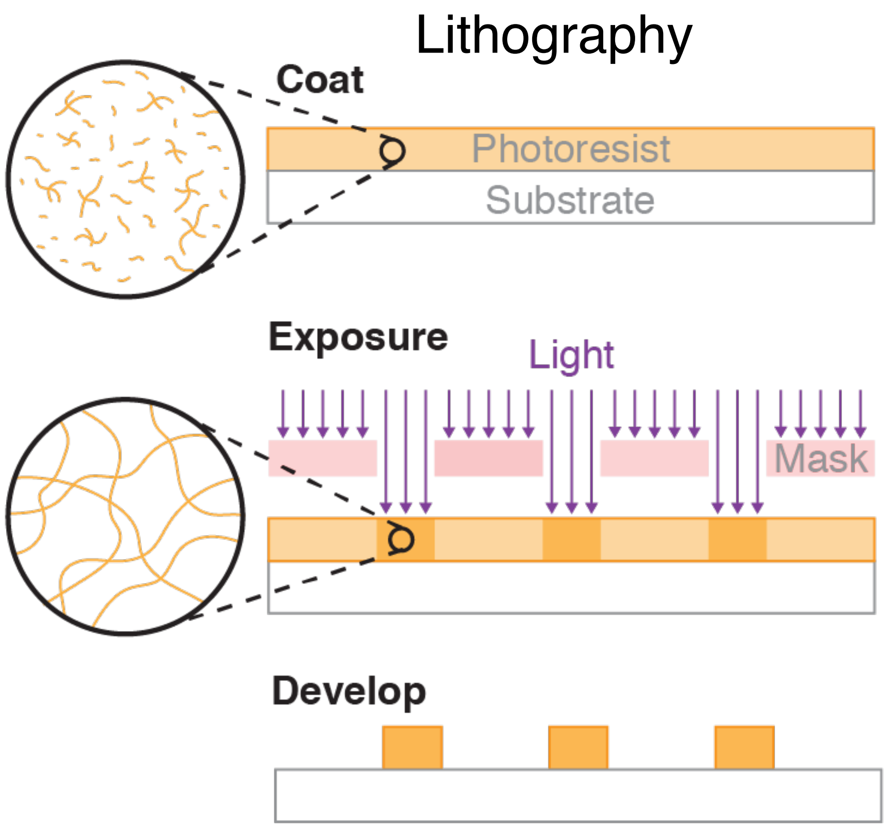
Lithography

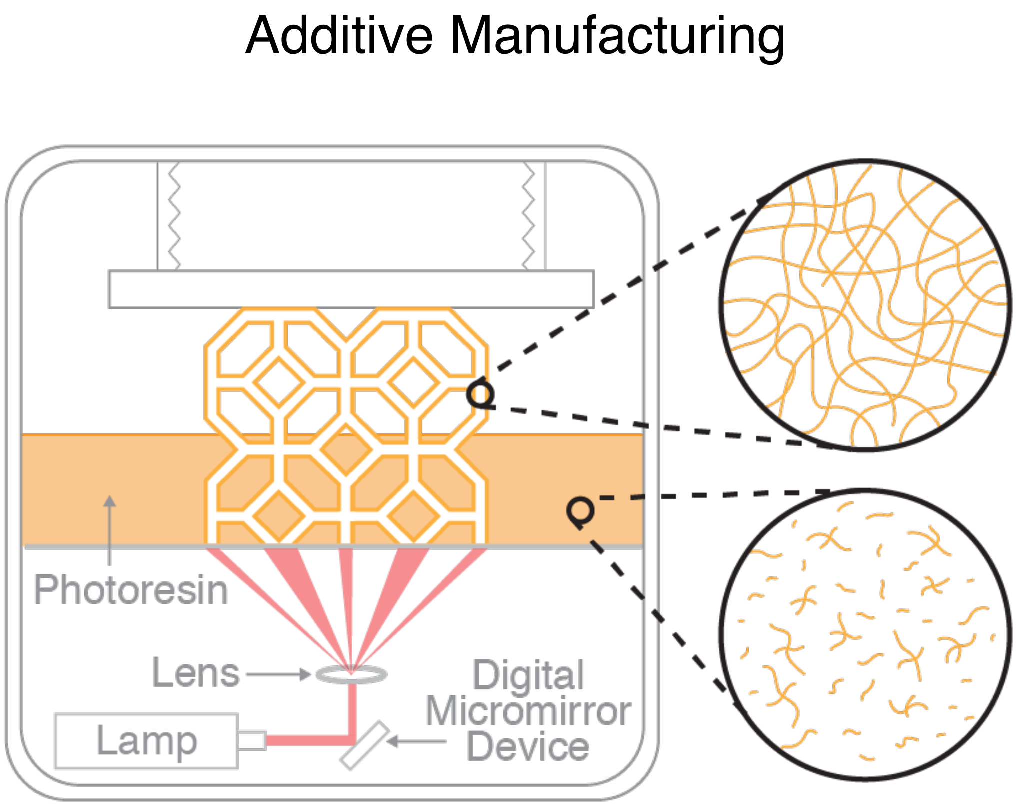


Additive Manufacturing



Polymer Synthesis in Microengineering and Advanced Manufacturing





Learning polymer synthesis → Understand manufacturing
+ Understand how to tune their properties

Today's Lesson: How does 2 part epoxy work?

Need to add proper amounts of each part

Left: Correct ratio

Right: Incorrect ratio

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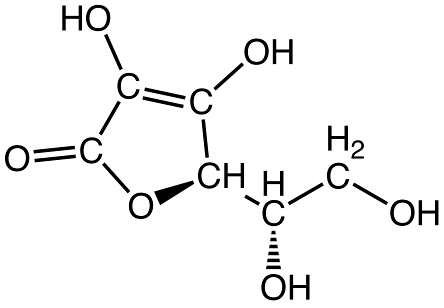
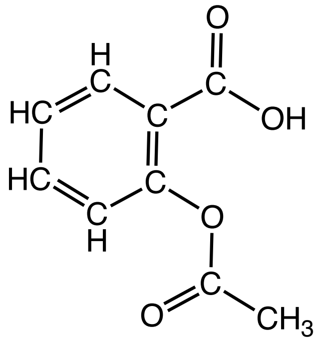
To understand synthesis, we need to know some chemistry

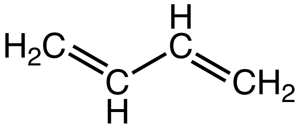
The goal here is not to be an expert in chemistry but to understand some patterns and *start* to think molecularly



Vitamin C



Aspirin

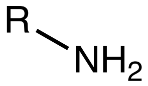


Acrolein

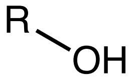
Functional groups:

- Parts of a molecule where reactions take place
- The reaction is the same or similar each time
- Allows for systematic prediction of reactions

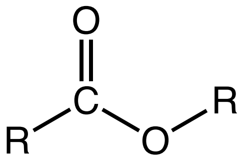
Functional groups commonly seen in polymerization*



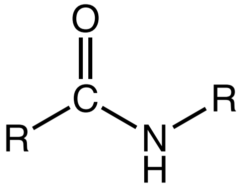
Amines



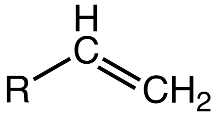
Hydroxyl



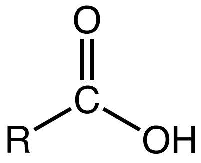
Ester



Amide



Vinyl



Carboxylic acid

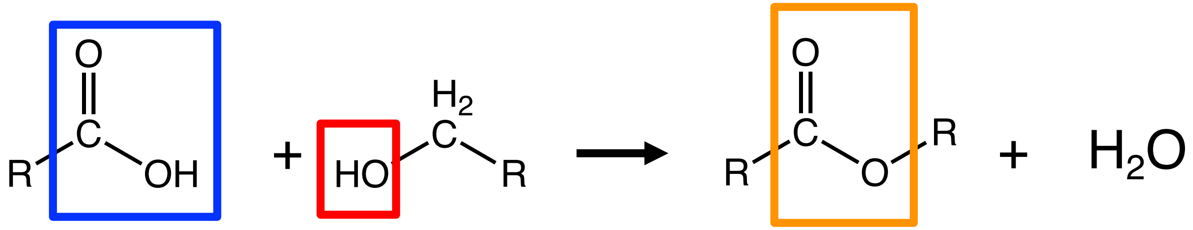
R is used here to denote the rest of the molecule

Adding a certain functional group could make a molecule "polymerizable" and vice versa

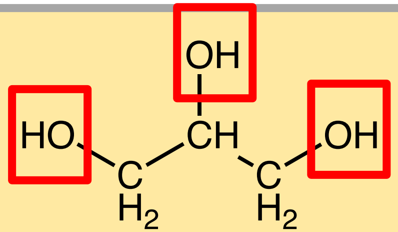
*This is a tiny fraction of all the functional groups out there

Some common polymerization reactions

Ester formation

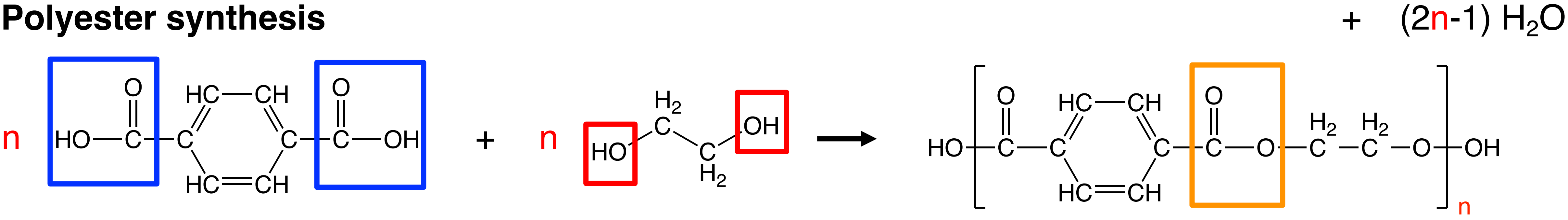


Carboxylic acid   Hydroxyl   Ester



What happens if we use this instead?
Assume all the -OH reacts similarly

Polyester synthesis

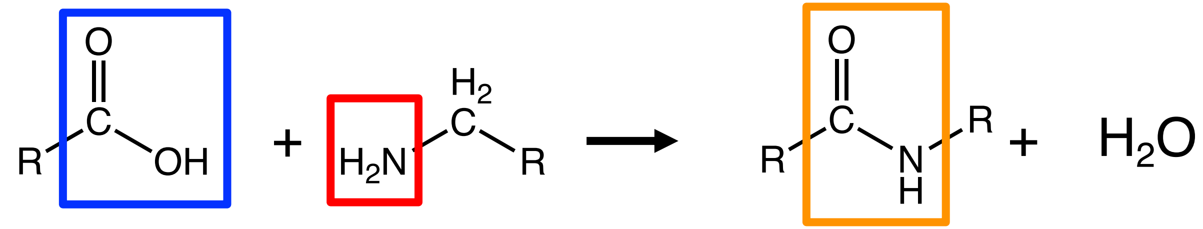


Terephthalic acid   Ethylene glycol   Poly(ethylene terephthalate) → PET

What kind of polymer architecture does this synthesis give us?

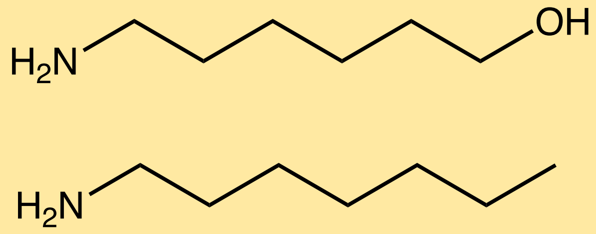
Some common polymerization reactions

Amide formation



Carboxylic acid Amine Amide

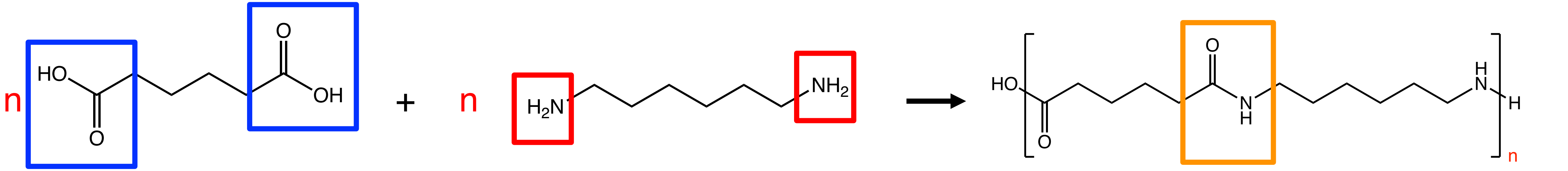
1.
2.



What happens if we use these instead?

Polyamide synthesis

$+ \quad (2n\text{-}1)\ H_2O$

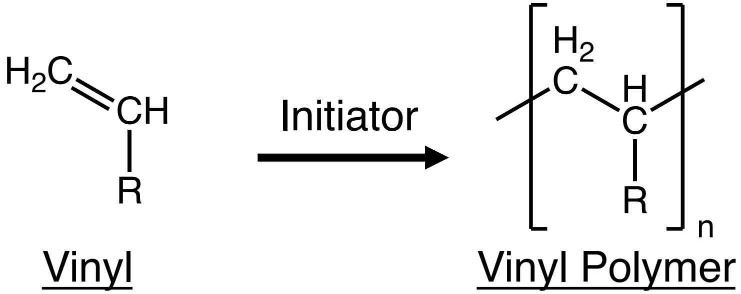


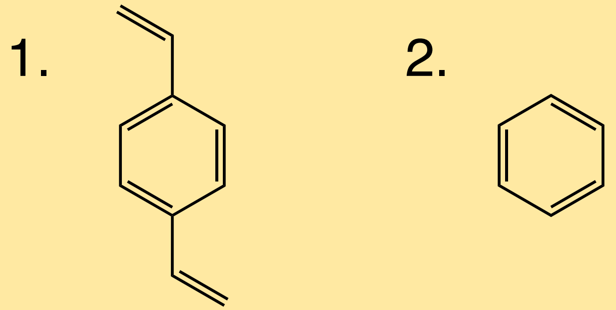
Adipic acid Hexamethylenediamine Nylon 66 → Cable ties

What kind of polymer architecture does this synthesis give us?

Some common polymerization reactions

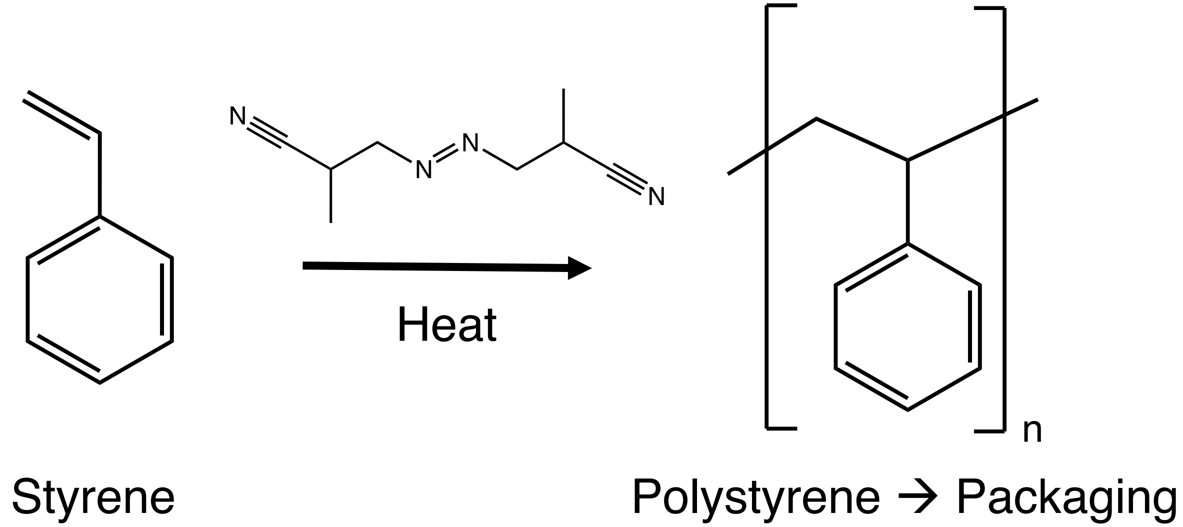
Free Radical Vinyl Polymerization





What happens if we use these instead?

Polystyrene synthesis

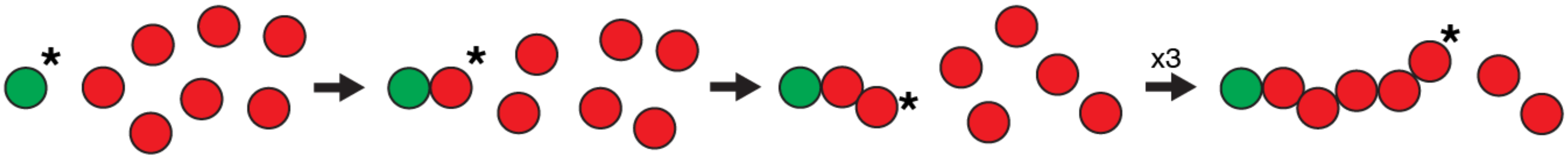


What kind of polymer architecture does this synthesis give us?

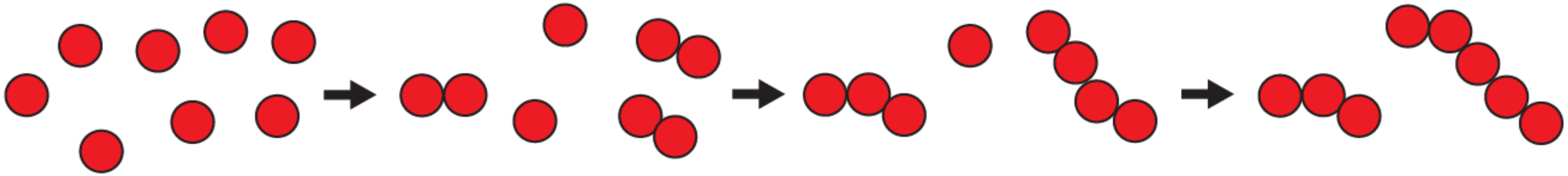
Week 1 Recap

Classifying polymers via polymerization mechanism

Chain-growth*: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain
Active site(s) regenerated at the end of each growth step



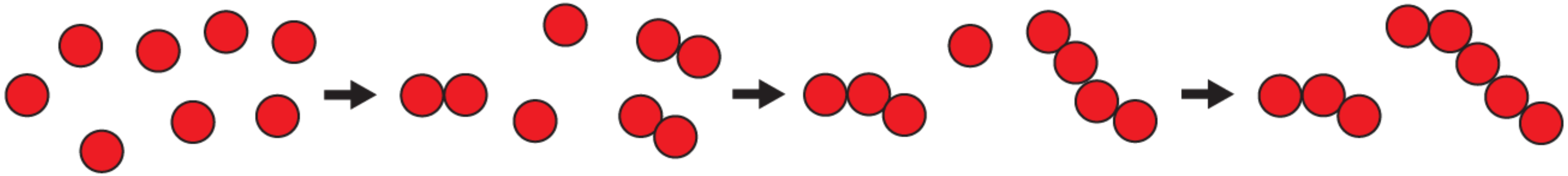
Step-growth*: Polymer grows via the reaction between any pairs of reactive species



*Deprecated by IUPAC but still very very widely used. Taught here so you'll be familiar with the literature.

STEP-GROWTH POLYMERIZATION

Step-growth*: Polymer grows via the reaction between any pairs of reactive species



Step-growth Polymerization: A word about terminology

Active discussion within the polymer community about the appropriate terminology.

– The literature has multiple terms that refer to the same/similar thing → Confusing!

1. **Step-growth polymerization** is also sometimes called **step polymerization**. This is fine.
2. Some treat **condensation polymerization** as synonymous with **step polymerization**. Not ok.
3. **Condensation polymerization ≠ polycondensation**

Most common terms used in literature:

- **Step-growth polymerization**
- **Step-polymerization**.

This year we will teach this. But be aware of the IUPAC definition

IUPAC recommendation for mechanisms where molecules of all sizes react together

- **Polycondensation (with byproduct)**
- **Polyaddition (with no byproduct)**

Step-growth Polymerization — Let’s Play a Game

Step-growth rules:

- Shake hands to form a bond!
- Anyone can shake hands with anyone
- You cannot form 2 bonds with the same person
- Held hands cannot be un-held

- **If you can, form a bond each time I say “Go”**

→ What can this simple game tell us about step-growth polymerization?

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STEP GROWTH POLYMERIZATION
LET'S PLAY A MORE COMPLEX GAME

Step-growth Polymerization — Let's Play a Game

Step-growth rules (more complex version):

- Shake hands to form a bond!
- Anyone can shake hands with anyone
- You cannot form 2 bonds with the same person
- **To shake hands, play Rock-Paper-Scissors**
  - **If there is a winner – shake hands**
  - **If it's a draw, do not shake hands**
- Held hands cannot be un-held
- **If you can, try forming a bond each time I say "Go"**

→ What can this simple game tell us about step-growth polymerization?

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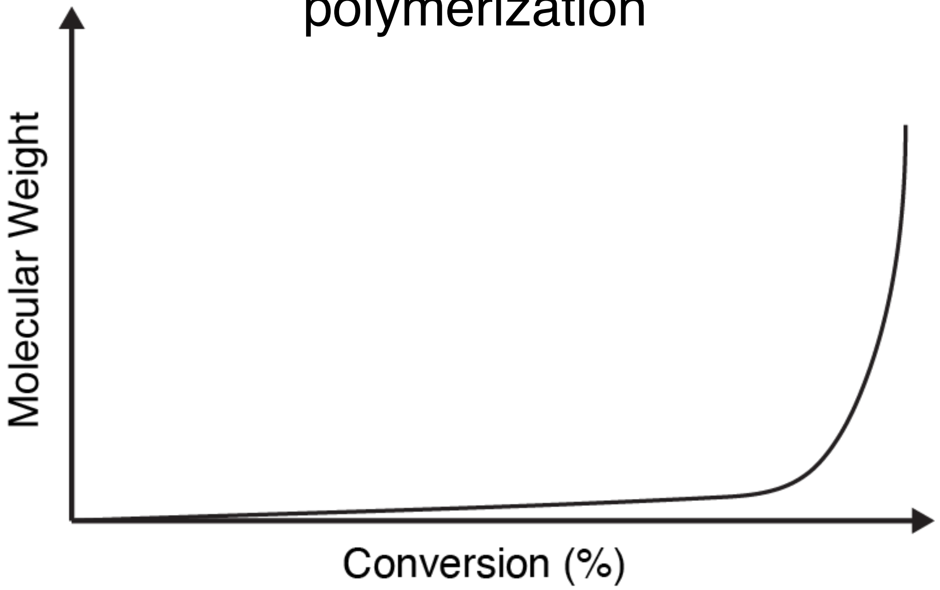
Step-growth Polymerization and Molecular Weight

Step-growth: Polymer grows via the reaction between any pairs of reactive species

Recall: Molecular weight influences polymer properties

<u>How do we control molecular weight during step-growth polymerization?</u>

Typical step-growth polymerization



monomer + monomer	→ dimer
dimer + monomer	→ trimer
dimer + dimer	→ tetramer
trimer + monomer	→ tetramer
trimer + dimer	→ pentamer
trimer + trimer	→ hexamer
tetramer + monomer	→ pentamer
tetramer + dimer	→ hexamer
tetramer + trimer	→ heptamer
tetramer + tetramer	→ octamer

⋮

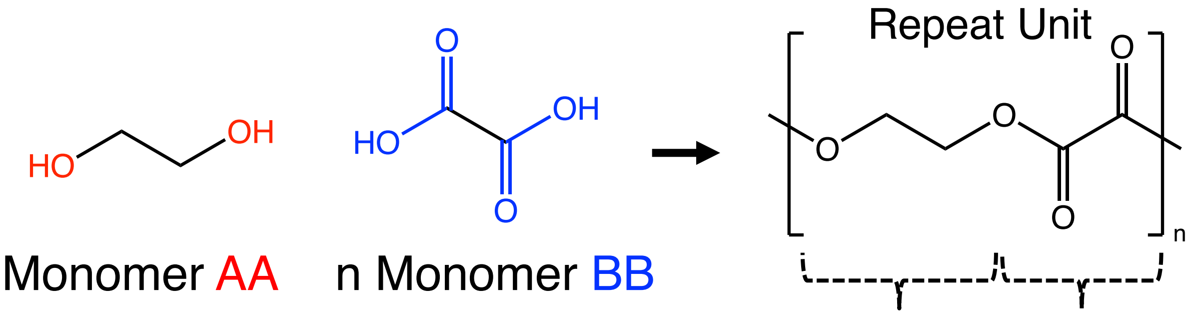
Assume reactivity of functional groups are independent of *x–mer* length

Molecular weight increases slowly!

Step-growth Polymerization and Molecular Weight

For a desired polymer length, how much monomer do we need to react?

Example system:
(Polyester)



+ (2n-1) H_2O

Structural/ Monomeric Unit AA

Structural/ Monomeric Unit BB

Assume equimolar bifunctional monomers

Since A can only react with B, we can simplify our reaction system as such:

1. The number of unreacted A **or** B is equal to the total number of molecules in the system at time t

2. The total number of structural/monomeric units and monomers in the system
= total number of AA + BB **initially present**

Step-growth Polymerization and Molecular Weight

1. The number of unreacted A **or** B is equal to the total number of molecules in the system at time t
2. The total number of monomeric units + monomers in the system is conserved

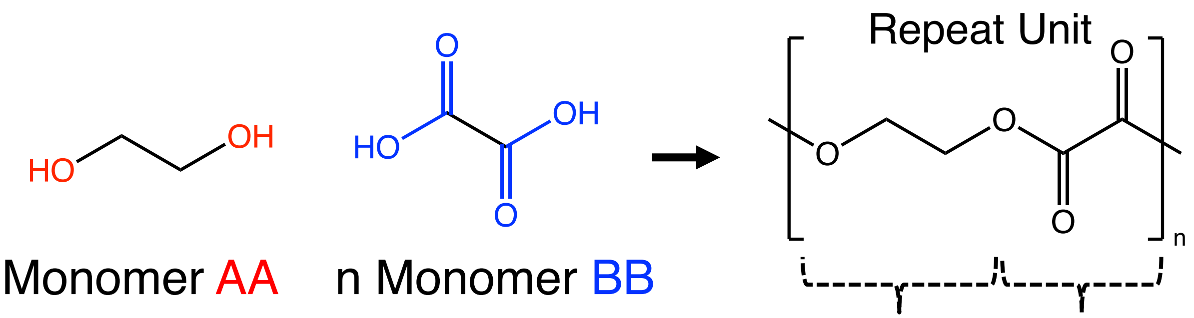
Number of AA molecules	Number of BB molecules	Oligomer sequences	Number of monomeric units + unreacted monomers	Total number of molecules	Total number of unreacted A
n	n	-	2n	2n	2n
n-1	n-1	AABB	2 + 2(n-1) = 2n	2n-1	2(n-1) + 1 = 2n-1
n-2	n-1	AABBAA	3 + (n-2) + (n-1) = 2n	2n-2	2(n-2) + 2 = 2n-2
n-3	n-3	BBAABBAA AABB	6 + (n-3) + (n-3) = 2n	2n-4	2(n-3) + 2 = 2n-4
n-3	n-5	BBAABBAABB BBAABB	8 + (n-3) + (n-5) = 2n	2n-6	2(n-3) = 2n-6
n-11	n-13	3 BBAABBAABB BBAABBAABBAA AABBAA	5 + 5 + 5 + 6 + 3 + (n-11) + (n-13) = 2n	n-11 + n-13 + 5 = 2n-19	2(n-11) + 3 = 2n-19
0	0	n AABB	2n	n	n
0	0	n/5 AABBAABBAABB n/5 AABBAABB	$\frac{6n}{5} + \frac{4n}{5} = 2n$	$\frac{2n}{5}$	$\frac{n}{5} + \frac{n}{5} = \frac{2n}{5}$

For an equimolar system, tracking either A or B is sufficient to measure the reaction

Step-growth Polymerization and Molecular Weight

For a desired polymer length, how much monomer do we need to react?

Example system:
(Polyester)



+ (2n-1) H_2O

n Monomer AA   n Monomer BB

Structural/ Monomeric Unit AA   Structural/ Monomeric Unit BB

Assume equimolar bifunctional monomers

Conversion (p): $$p = \frac{[M]_0 - [M]}{[M]_0}$$

Fraction of reactant that has reacted at time t

[M]$_0$ = Concentration of unreacted **groups** OH **or** COOH at t = 0
[M] = Concentration of unreacted **groups** OH **or** COOH at t

Number average degree of polymerization ($\bar{X}_n$) $$\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1-p}$$

Carothers Equation

$$\frac{\textit{Total number of molecules initially present}}{\textit{Total number of molecules at time t}}$$

Average number of **monomeric units** per chain

Step-growth Polymerization and Molecular Weight

Number average degree of polymerization ($\bar{X}_n$) $\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1-p}$

Carothers Equation

$$\frac{Total\ number\ of\ molecules\ initially\ present}{Total\ number\ of\ molecules\ at\ time\ t}$$

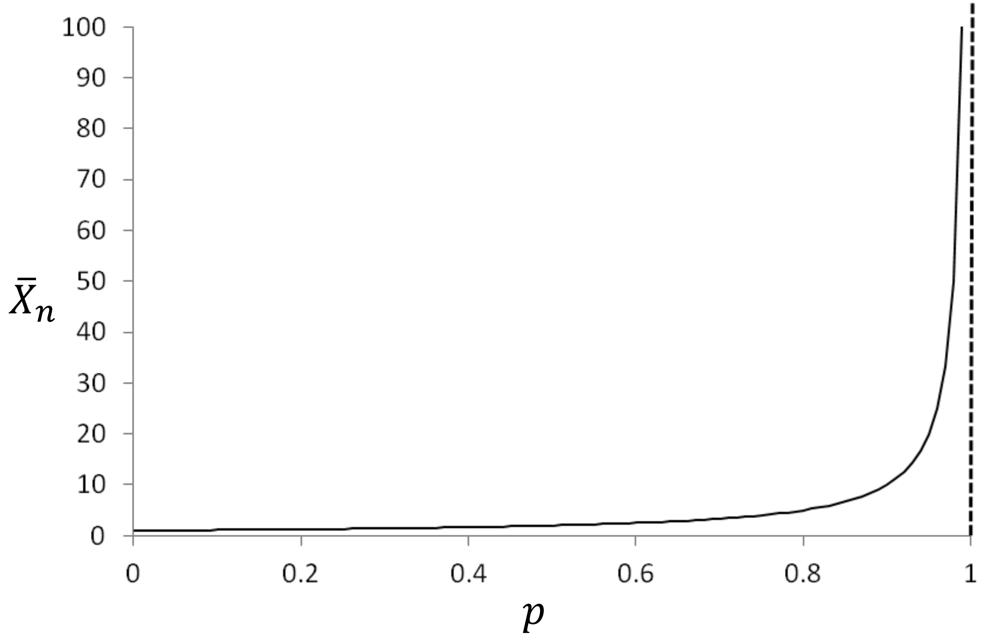
Average number of **monomeric units** per chain

Number average molecular weight $\bar{M}_n = \frac{total\ weight\ of\ polymers}{total\ number\ of\ polymers}$

$= M_0\bar{X}_n + M_{eg} \approx M_0\bar{X}_n$, i.e. M_{eg} is small

$= \frac{M_0}{1-p}$

M_0 = Mean of the molecular weights of the two monomeric units
M_{eg} = Molecular weight of the end groups
p = Conversion



Assuming equimolar reagents:

To achieve high molecular weight polymers, the reaction needs to be very near completion!

At $p = 0.9$, $\bar{X}_n = 10$
At $p = 0.98$, $\bar{X}_n = 50$
At $p = 0.999$, $\bar{X}_n = 1000$

→ High Temperatures
Long reaction times

Step-growth Polymerization and Molecular Weight

Where do we see this relationship manifesting?

2-part epoxy

Contains A →

Contains ← B

PDMS

Long cure times: 24 – 48 hrs
Temperature dependent curing

For bifunctional stoichiometric systems:

$$\bar{X}_n = \frac{1}{1-p}$$

In general for step-growth systems*:

$$\bar{X}_n \propto \frac{1}{f(p)}$$

High conversions needed for "useful" polymer → Long times needed

High temperatures are needed to achieve *p* rapidly

EPFL

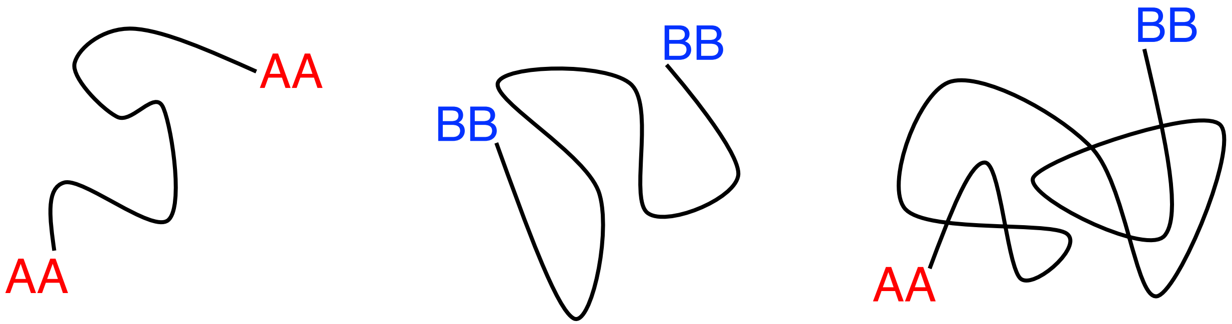
*this is a simplification since factors like crosslinking, functionality, viscosity, stoichiometry, etc. all play a role. But the idea holds.

Controlling Molecular Weight in Step-Growth Polymerization

At $p = 0.98$, $\bar{X}_n = 50$
At $p = 0.99$, $\bar{X}_n = 100$
At $p = 0.999$, $\bar{X}_n = 1000$

→ At large p, small changes in p leads to large changes in $\bar{X}_n$.
Not practical to control $\bar{X}_n$ solely using p

Even if you could stop the reaction perfectly, what happens if the polymers are heated again?



→ End groups can react further with each other → Growth!

Nonstoichiometric reaction → Polymerization stops when one reagent is completely used up

1. Adjust relative concentration of bifunctional reagents
2. Introduce monofunctional monomer (chain stopper)

Controlling Molecular Weight in Step-Growth Polymerization

Case 1. AA and BB, with BB in excess

Number of A groups = N_A
Number of B groups = N_B

Stoichiometric ratio, $r = \frac{N_A}{N_B}$

Total number of monomers = $\frac{N_A + N_B}{2}$

$$= \frac{N_A\left(1+\frac{1}{r}\right)}{2}$$

Fraction of A that have reacted at time t → p

Fraction of B that have reacted at time t → rp

Number of unreacted A at time t → $N_A(1-p)$

Number of unreacted B at time t → $N_B(1-rp)$

Total number of polymer chain ends = sum of the total number of unreacted A and B groups

Since each polymer has 2 ends, the total number of polymer molecules = $\frac{1}{2}$ the total number of chain ends

$$= \frac{N_A(1-p)+N_B(1-rp)}{2}$$

$$\bar{X}_n = \frac{Total\ number\ of\ molecules\ initially\ present}{Total\ number\ of\ molecules\ at\ time\ t}$$

$$= \frac{\frac{N_A\left(1+\frac{1}{r}\right)}{2}}{\frac{N_A(1-p)+N_B(1-rp)}{2}} = \frac{1+r}{1+r-2rp}$$

Controlling Molecular Weight in Step-Growth Polymerization

Case 1. AA and BB, with BB in excess

$$\bar{X}_n = \frac{1+r}{1+r-2rp}, \quad r = \frac{N_A}{N_B} \leq 1$$

If $N_A = N_B$ → r = 1 → $\bar{X}_n = \frac{1}{1-p}$

If $p = 1$ → $\bar{X}_n = \frac{1+r}{1-r}$ Growth is now limited!
(Realistically, p is never 1)

Some perspective:

At $p = 1$, $r = 0.99$, $\bar{X}_n = 201$
At $p = 1$, r = 0.999, $\bar{X}_n = 2001$
At $p = 0.99$, r = 0.99, $\bar{X}_n = 67$
At $p = 0.99$, r = 1, $\bar{X}_n = 100$

Stoichiometric control is important!

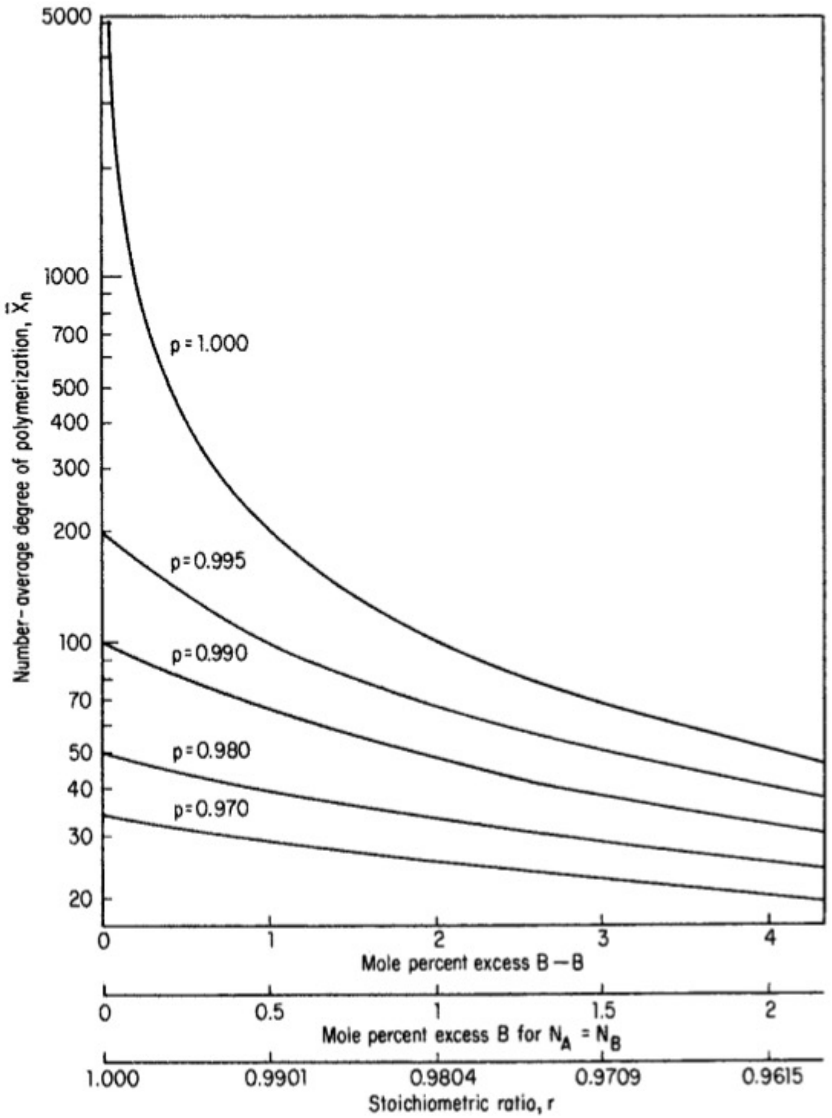


Fig. 2-8 Dependence of the number-average degree of polymerization $\bar{X}_n$ on the stoichiometric ratio r for different extents of reaction p in the polymerization of A—A with B—B.

Adapted from Odian 2004

*Case 2 will be described in an exercise

EPFL

Controlling Molecular Weight in Step-Growth Polymerization

Stoichiometric control is important! Example: Mixing 2-part epoxy

Left: Correct ratio
Right: Incorrect ratio

A quick refresher about kinetics

Molecularity	Elementary Step	Rate Law	Example
Unimolecular	$A \rightarrow Products$	$rate = k[A]$	$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
Bimolecular	$A + A \rightarrow Products$	$rate = k[A]^2$	$2NOCl \rightarrow 2NO_{(g)} + Cl_{2(g)}$
	$A + B \rightarrow Products$	$rate = k[A][B]$	$CO_{(g)} + NO_{3(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$
Termolecular	$A + A + A \rightarrow Products$	$rate = k[A]^3$	
	$A + A + B \rightarrow Products$	$rate = k[A]^2[B]$	$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ [2]
	$A + B + C \rightarrow Products$	$rate = k[A][B][C]$	$H + O_{2(g)} + M \rightarrow HO_{2(g)} + M$ [3]

Kinetics of Step Growth Polymerization

How long does it take to reach high conversions?

In a generic case of bifunctional stoichiometric monomers*: n AA + n BB → P(AABB)$_n$ + some by products

$$Rate = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

$$= k[A][B]$$

Since [A] and [B] are the same (stoichiometric),

$$\rightarrow [A] = [B] = [M]$$

$$Rate = \frac{d[P]}{dt} = -\frac{d[M]}{dt} = k[M]^2$$

Integrating → $\frac{1}{[M]} - \frac{1}{[M]_0} = kt$

$$\frac{[M]_0}{[M]} - \frac{[M]_0}{[M]_0} = [M]_0 kt$$

Recall that $\bar{X}_n = \frac{[M]_0}{[M]} = \frac{1}{1-p}$

$$\rightarrow \bar{X}_n - 1 = [M]_0 kt$$

$$\bar{X}_n = [M]_0 kt + 1$$

If we assume that $[M]_0kt >> 1$ then $\bar{X}_n \approx [M]_0 kt$

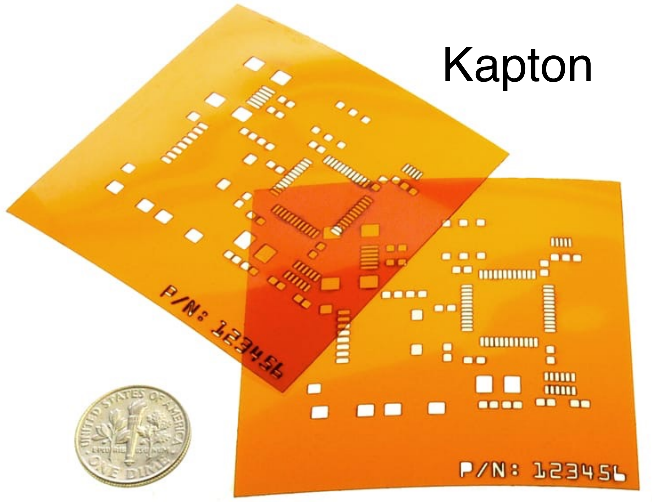
At $p = 0.98$, $\bar{X}_n = 50$, time t
At $p = 0.99$, $\bar{X}_n = 100$, time 2t

→ 2x time for only a 1% increase in conversion!

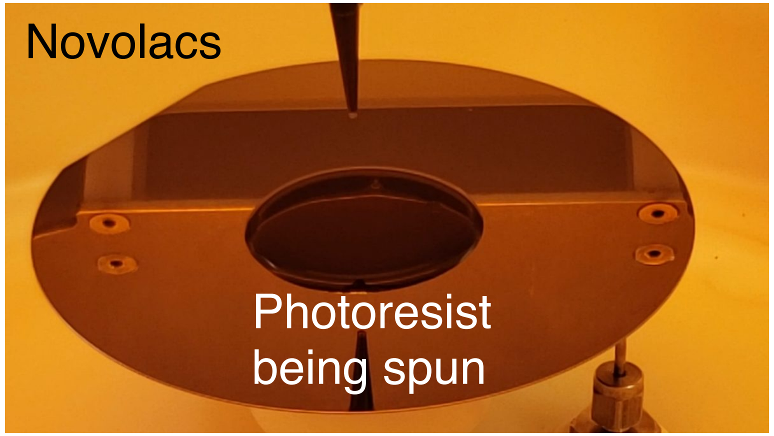
*We assume no catalysis is needed for this reaction, self or otherwise

Some Industrially Relevant Step-Growth Polymers

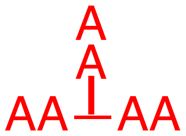
- Polyesters
- Polyethylene terephthalate (PET)
- Polycarbonates
- Polyether ether ketone (PEEK)
- Kevlar
- Kapton
- Novolacs (used as photoresists in photolithography)
- Epoxy resins
- Polyurethane foams
- Silicones



Kapton



Step-growth Polymerization: What we did not cover

- Stoichiometric multifunctional monomers: What about 

BBBB
- Stoichionetric bifunctional monomers with chain stoppers
- Nonstoichiometry with multifunctional monomers
- Kinetics of self-catalyzed step-growth polymerizations
- Kinetics of catalyzed step-growth polymerizations
- Molecular weight distributions
- Dispersity of step-growth polymers

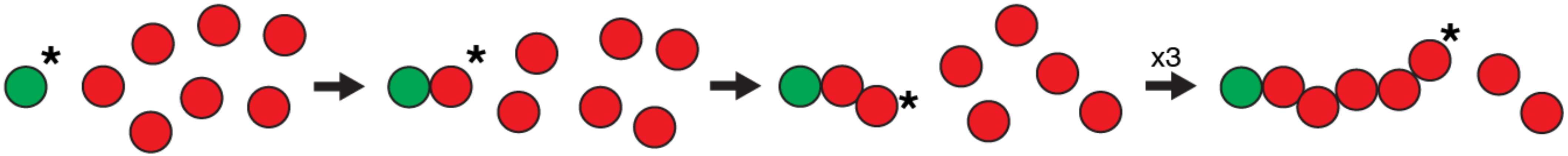
More advanced models that explains what you see in your day to day life but this isn't Polymer Chemistry 101

Key Takeaways

- Step-growth polymerization occurs between any species present in the reaction system
- High conversions required to obtain large molecular weights
- Stoichiometric control is important for high molecular weights
- Long reaction times often needed for high molecular weights

CHAIN-GROWTH POLYMERIZATION

Chain-growth*: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain
Active site(s) regenerated at the end of each growth step



Chain-growth Polymerization: A word about terminology

Active discussion within the polymer community about the appropriate terminology.

– The literature has multiple terms that refer to the same/similar thing → Confusing!

1. **Chain-growth polymerization** is also sometimes called **chain polymerization**. This is fine.
2. Some treat **addition polymerization** as synonymous with **chain polymerization**. Not ok.
3. **Addition polymerization ≠ polyaddition**

Most common terms used in literature:

- **Chain-growth polymerization**
- **Chain-polymerization**.

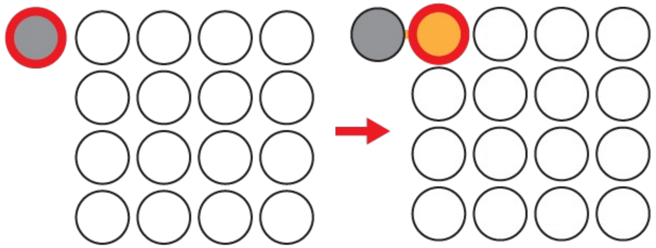
This year we will teach this. But be aware of the IUPAC definition

IUPAC recommendation for mechanisms where molecules react with active chains

- **Condensative chain polymerization (with byproduct)**
- **Chain polymerization (with no byproduct)**

Chain-growth Polymerization: The Three Phases

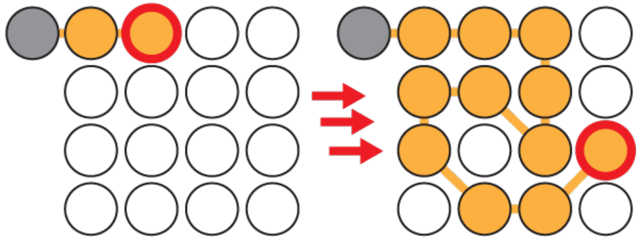
Initiation



$$I \rightarrow I^*$$

$$I^* + M \rightarrow I\text{-}M^*$$

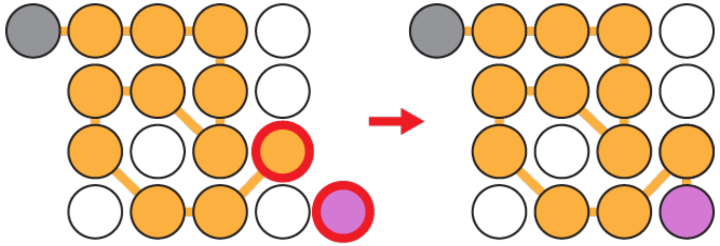
Propagation



$$I\text{-}M^* + M \rightarrow I\text{-}M\text{-}M^*$$

$$I\text{-}M\text{-}M^* \xrightarrow{M} I\text{-}M\text{-}(M)_n\text{-}M^*$$

Termination



$$I\text{-}M\text{-}(M)_n\text{-}M^* + Y^* \rightarrow I\text{-}M\text{-}(M)_n\text{-}M\text{-}Y$$

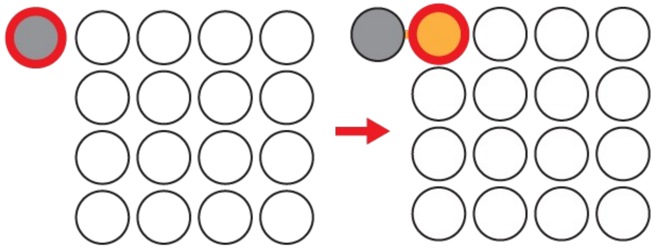
Active site is a high-energy state
→ Lower energy by forming a bond between monomer and polymer

High energy state is transferred from one molecule to another until termination
→ One monomer at a time

Note: Color here is just a guide to the eye, color is not used normally to denote different phases

Chain-growth Polymerization: The Three Phases

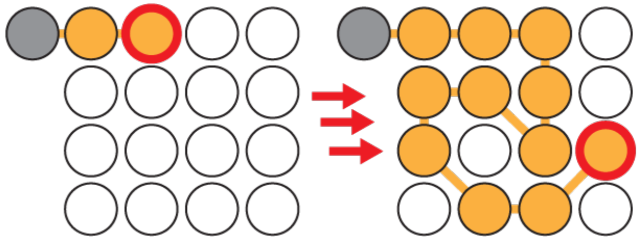
Initiation



$I \longrightarrow I^*$

$I^* + M \longrightarrow I\text{-}M^*$

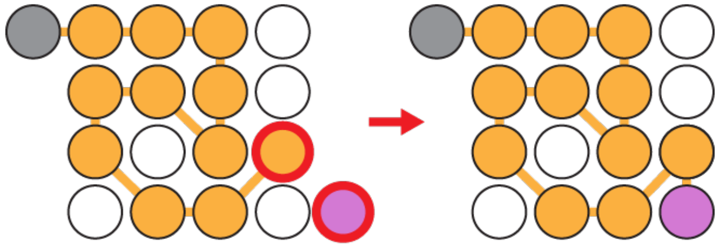
Propagation



$I\text{-}M^* + M \longrightarrow I\text{-}M\text{-}M^*$

$I\text{-}M\text{-}M^* \xrightarrow{M} I\text{-}M\text{-}(M)_n\text{-}M^*$

Termination



$I\text{-}M\text{-}(M)_n\text{-}M^* + Y^* \longrightarrow I\text{-}M\text{-}(M)_n\text{-}M\text{-}Y$

Termination often occurs before complete consumption of monomers

Termination **often** occurs via reaction with another active site → Loss of active site(s)

There can be multiple active sites in the system at the same time.
Active sites can also be generated

Note: Color here is just a guide to the eye, color is not used normally to denote different phases

Chain-growth Polymerization: Initiation

Initiation

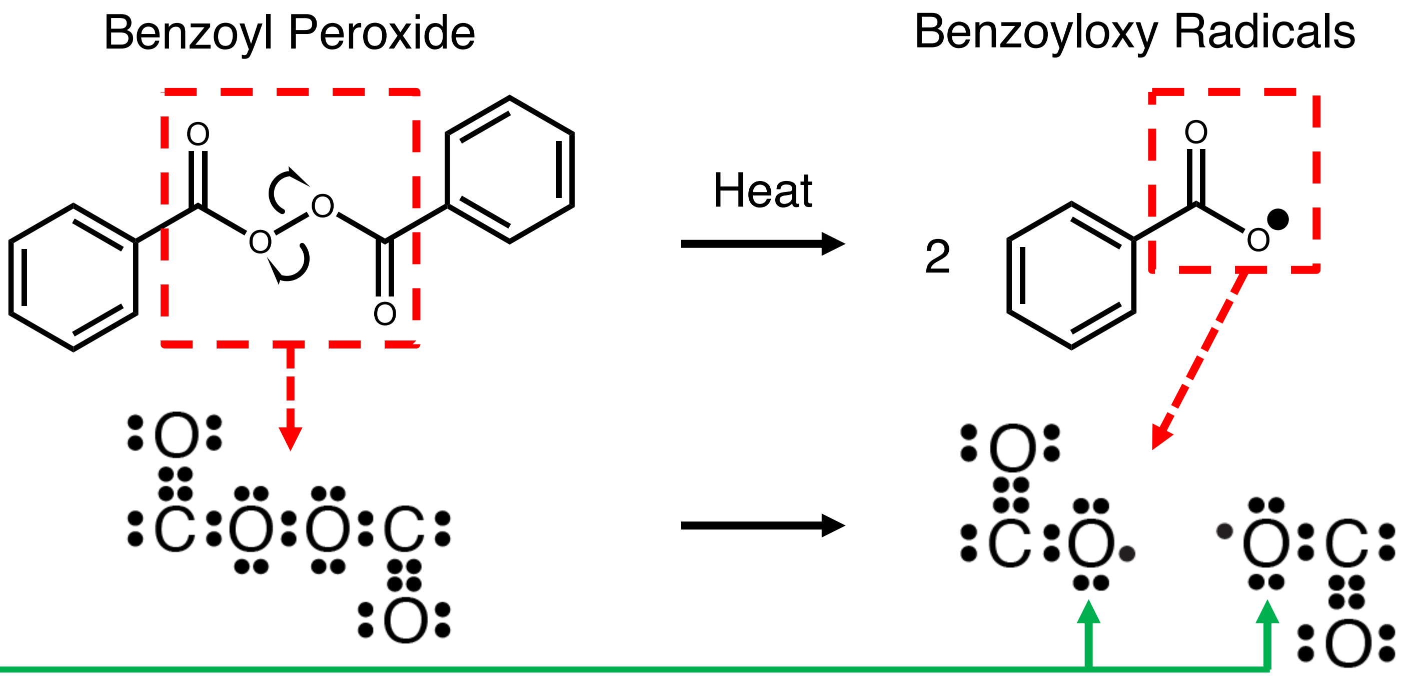
$I \longrightarrow I^*$

Step-growth polymerization: all species can react

Chain-growth polymerization: **initiated** by a reactive species I^* produced from an **initiator** I

I^* can be a free radical, $I^\bullet$, cation, I^+, or anion, I^- → We will focus on just free radicals, $I^\bullet$

A radical is an atom, molecule, or ion that has at least one unpaired valence electron



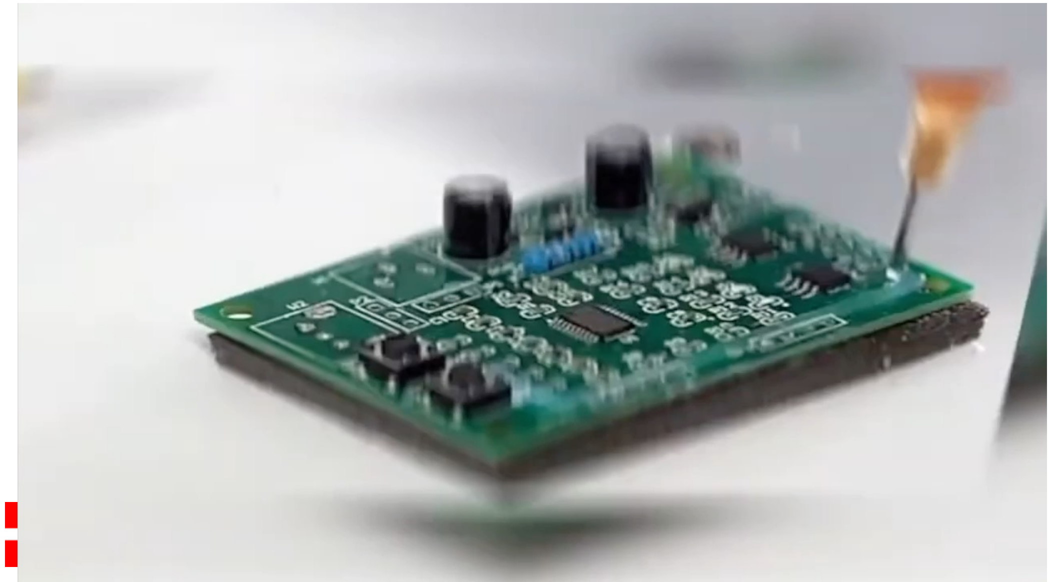
Chain-growth Polymerization: Initiation

Initiation ⟶ Two reactions

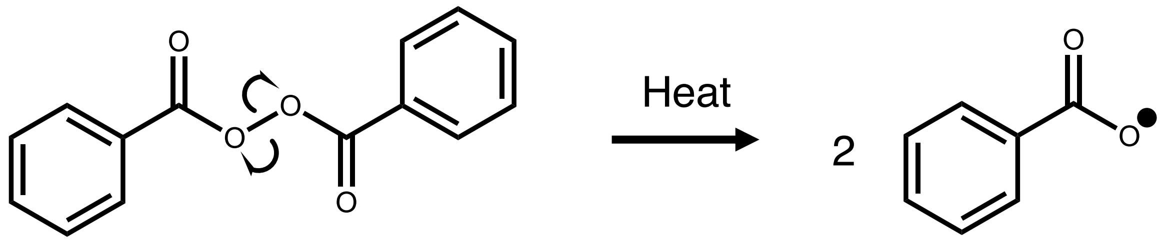
1. $I \longrightarrow 2I^{\bullet}$ (Primary radical)

Depending on the initiator, primary radicals can be formed via heat, redox reactions, radiation, and electricity.

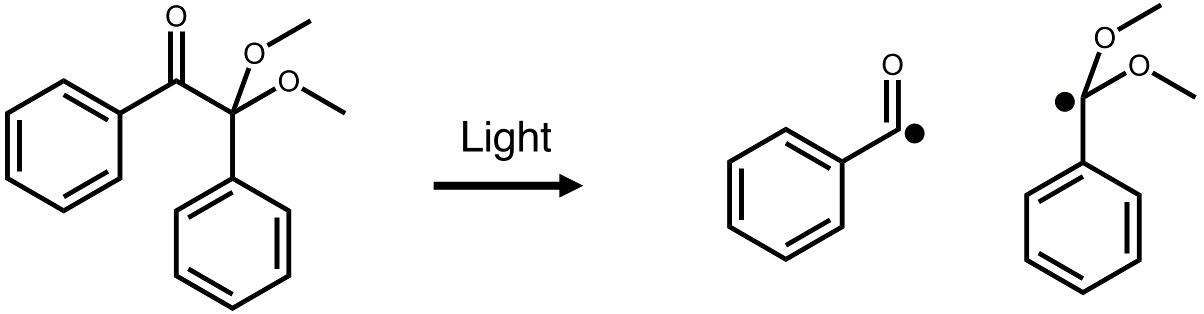
One of the reasons why some polymers are cured with heat or light!



Benzoyl Peroxide Benzoyloxy Radicals



2,2-Dimethoxy-2-phenylacetophenone Benzoyl Radical Methoxybenzyl Radical



Chain-growth Polymerization: Initiation

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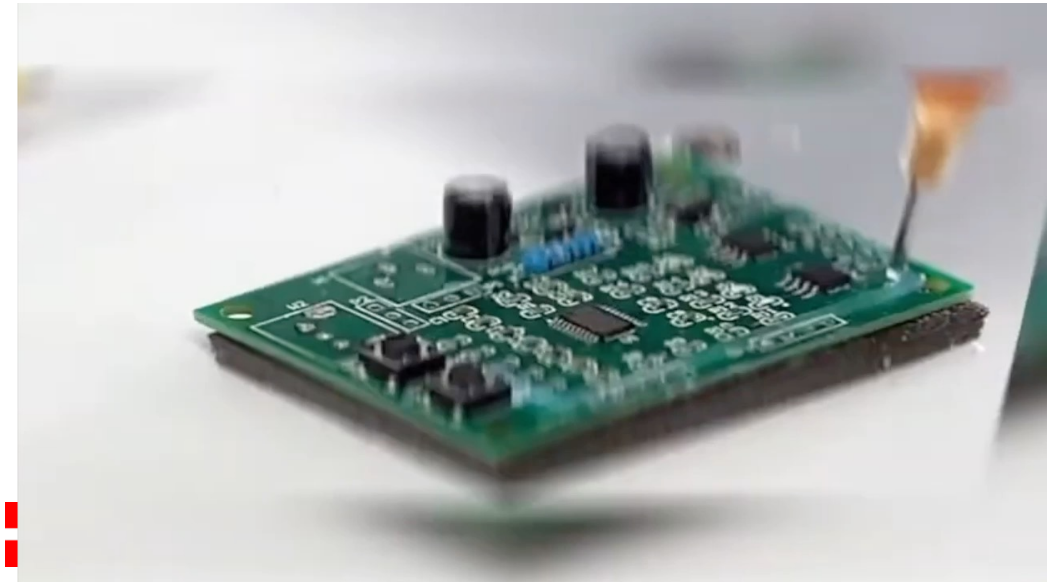
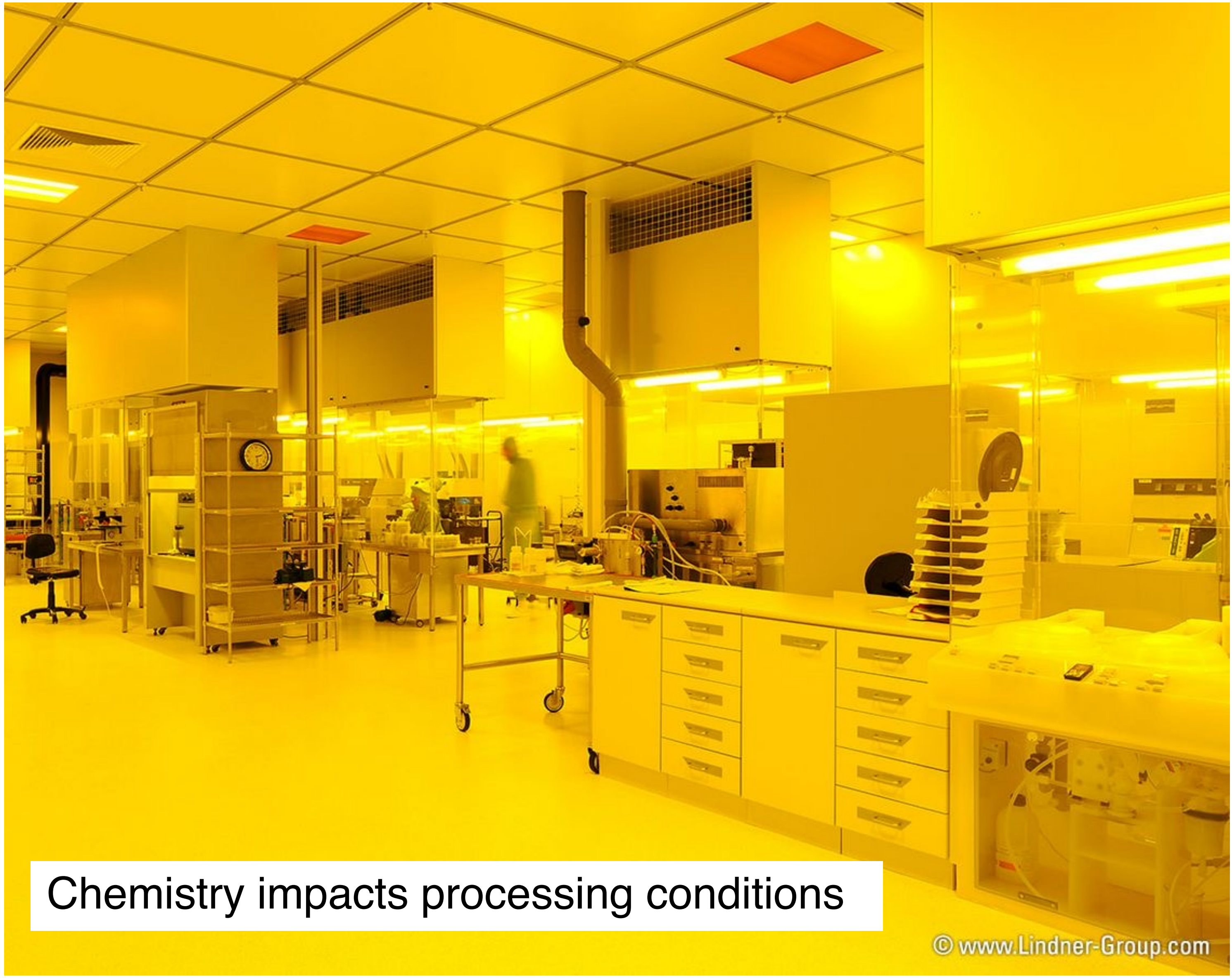




Chemistry impacts processing conditions

Chain-growth Polymerization: Initiation

Initiation → Two reactions

1. $I \rightarrow 2I^{\bullet}$ (Primary radical)

Depending on the initiator, primary radicals can be formed via heat, redox reactions, radiation, and electricity.

One of the reasons why some polymers are cured with heat or light!

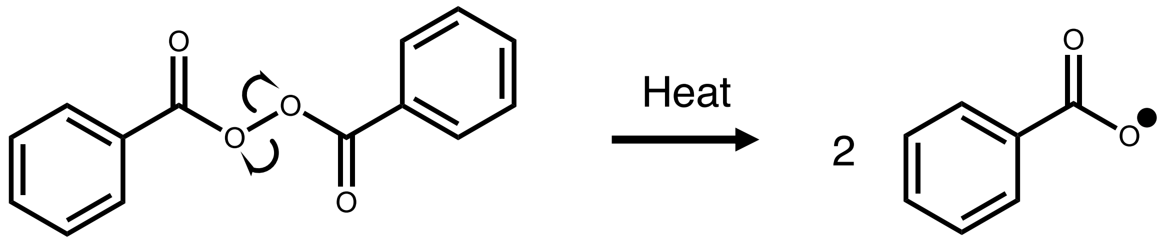
<u>Some notes</u>

Not all primary radicals are created equal
→ some radicals initiate polymerization less

Recombination of primary radicals can occur
→ no polymerization

Benzoyl Peroxide

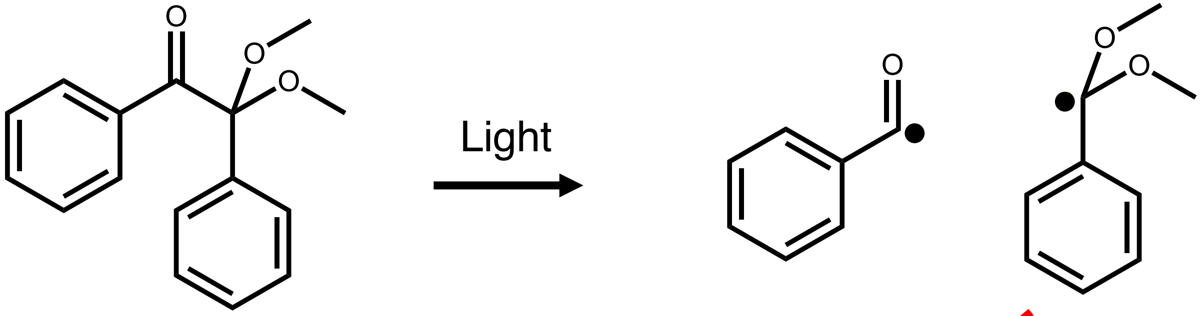
Benzoyloxy Radicals



2,2-Dimethoxy-2-phenylacetophenone

Benzoyl Radical

Methoxybenzyl Radical



This radical is less reactive than the benzoyl radical

I uploaded old slides. The last part on chain-growth were not there. Sorry!

I just uploaded the correct one.

Week 2 Learning Objectives

- **Recognize some basic functional groups and their use in polymer synthesis**
- **Step-growth Polymerization**
  – Terms: Polyaddition, polycondensation, conversion, Carothers equation
- **Understand the molecular mechanisms of controlling molecular weight during step-growth polymerization**
- **Chain-growth Polymerization**
  – Terms: Chain polymerization, condensative chain polymerization, conversion, initiation, propagation, termination