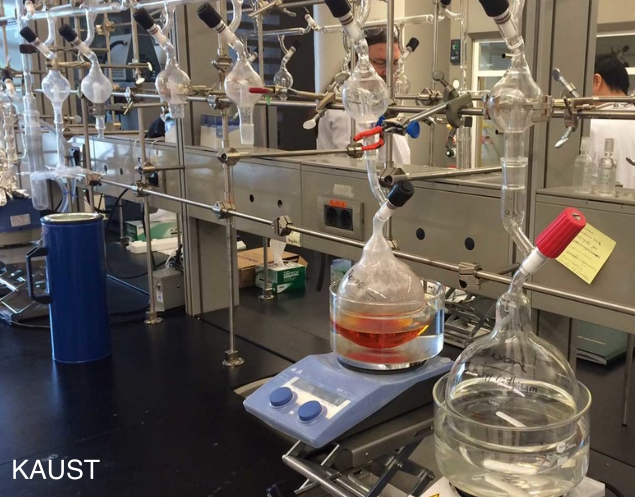
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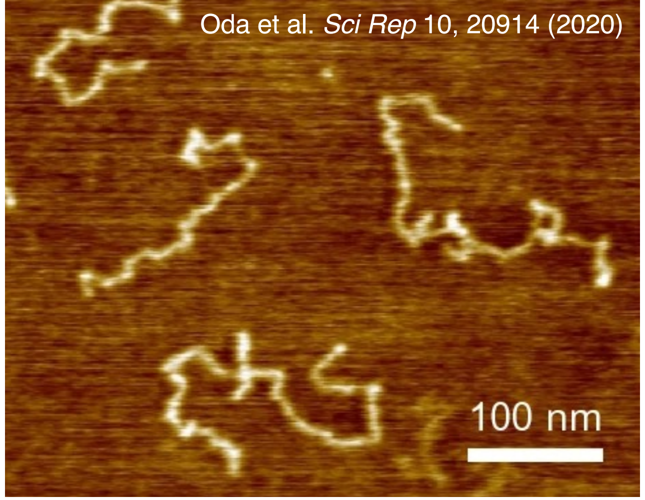

Oda et al. *Sci Rep* 10, 20914 (2020)

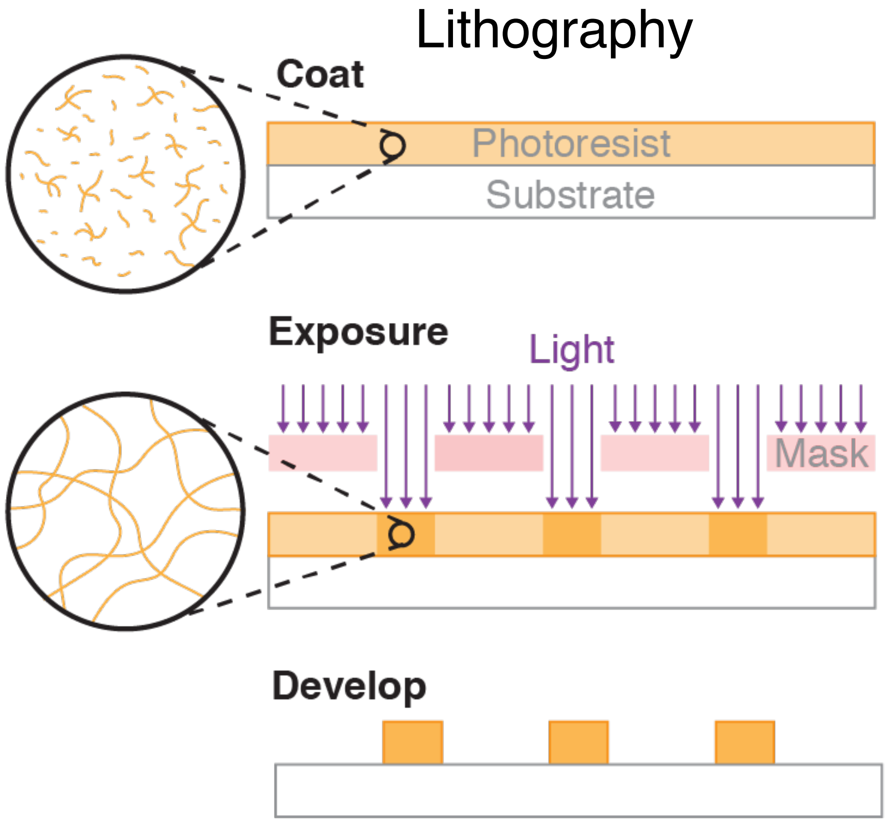
Materials Engineering I (MSE 214)

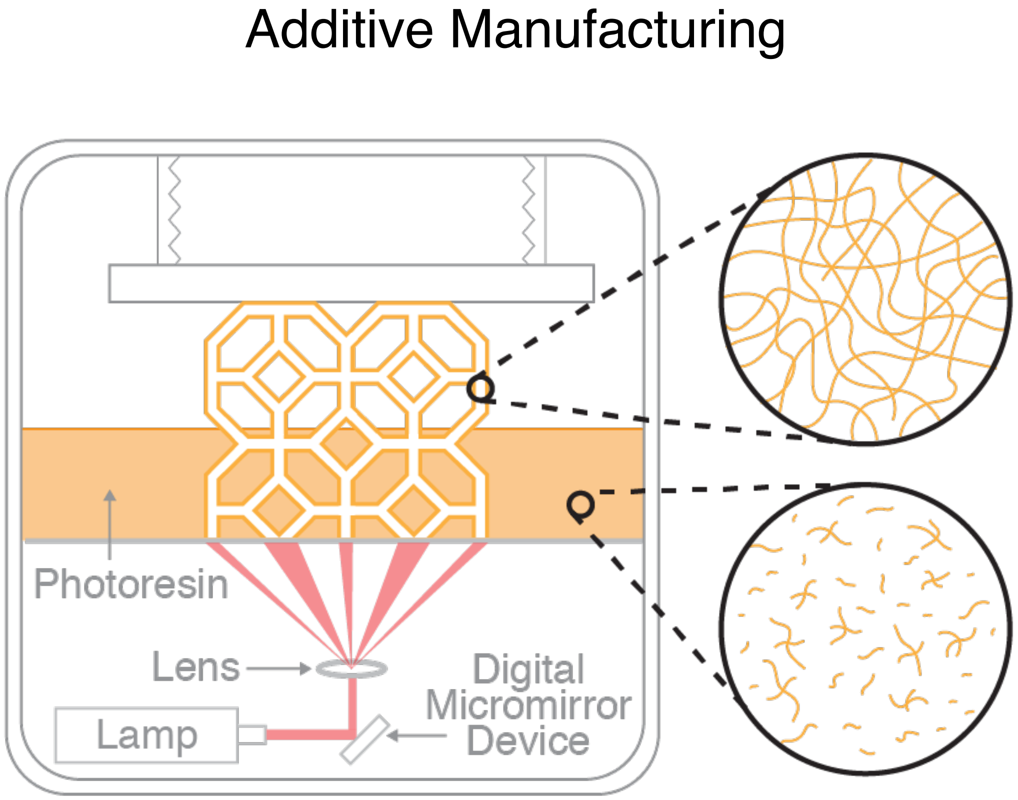
Lecture 3: Making Polymers (II) + Microstructure (I)

Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

Polymer Synthesis in Microengineering and Advanced Manufacturing

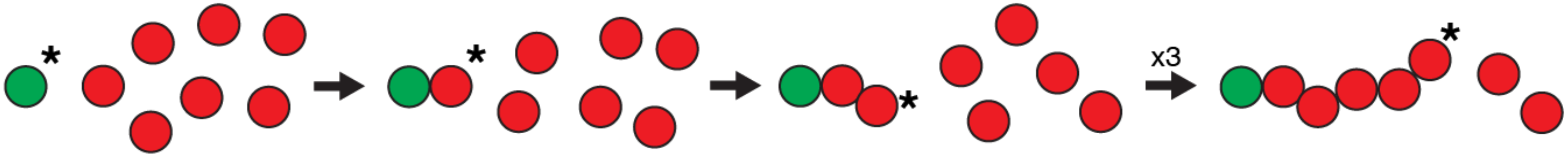




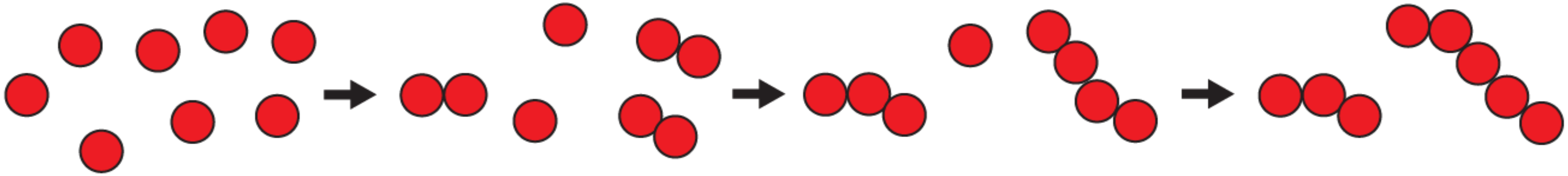
Learning polymer synthesis → Understand manufacturing
+ Understand how to tune their properties

Week 2 Recap

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



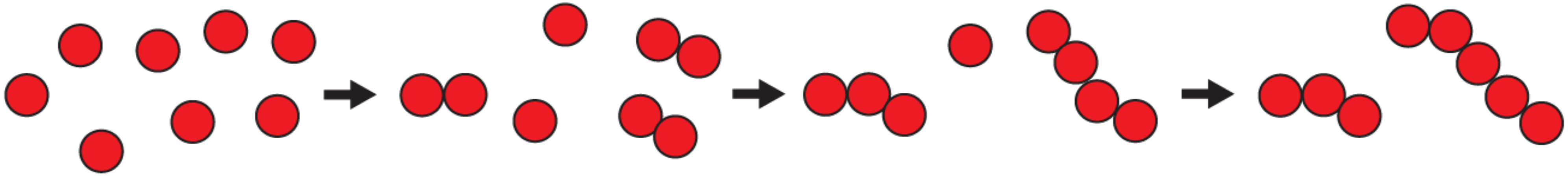
Step-growth*: Polymer grows via the reaction between any pairs of reactive species



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

Week 2 Recap

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

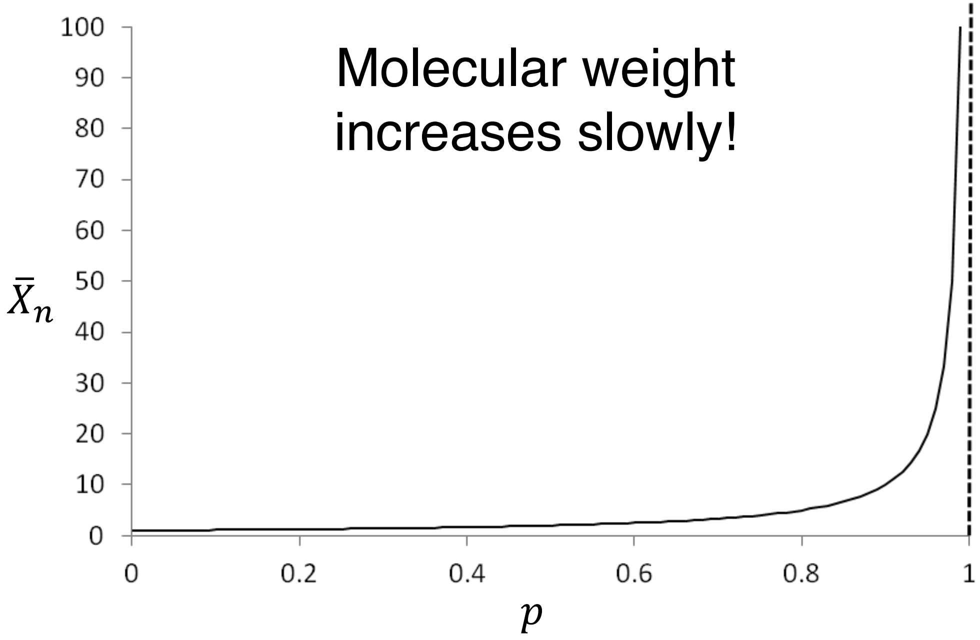


Number average degree of polymerization ($\bar{X}_n$) $\bar{X}_n = \dfrac{[M]_0}{[M]} = \dfrac{1}{1-p}$

Carothers Equation

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

Average number of **structural units** per chain



Molecular weight increases slowly!

Week 2 Recap

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

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

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

Case 1. AA and BB, with BB in excess

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

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

Stoichiometric control is important!

Week 2 Recap

Stoichiometric control is important!

→ **Where do we see this manifesting?**

2-part epoxy

Contains A →

← Contains B

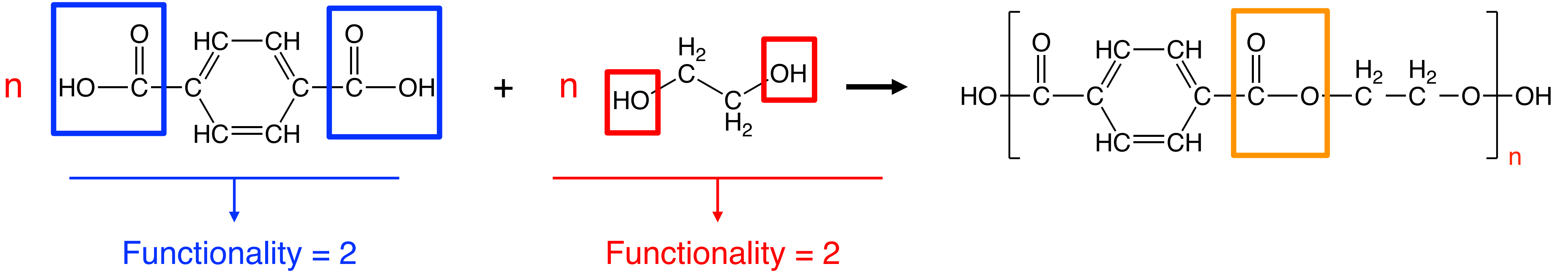
Week 2 Recap: Common questions

How to tell if a polymer is linear or not?

It depends on the functionality of the monomer(s) → Functionality (f) = # of polymerizable groups

Step Growth:

+ (2n-1) H_2O



Linear polymers: Most of the monomers have f = 2. Some monomers have f = 1

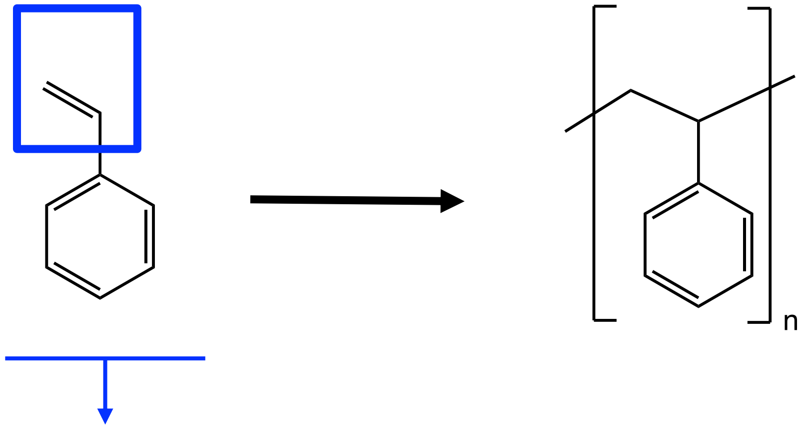
Case 1:	Case 2:	Case 3:
95% of monomers have f=2	95% of monomers have f=2	95% of monomers have f=3
5% of monomers have f=1	5% of monomers have f=3	5% of monomers have f=2

Week 2 Recap: Common questions

How to tell if a polymer is linear or not?

It depends on the functionality of the monomer(s) → Functionality (f) = # of polymerizable groups

Chain Growth:



Functionality = 1

Linear polymers: Only if all the monomers have f = 1 and no chain transfer

Case 1:

100% of monomers have f=1

Case 2:

95% of monomers have f=1

5% of monomers have f=2

Week 2 Recap: Common questions

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

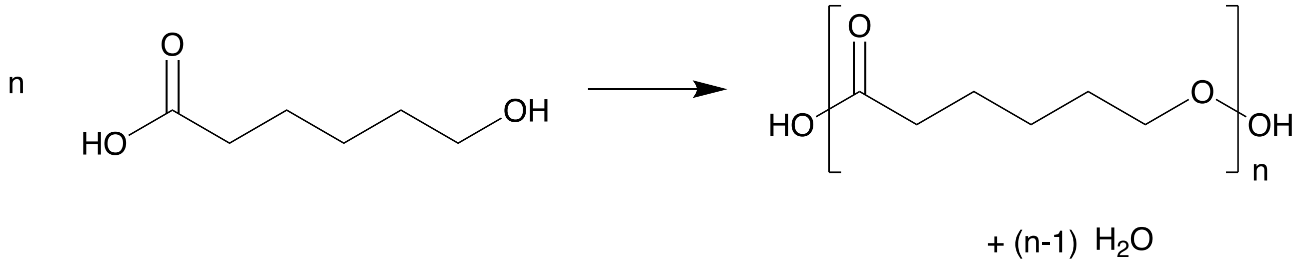
Number of AA molecules	Number of BB molecules	Oligomer sequences	Number of monomeric units + unreacted monomers	Total number of molecules	Total number of unreacted A
n	n	-	2n	2n	2n
n-1	n-1	AABB	2 + 2(n-1) = 2n	2n-1	2(n-1) + 1 = 2n-1
n-2	n-1	AABBAA	3 + (n-2) + (n-1) = 2n	2n-2	2(n-2) + 2 = 2n-2
n-3	n-3	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

Week 2 Recap: Notes about Exercise 1

Question 4: Classify the polymers that are formed from the reactions below

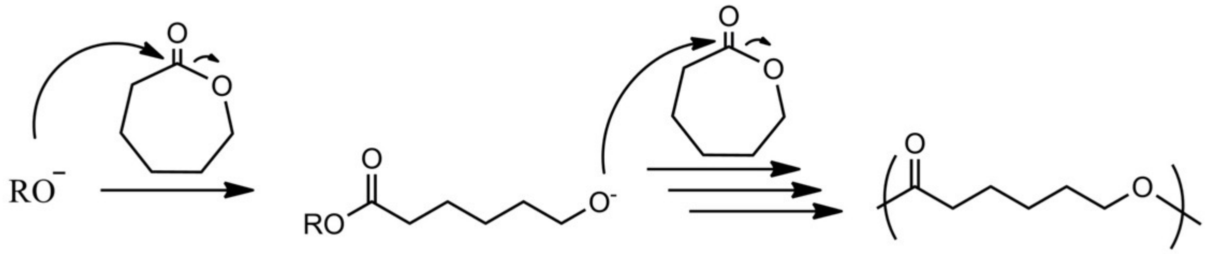
a)



Ans: Homopolymer. Linear polymer. Step-growth polymer. Condensation polymerization

Ignoring end groups, these are the same!

b)



Ans: Homopolymer. Linear polymer. Chain-growth polymer. Addition polymerization

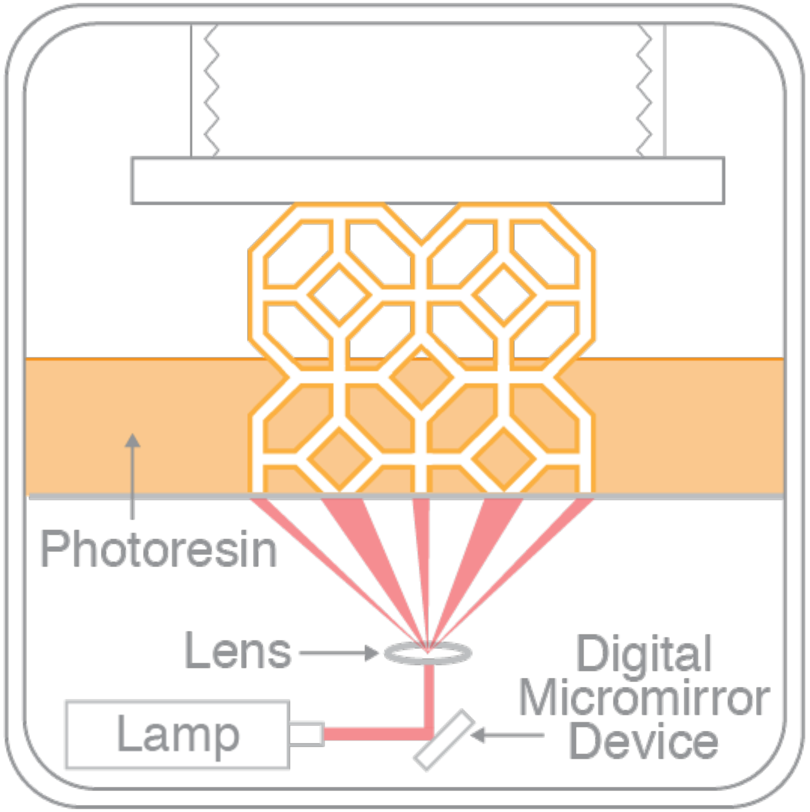
Same polymer can be made via multiple routes!

Without specialist knowledge you cannot tell just from looking at it / the name of the polymer

Week 3 Learning Objectives

- **Chain-growth Polymerization**
  - Terms: Chain polymerization, condensative chain polymerization, conversion, initiation, propagation, termination, chain transfer, inhibition, Mayo equation, kinetic chain length
- **Understand the molecular mechanisms of controlling molecular weight**
- **Understand the difference between amorphous and semi-crystalline polymers**
- **Understand what the glass transition temperature is**

Today’s Lesson: How does resin 3D printing work?



How do we go from a liquid to a solid?

How does the part form?

CHAIN-GROWTH POLYMERIZATION
LET’S PLAY A GAME

Chain-growth Polymerization — Let’s Play a Game

Chain-growth rules (more complex version):

- Everyone is a monomer!
- Shake hands to form a bond!
- A select few start with a chocolate bar. These individuals only have one hand
- **If you have the chocolate, you HAVE to give it away each time I say “Go”.**

  You decide who to give to.
- When you give the chocolate to someone, you have to hold their hand.
- You can only receive chocolate if you have free hands.
- Holding chocolate does not count as using a hand.
- Held hands cannot be un-held.

- **Whoever ends up with the chocolate keeps it.**

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

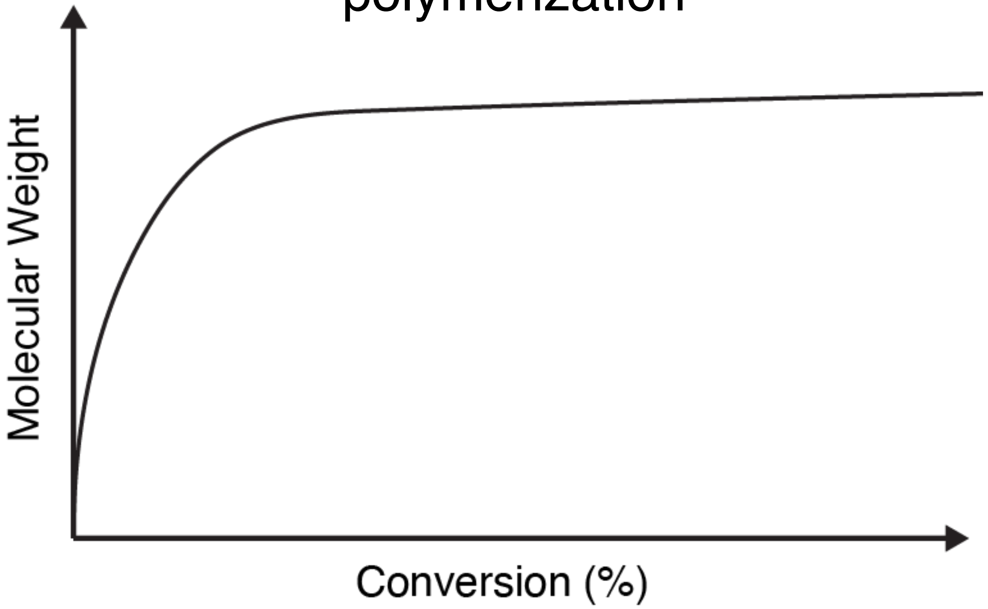
Strategy time: Sticking to the rules of the game, how do you end up with the chocolate?

Chain-growth Polymerization and Molecular Weight

Chain-growth: Polymer grows via the reaction of monomer(s) onto **active site(s)** on the polymer chain

Recall: Molecular weight influences polymer properties

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



Typical chain-growth polymerization

monomer + monomer → nothing
monomer* + monomer → dimer*
dimer* + monomer → trimer*
trimer* + monomer → tetramer*
tetramer* + monomer → pentamer*

x-mer* + monomer → (x+1)-mer*
x-mer* + y-mer* → (x+y)-mer
x-mer + y-mer → nothing

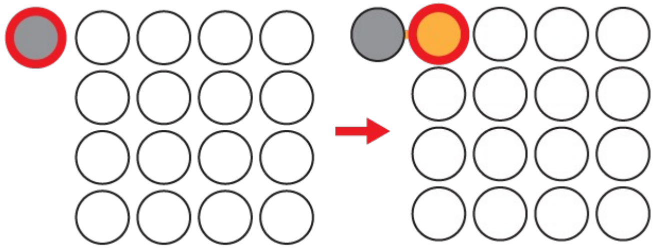
Only molecules with * can react!

Only a limited number of * in system

But molecules with * grow quickly!
The other monomers are not doing anything

Chain-growth Polymerization: The Three Phases

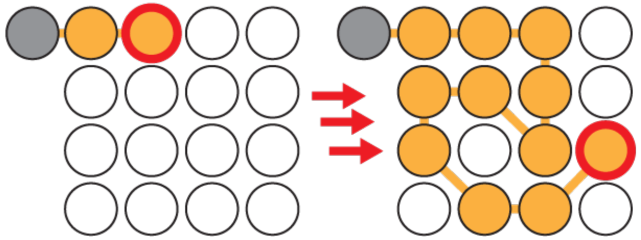
Initiation



$I \longrightarrow I^*$

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

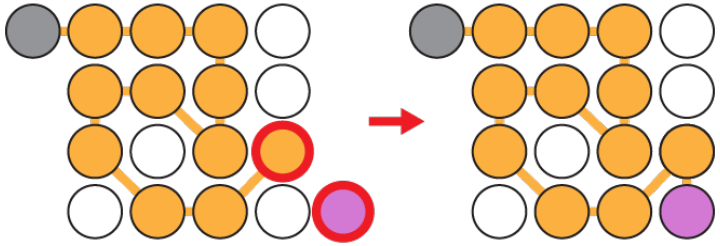
Propagation



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

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

Termination



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

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

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

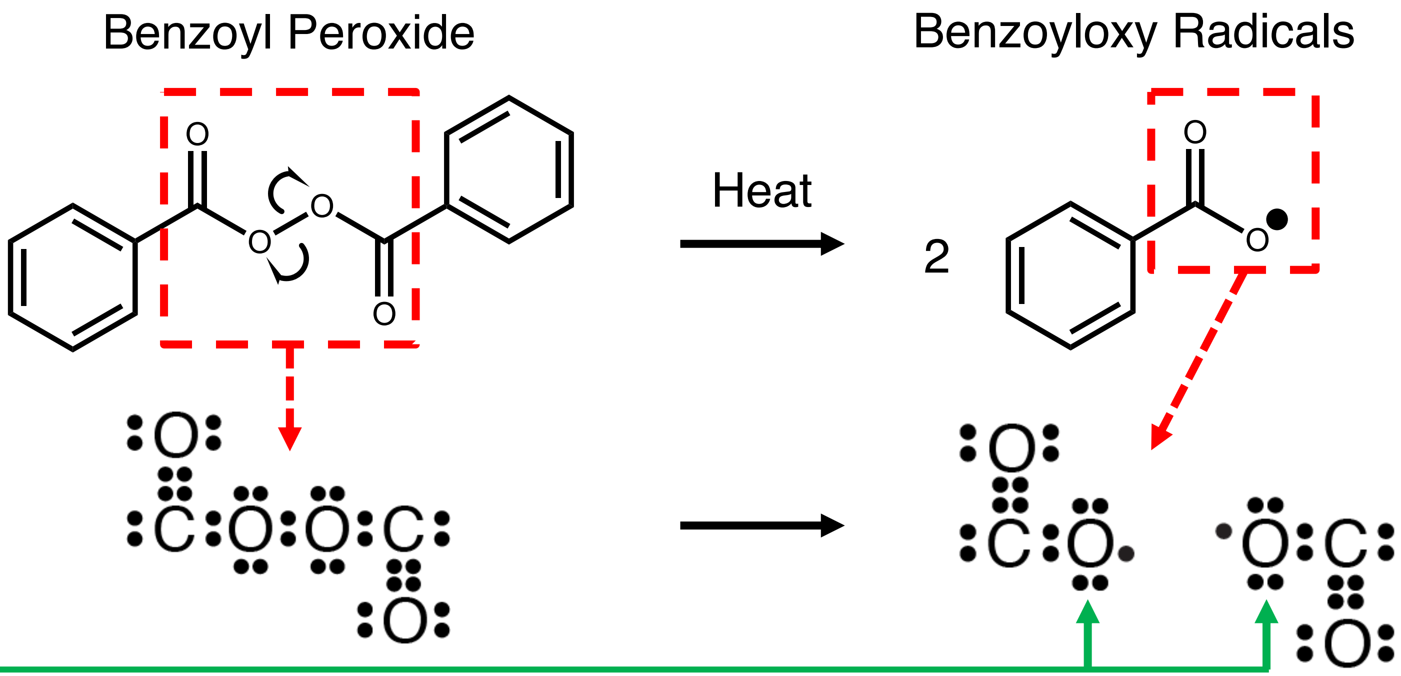
Initiation

$I \longrightarrow I^*$

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

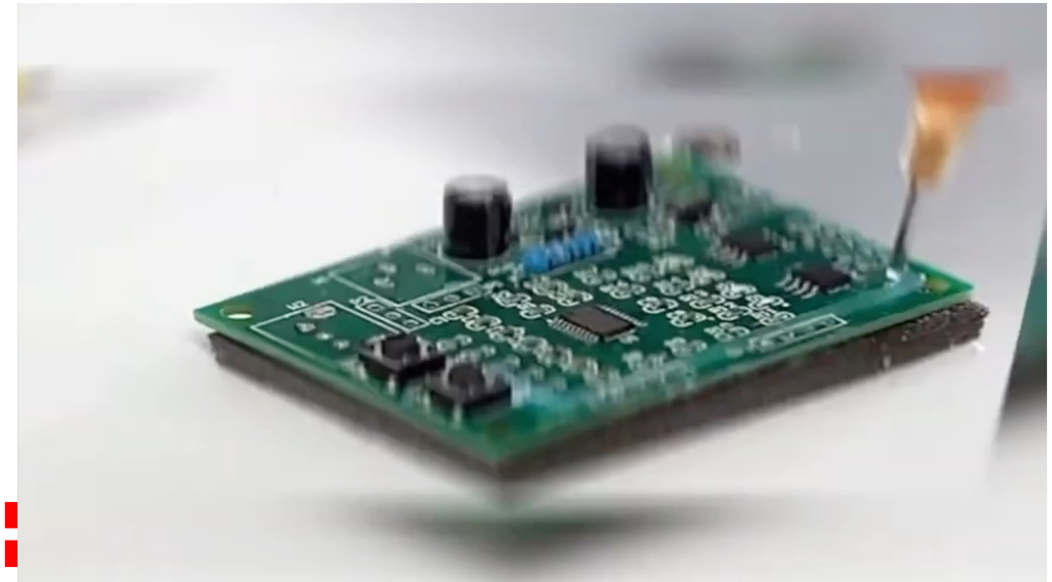
Chain-growth Polymerization: Initiation

Initiation → Two reactions

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

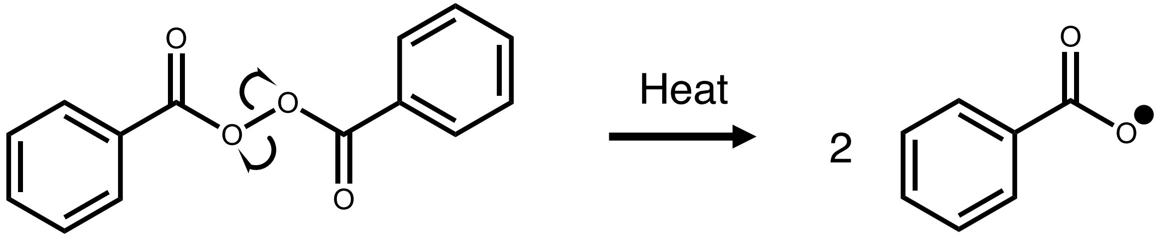
Depending on the initiator, primary radicals can be formed via heat, redox reactions, radiation, and electricity.

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



Benzoyl Peroxide

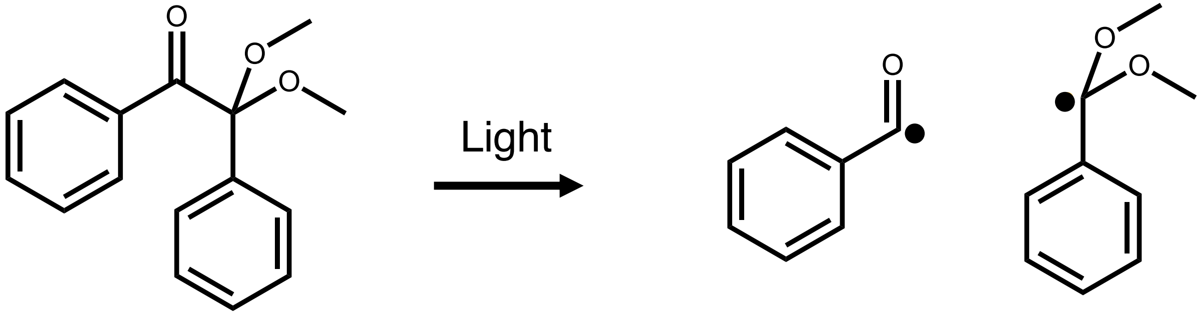
Benzoyloxy Radicals



2,2-Dimethoxy-2-phenylacetophenone

Benzoyl Radical

Methoxybenzyl Radical



Chain-growth Polymerization: Initiation

Initiation → Two reactions

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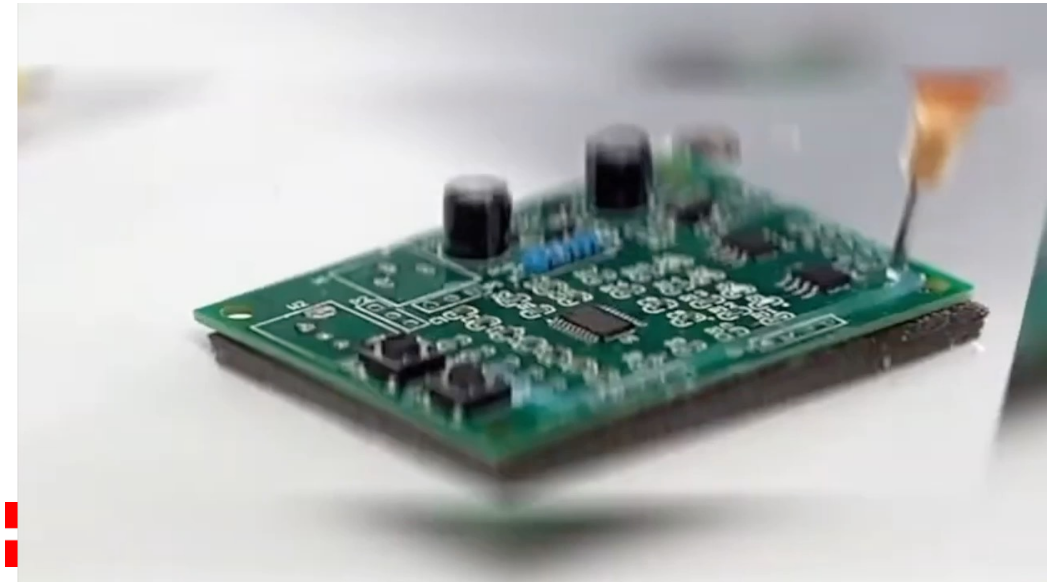

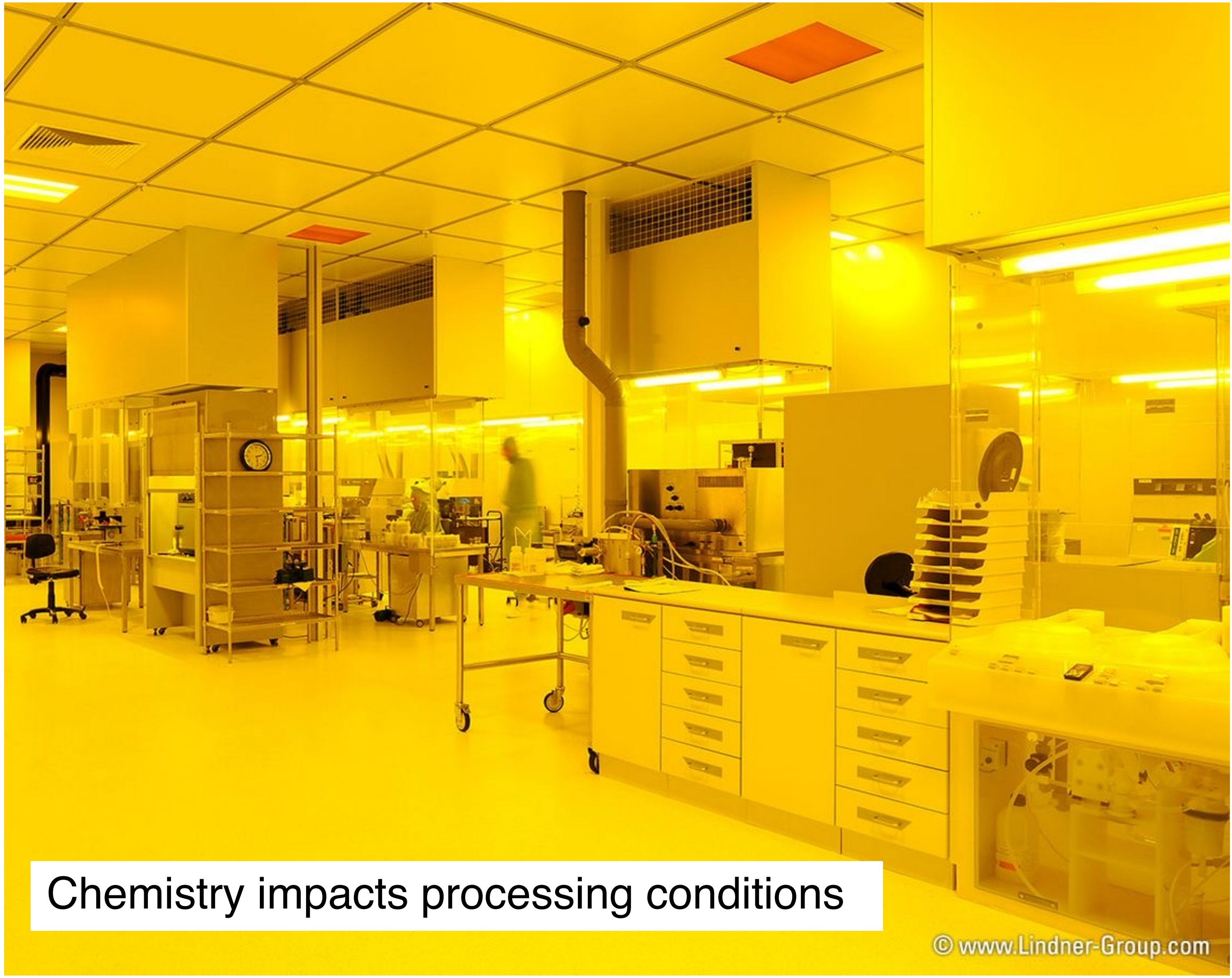

Chemistry impacts processing conditions

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Chain-growth Polymerization: Initiation

Initiation ⟶ Two reactions

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

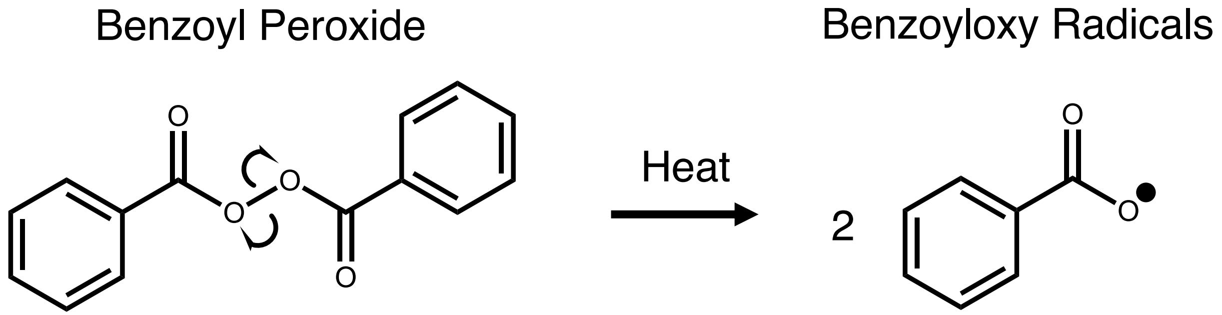
Depending on the initiator, primary radicals can be formed via heat, redox reactions, radiation, and electricity.

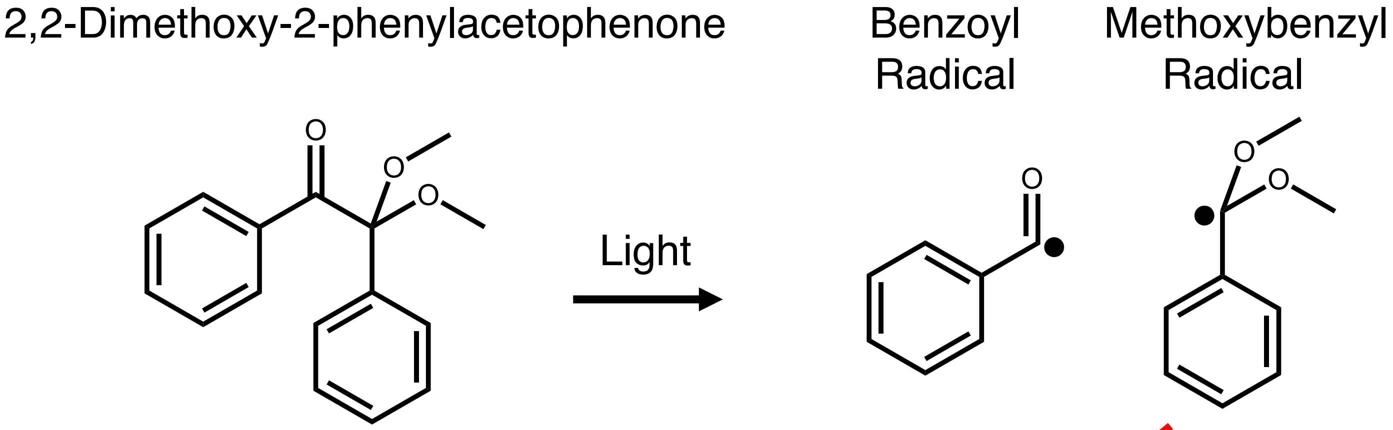
One of the reasons why some polymers are cured with heat or light!

Some notes

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

Recombination of primary radicals can occur
→ no polymerization



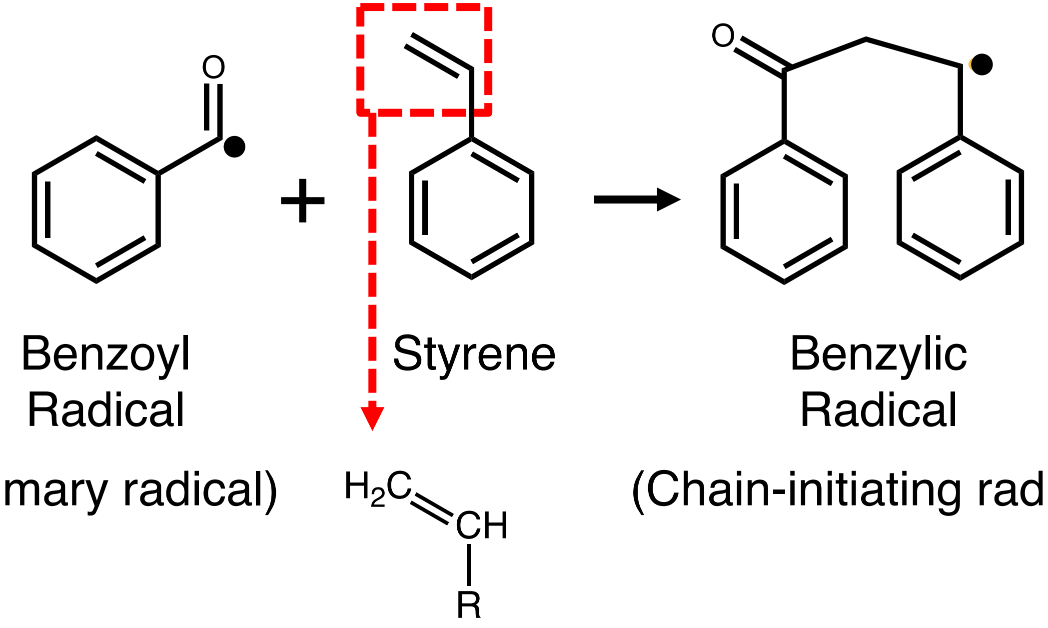


This radical is less reactive than the benzoyl radical

Chain-growth Polymerization: Initiation

Initiation → Two reactions

1. $I \rightarrow 2I^{\bullet}$ (Primary radical)
2. $I^{\bullet} + M \rightarrow I\text{-}M^{\bullet}$ (Chain-initiating radical)



Benzoyl Radical

(Primary radical)

Styrene

Benzylic Radical

(Chain-initiating radical)

Vinyl

Kinetics of Initiation

$$I \xrightarrow{k_d} 2I^{\bullet}$$

k_d = rate constant for thermal dissociation

$$I^{\bullet} + M \xrightarrow{k_i} I\text{-}M^{\bullet}$$

k_i = rate constant for initiation step

$$R_d = 2\, f\, k_d [\, I \,]$$

R_d = Rate of dissociation
f = initiator efficiency

Step 2 is significantly faster than Step 1
→ Rate of initiation is dominated by rate of Step 1

$$R_i = 2\, f\, k_d [\, I \,]$$

R_i = Rate of initiation as a whole process

$$R_i = 2\, \phi\, I_a([\, I \,])$$

(For photochemical initiation)

ϕ = Quantum yield for initiation

I_a = Intensity of light absorbed. Function of [I]

Chain-growth Polymerization: Propagation

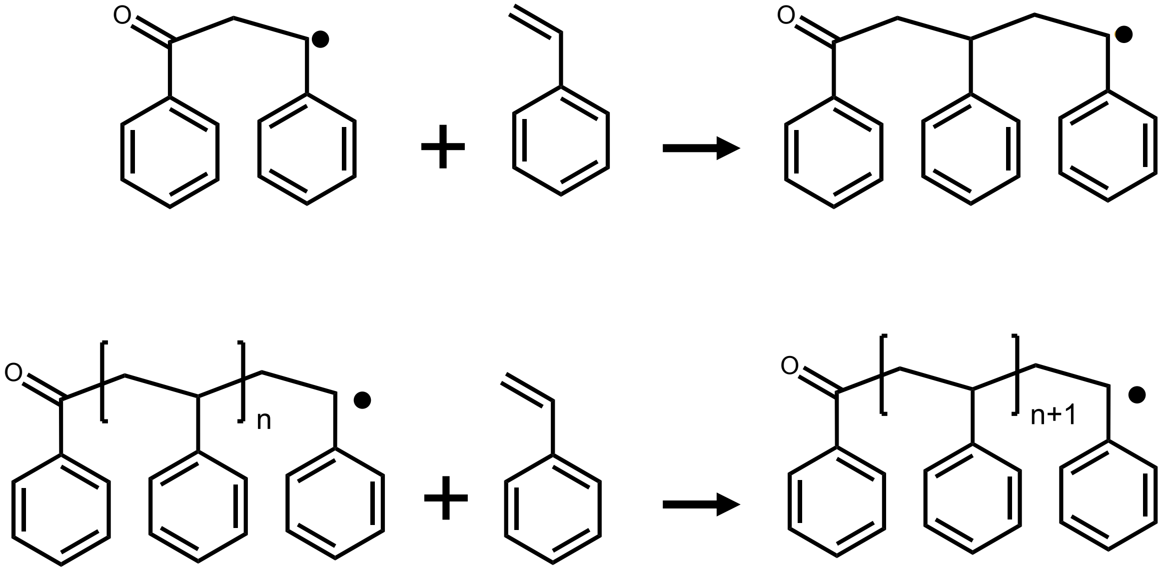
Propagation ⟶ Multiple reactions (up to 10^6 !)

$$\text{I-M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{I-M-M}^{\bullet}$$

$$\text{I-M-M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{I-M-M-M}^{\bullet}$$

$$\text{I-(M)}_2\text{-M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{I-M-(M)}_3\text{-M}^{\bullet}$$

k_p = rate constant for propagation



In general

$$\text{M}_n^{\bullet} + \text{M} \xrightarrow{k_p} \text{M}_{n+1}^{\bullet}$$

- I is ignored
- M_n → polymer with n monomeric units

Monomer added one at a time

Radical is consumed and regenerated

k_p is assumed to be independent of radical size

Chain-growth Polymerization: Propagation

Propagation ⟶ Multiple reactions (up to 10^6 !)

$$I\text{-}M^{\bullet} + M \xrightarrow{k_p} I\text{-}M\text{-}M^{\bullet}$$

k_p = rate constant for propagation

$$I\text{-}M\text{-}M^{\bullet} + M \xrightarrow{k_p} I\text{-}M\text{-}M\text{-}M^{\bullet}$$

$$I\text{-}(M)_2\text{-}M^{\bullet} + M \xrightarrow{k_p} I\text{-}M\text{-}(M)_3\text{-}M^{\bullet}$$

In general

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

- I is ignored
- M_n → polymer with n monomeric units

Monomer added one at a time

Radical is consumed and regenerated

k_p is assumed to be independent of radical size

Kinetics of Propagation

$$\frac{d[P]}{dt} = -\frac{d[M]}{dt} = R_i + R_p$$

R_i = Rate of initiation

R_p = Rate of propagation

Rate of polymerization =
Rate of monomer consumption

Number of monomers involved in propagation ≫ Number of monomers involved in initiation

$$\rightarrow \quad \frac{d[P]}{dt} = -\frac{d[M]}{dt} \approx R_p$$

$$R_p = k_p\,[\,M^{\bullet}]\,[\,M\,]$$

$[\,M^{\bullet}]$ is the total concentration of **all** chain radicals

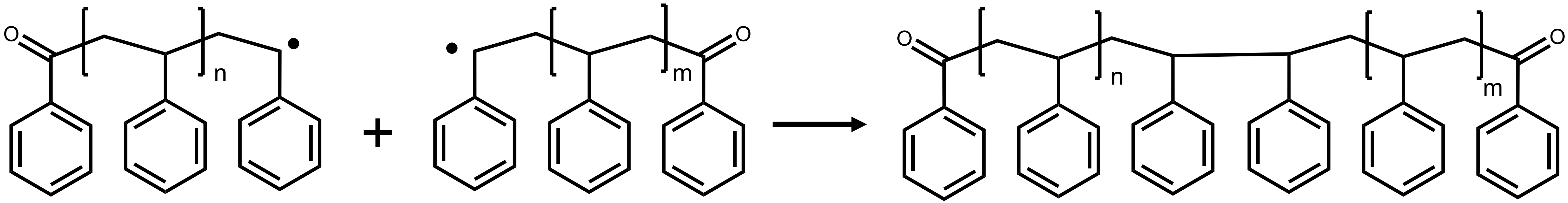
Chain-growth Polymerization: Termination

Termination → 2 types

Coupling

$$\text{I-(M)}_n\text{-M}^{\bullet} + {}^{\bullet}\text{M-(M)}_y\text{-I} \xrightarrow{k_{tc}} \text{I-(M)}_{n+y+2}\text{-I}$$

k_{tc} = rate constant for termination coupling



$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_{tc}} M_{n+m}$$

2 polymer chains → 1 polymer chain

"Dead" polymer → No more radical / active site

→ How does this impact molecular weight?

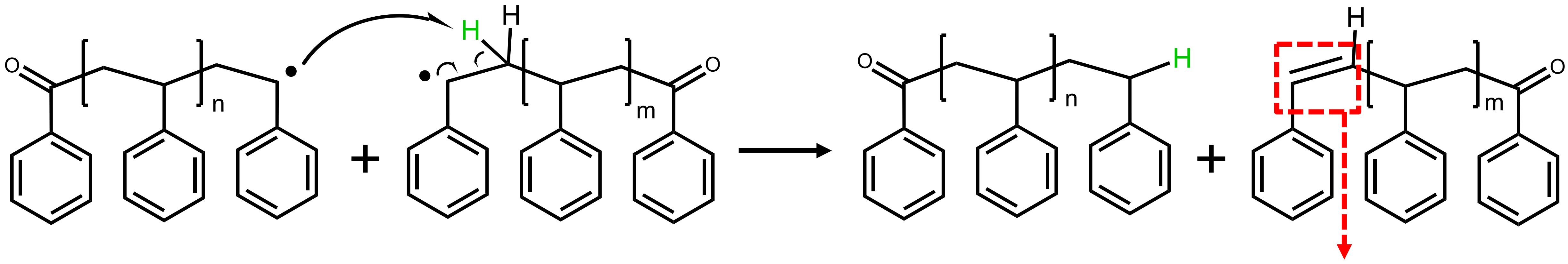
Chain-growth Polymerization: Termination

Termination → 2 types

<u>Disproportionation</u>

$$I\text{-}(M)_n\text{-}M^\bullet + {}^\bullet M\text{-}(M)_y\text{-}I \xrightarrow{k_{td}} I\text{-}(M)_n\text{-}M + M{=}M\text{-}(M)_{y-1}\text{-}I$$

k_{td} = rate constant for termination disproportionation



Note: Not a vinyl group, just a double bond

$$M_n^\bullet + M_m^\bullet \xrightarrow{k_{td}} M_n + M_m$$

2 polymer chains → 2 polymer chains

"Dead" polymer → No more radical / active site

→ How does this impact molecular weight?

Chain-growth Polymerization: Termination

Termination ⟶ 2 types

If the mode of termination is not specified, i.e. termination in general terms:

$M_n^\bullet + M_m^\bullet \xrightarrow{k_t}$ dead polymer $\qquad k_t = a\,k_{tc} + (1 - a)\,k_{td}$

a and (1 – *a*) are the fractions of termination by coupling and disproportionation respectively

Rate of termination, $R_t = -\dfrac{d[M^\bullet]}{dt} = 2k_t[M^\bullet]^2$

Note: Termination is a bimolecular reaction.
Factor of 2 → termination occurs in pairs

Termination rate constant significantly larger than propagation's
→ $k_t >> k_p$

→ How does polymerization work if termination is so fast? →

Concentration of [M•] is small!

Chain-growth Polymerization: Kinetics

Initiation ⟶ **Propagation** ⟶ **Termination** (Putting it all together)

$R_i = 2\, f\, k_d[\,I\,]$ or $2\,\phi\, I_a([\,I\,])$

$R_p = k_p[\,M^{\bullet}][\,M\,]$

$R_t = 2\,k_t[\,M^{\bullet}]^2$

Measuring [M$^{\bullet}$] is hard!

Use steady-state assumption

$\rightarrow \frac{d[M^{\bullet}]}{dt} = 0$

Concentration of radicals increases initially but almost instantly reaches a constant steady-state.

$\rightarrow R_i = R_t = 2\,k_t\,[M\bullet]^2$

$$[M^{\bullet}] = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$\rightarrow \quad R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$R_p = k_p[M]\left(\frac{f k_d[I]}{k_t}\right)^{\frac{1}{2}} \quad \text{or} \quad k_p[M]\left(\frac{\phi I_a([I])}{k_t}\right)^{\frac{1}{2}}$$

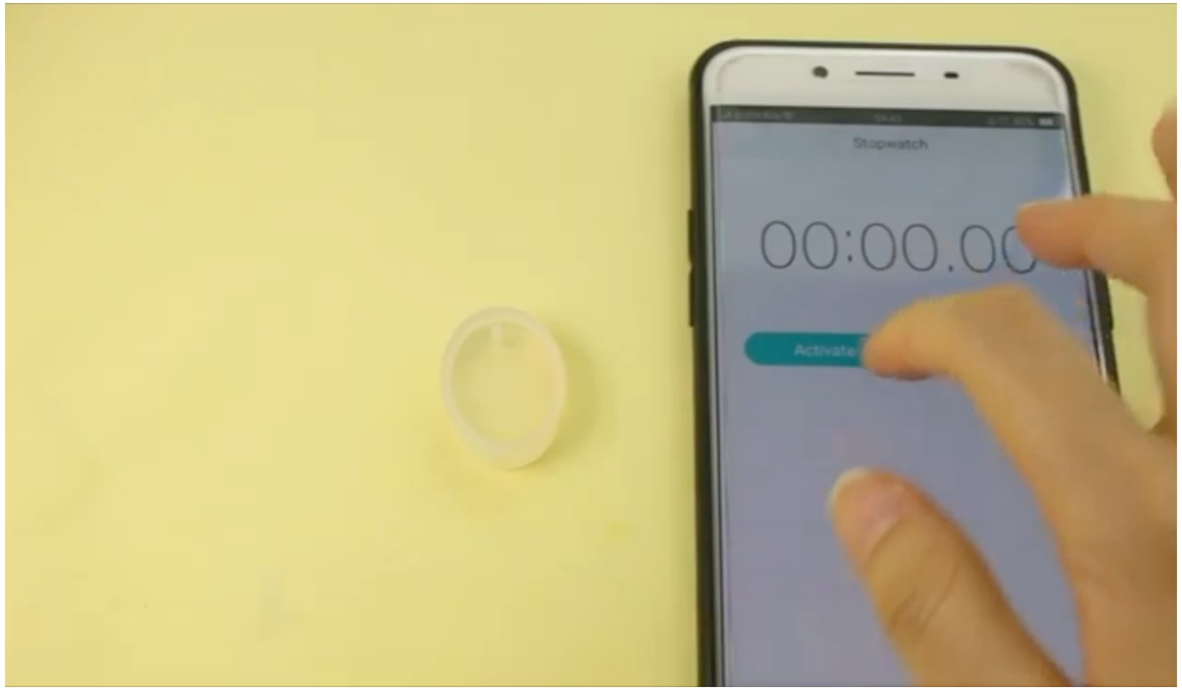
(Thermal) (Photochemical)

Thermal: Polymerization rate depends on the square root of the initiator concentration!

Photothermal: Polymerization rate depends on the square root of the intensity + initiator concentration + distance!

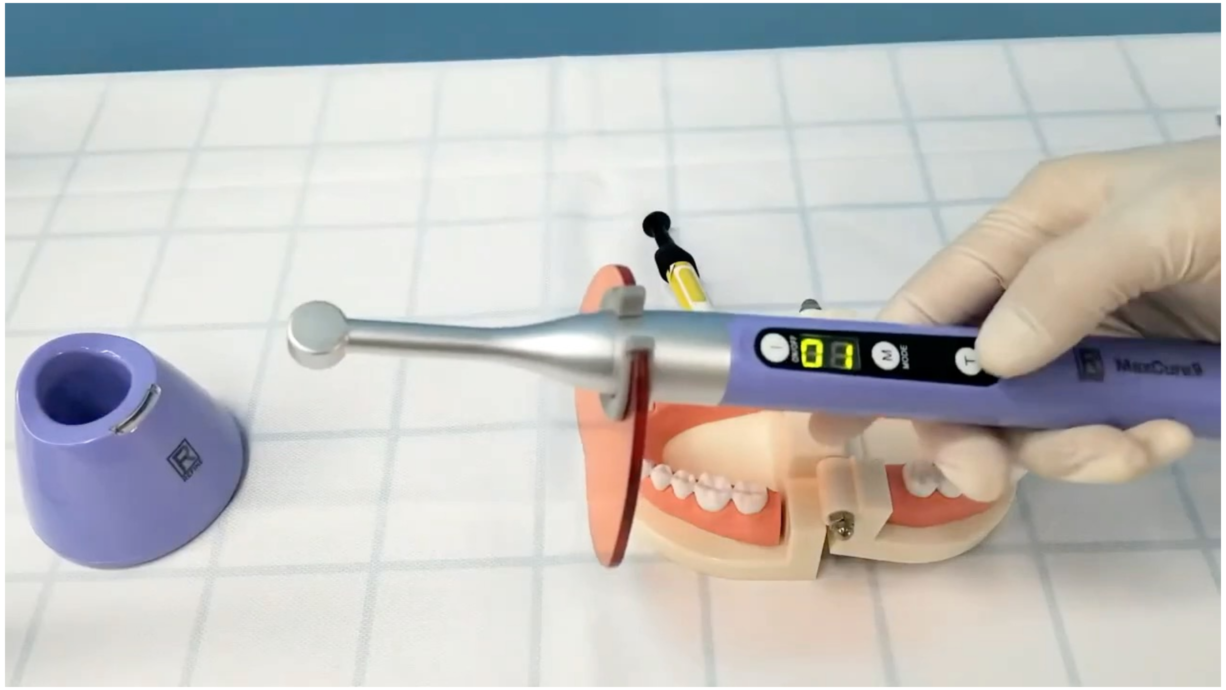
Light intensity vs Polymerization Rate

Low Intensity



Youtube: Monsterkraft

High Intensity



Youtube: Senmy Dental

Caveat: Different resin formulations used → Will impact polymerization speed also

But point still stands: $R_p = k_p[M]\left(\frac{\phi \, \boxed{I_a} \, ([I])}{k_t}\right)^{\frac{1}{2}}$

Chain-growth Polymerization: Molecular Weight

How many monomers are added to each radical chain before termination?

Kinetic chain length υ: Average number of monomers consumed per radical which initiates a polymer chain

$$\upsilon = \frac{Rate\ of\ monomer\ addition\ to\ chain}{Rate\ of\ new\ chain\ formation}$$

$$\upsilon = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$ Steady state approximation: initiation = termination rate

$$R_p = k_p[\,M\,]\left(\frac{f k_d[\,I\,]}{k_t}\right)^{\frac{1}{2}}$$

$$R_i = 2\,f\,k_d[\,I\,]$$

(For thermal initiation)

$$\upsilon = \frac{k_p[M]\left(\frac{f k_d[I]}{k_t}\right)^{\frac{1}{2}}}{2\,f\,k_d\,[\,I\,]} = \frac{k_p[\,M\,]}{2\,(f\,k_d\,k_t\,[\,I\,])^{\frac{1}{2}}}$$

Changing [M] or [I] to change kinetic chain length will also change the rate of polymerization

Chain-growth Polymerization: Molecular Weight

Number average degree of polymerization $\bar{X}_n$ is related to $\boldsymbol{v}$

Termination by coupling: $\bar{X}_n = 2\boldsymbol{v}$

Termination by disproportionation: $\bar{X}_n = \boldsymbol{v}$

Number average molecular weight: $M_n = M_o\,\bar{X}_n$
(M_o is the molecular weight of the monomer)

Let ***a*** be the fraction of chains that terminate by coupling
→ (***1 – a***) is the fraction of chains that terminate by disproportionation

$$\mathrm{I{-}(M)_n{-}M^{\bullet} + {}^{\bullet}M{-}(M)_y{-}I \xrightarrow{k_{tc}} I{-}(M)_{n+y+2}{-}I}$$

$$\mathrm{I{-}(M)_n{-}M^{\bullet} + {}^{\bullet}M{-}(M)_y{-}I \xrightarrow{k_{td}} I{-}(M)_n{-}M + M{=}M{-}(M)_{y-1}{-}I}$$

We can use the number of initiator fragments per chain to determine the mode of termination

Chain-growth Polymerization: Molecular Weight

Number average degree of polymerization $\bar{X}_n$ is related to υ

Let ***a*** be the fraction of chains that terminate by coupling
→ (***1 – a***) is the fraction of chains that terminate by disproportionation

Let ***b*** be the average number of initiator fragments per polymer → $b = \frac{Total\ number\ of\ initiator\ fragments}{Total\ number\ of\ polymer\ molecules}$

For a system composed of ***n*** propagating chains:

Coupling yields ***a n*** initiator fragments

Disproportionation yields (**1–*a)*** initiator fragments

$$b = \frac{\overline{a\,n} + \overline{(1-a)n}}{\underline{\frac{a\,n}{2}} + \underline{(1-a)n}}$$

Coupling yields $\frac{\boldsymbol{a\,n}}{\boldsymbol{2}}$ chains

Disproportionation yields ***(1–a)n*** chains

Chain-growth Polymerization: Molecular Weight

Number average degree of polymerization $\bar{X}_n$ is related to $\boldsymbol{v}$

Let ***a*** be the fraction of chains that terminate by coupling
→ (***1 – a***) is the fraction of chains that terminate by disproportionation

Let ***b*** be the average number of initiator fragments per polymer → $b = \frac{Total\ number\ of\ initiator\ fragments}{Total\ number\ of\ polymer\ molecules}$

b is a value between 1 and 2 and represents the extent of mixed mode termination

$$\overline{X_n} = bv = \frac{2v}{2-a} = \frac{2R_p}{(2-a)R_t} = \frac{2\,k_p[\,M\,]}{4-2a\,(f\ k_d\ k_t\ [\,I\,])^{\frac{1}{2}}}$$

$$R_p = k_p[\,M\,]\left(\frac{f k_d[\,I\,]}{k_t}\right)^{\frac{1}{2}}$$

Two Problems:

1. Degree of polymerization and rate of polymerization are coupled
2. Experimental degree of polymerization observed to be lower than predicted

Chain-growth Polymerization: Chain Transfer

Premature termination via transfer of radical to another species

$$M_n\bullet + XA \xrightarrow{k_{tr}} M_n{-}X + A\bullet$$

(k_{tr} is the chain-transfer rate constant)

XA could be monomer, initiator, solvent, polymer, or other substance.
X is the atom or species transferred to the chain

$$A\bullet + M \xrightarrow{k_a} M\bullet$$

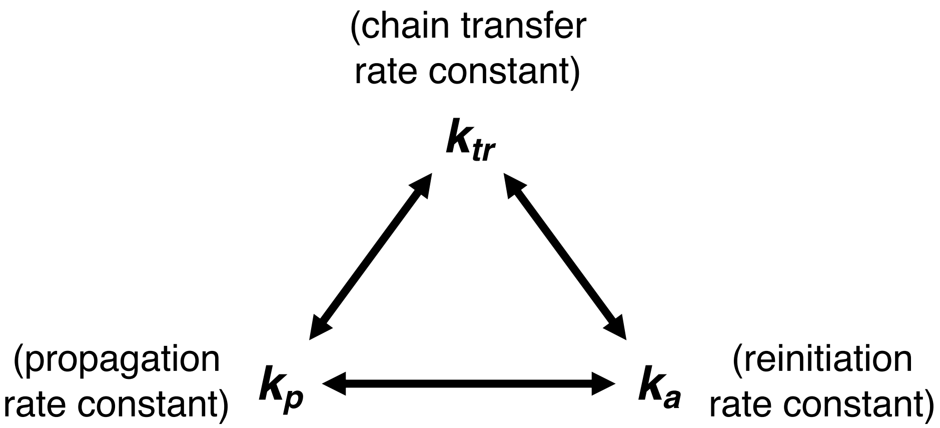
(k_a is the reinitiation rate constant)

Chain transfer results in the production of a new radical $A^{\bullet}$, which reinitiates polymerization

Chain transfer ≠ termination of radical

Chain transfer just causes a premature decrease in the size of the propagating polymer chain

Chain Transfer and Molecular Weight



The effect of chain transfer is dependent on the **relative rate constants** of chain transfer, reinitiation, and propagation

Case 1: $k_p >> k_{tr}$; $k_a \sim k_p$

Propagation faster than chain transfer
Reinitiation is rapid

Same number of monomers consumed per unit time but increased number of smaller-sized polymers

Little effect on R_p (rate of propagation)

$\overline{X_n}$ decreases

Case 2: $k_p << k_{tr}$; $k_a \sim k_p$

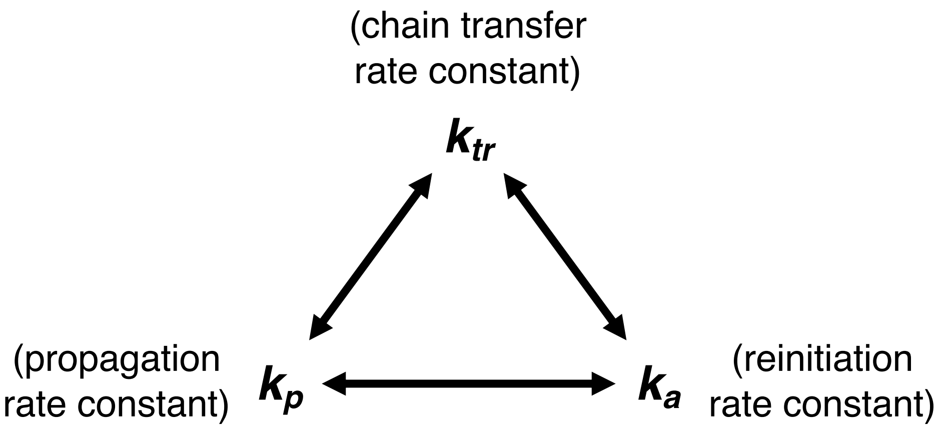
Chain transfer faster than propagation
Reinitiation is rapid

Same number of monomers consumed per unit time but significant number of smaller-sized polymers

Little effect on R_p (rate of propagation)

$\overline{X_n}$ decreases signficantly

Chain Transfer and Molecular Weight



The effect of chain transfer is dependent on the **relative rate constants** of chain transfer, reinitiation, and propagation

Case 3: $k_p >> k_{tr}$; $k_a < k_p$

Propagation faster than chain transfer
Reinitiation is slow

→ Smaller number of monomers consumed per unit time <u>and</u> increased number of smaller-sized polymers

→ R_p decreases (rate of propagation)

$\overline{X_n}$ decreases

Case 4: $k_p << k_{tr}$; $k_a < k_p$

Chain transfer faster than propagation
Reinitiation is slow

→ Much smaller number of monomers consumed per unit time <u>and</u> significant number of smaller-sized polymers

→ R_p decreases significantly (rate of propagation)

$\overline{X_n}$ decreases signficantly

Chain Transfer and Molecular Weight

Let us consider **Case 1**:

The degree of polymerization ($\overline{X_n}$) redefined:

$$\overline{X_n} = \frac{Rate\ of\ polymerization}{\sum chain\ breaking\ reactions}$$

Chain breaking reactions: termination + all chain transfer reactions

Chain transfer (general)

$$M_n\bullet + XA \xrightarrow{k_{tr}} M_n{-}X + A\bullet$$

Let's break this down into the different cases

In the low conversion regime

Chain transfer to monomer

$$M_n^{\bullet} + M \xrightarrow{k_{tr,\,M}} M_n - X + A^{\bullet}$$

Chain transfer to initiator

$$M_n^{\bullet} + I \xrightarrow{k_{tr,\,I}} M_n - X + A^{\bullet}$$

Chain transfer to chain-transfer agent

$$M_n^{\bullet} + S \xrightarrow{k_{tr,\,S}} M_n - X + A^{\bullet}$$

Chain Transfer and Molecular Weight

Let us consider **Case 1**:

The degree of polymerization ($\overline{X_n}$) redefined:

$$\overline{X_n} = \frac{Rate\ of\ polymerization}{\underline{\sum chain\ breaking\ reactions}}$$

Chain breaking reactions: termination + all chain transfer reactions

$$\overline{X_n} = \frac{R_p}{\underbrace{\frac{R_t(2-a)}{2}}_{\text{Rate of termination (coupling and disproportionation)}} + \underbrace{k_{tr,\,M}[\,M^{\bullet}][M]}_{\text{Rate of chain transfer to monomer}} + \underbrace{k_{tr,S}[\,M^{\bullet}][S]}_{\text{Rate of chain transfer to chain-transfer agent}} + \underbrace{k_{tr,I}[\,M^{\bullet}][I]}_{\text{Rate of chain transfer to initiator}}}$$

Rate of termination (coupling and disproportionation)

Rate of chain transfer to monomer

Rate of chain transfer to chain-transfer agent

Rate of chain transfer to initiator

Chain Transfer and Molecular Weight

Let us consider **Case 1**:

The degree of polymerization ($\overline{X_n}$) redefined:

$$\overline{X_n} = \frac{Rate\ of\ polymerization}{\sum chain\ breaking\ reactions}$$

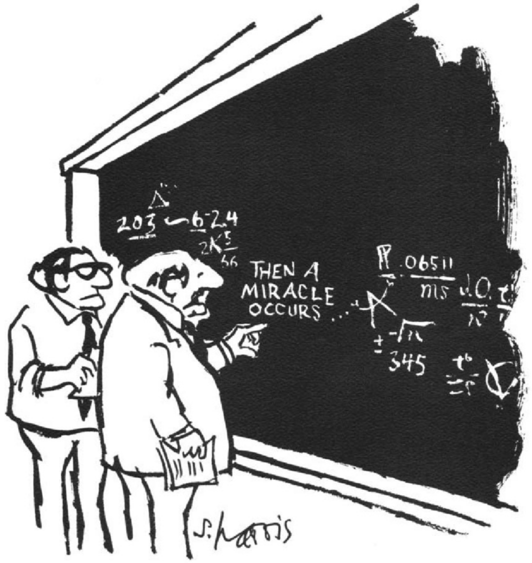
Chain breaking reactions: termination + all chain transfer reactions

$$\overline{X_n} = \frac{R_p}{\frac{R_t(2-a)}{2} + k_{tr,M}[M^\bullet][M] + k_{tr,S}[M^\bullet][S] + k_{tr,I}[M^\bullet][I]}$$

Let's try and simplify this by defining some **chain-transfer constants**:

$$C_M = \frac{k_{tr,M}}{k_p} \qquad C_I = \frac{k_{tr,I}}{k_p}$$

$$C_S = \frac{k_{tr,S}}{k_p}$$



"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

$$+ C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}$$

yo Equation

Chain Transfer Agents

$$\frac{1}{\overline{X}_n} = \frac{(2-a)R_i}{2R_p} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}$$

Mayo Equation

Mayo equation lets you adjust the reaction parameters to obtain the desired molecular weight

[S] provides a way to control the molecular weight of the polymer

This control can be wanted or unwanted!

These are solvents!

Regulators

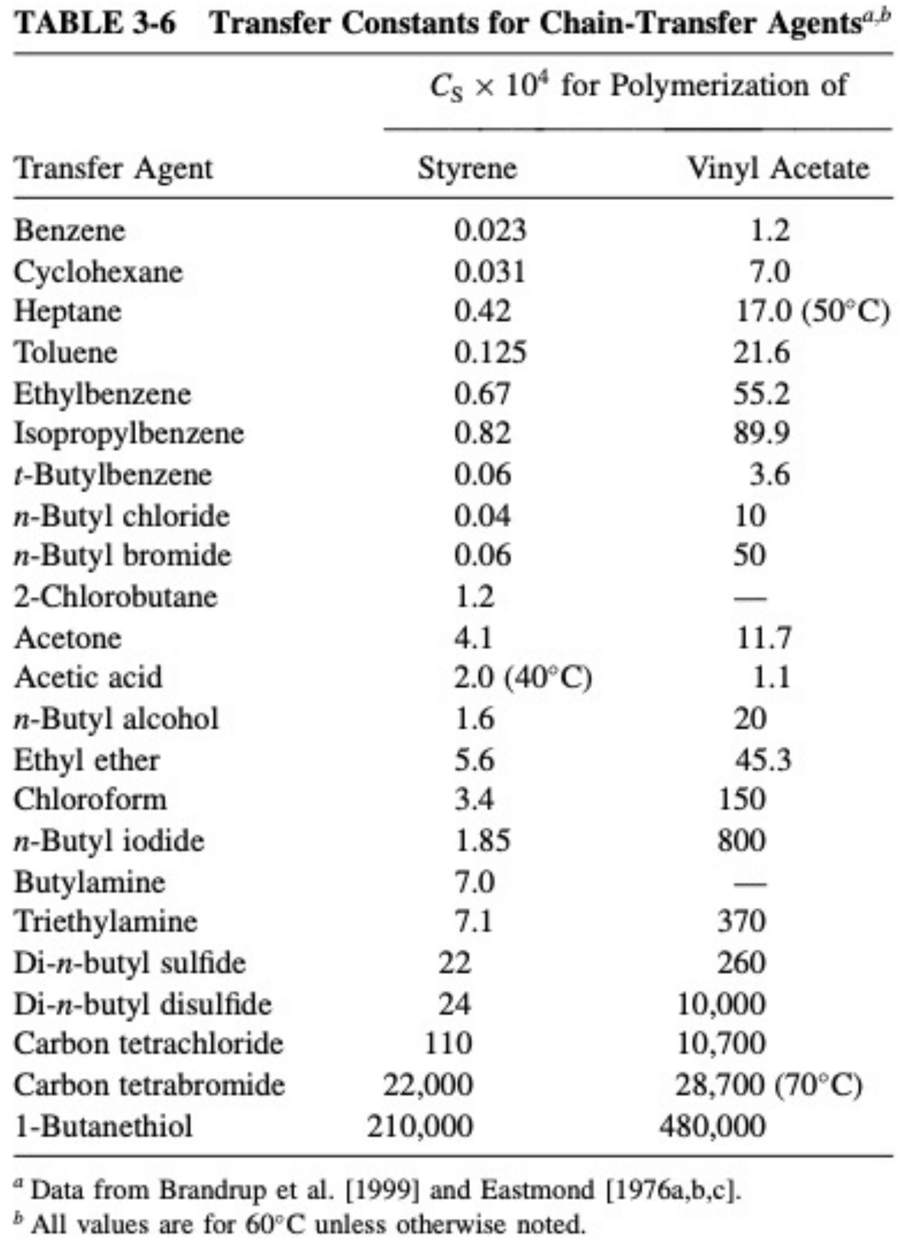


TABLE 3-6 Transfer Constants for Chain-Transfer Agents[a,b]

Transfer Agent	$C_S \times 10^4$ for Polymerization of Styrene	$C_S \times 10^4$ for Polymerization of Vinyl Acetate
Benzene	0.023	1.2
Cyclohexane	0.031	7.0
Heptane	0.42	17.0 (50°C)
Toluene	0.125	21.6
Ethylbenzene	0.67	55.2
Isopropylbenzene	0.82	89.9
t-Butylbenzene	0.06	3.6
n-Butyl chloride	0.04	10
n-Butyl bromide	0.06	50
2-Chlorobutane	1.2	—
Acetone	4.1	11.7
Acetic acid	2.0 (40°C)	1.1
n-Butyl alcohol	1.6	20
Ethyl ether	5.6	45.3
Chloroform	3.4	150
n-Butyl iodide	1.85	800
Butylamine	7.0	—
Triethylamine	7.1	370
Di-*n*-butyl sulfide	22	260
Di-*n*-butyl disulfide	24	10,000
Carbon tetrachloride	110	10,700
Carbon tetrabromide	22,000	28,700 (70°C)
1-Butanethiol	210,000	480,000

[a] Data from Brandrup et al. [1999] and Eastmond [1976a,b,c].

[b] All values are for 60°C unless otherwise noted.

Chain Transfer and Branching

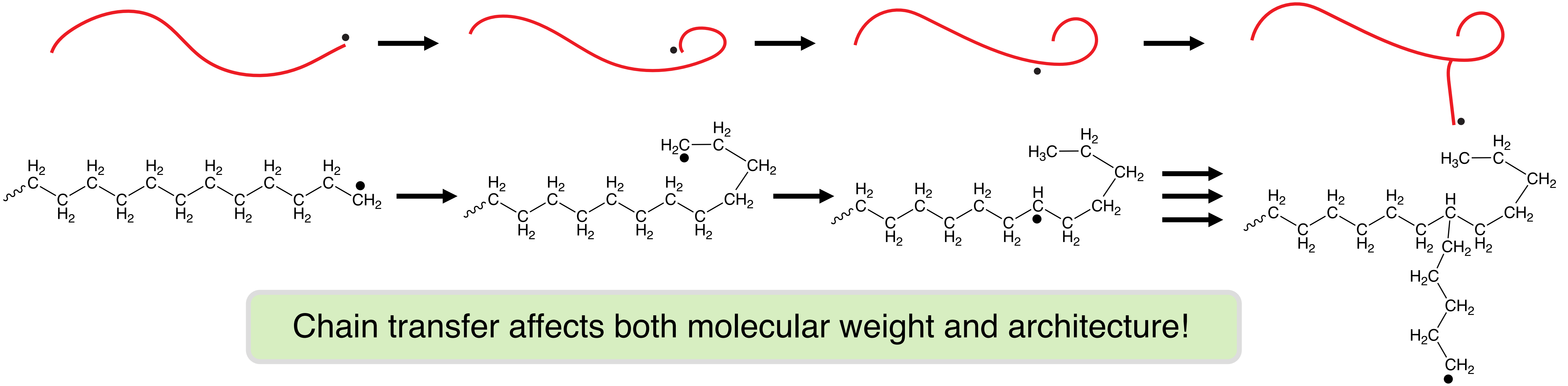
If chain growth can be summed up as:

$$I\text{-}M\text{-}M^{\bullet} + M \xrightarrow{k_p} I\text{-}M\text{-}M\text{-}M^{\bullet}$$

How do we get non-linear polymers?

Ans: At high conversions, chain transfer to polymer is possible!

Short branches* via "Backbiting"



Chain transfer affects both molecular weight and architecture!

*Long branches will be covered in the exercise

Inhibition and Retardation

Some compounds can suppress polymerization!

Chain transfer to these compounds with formation of less reactive radical*

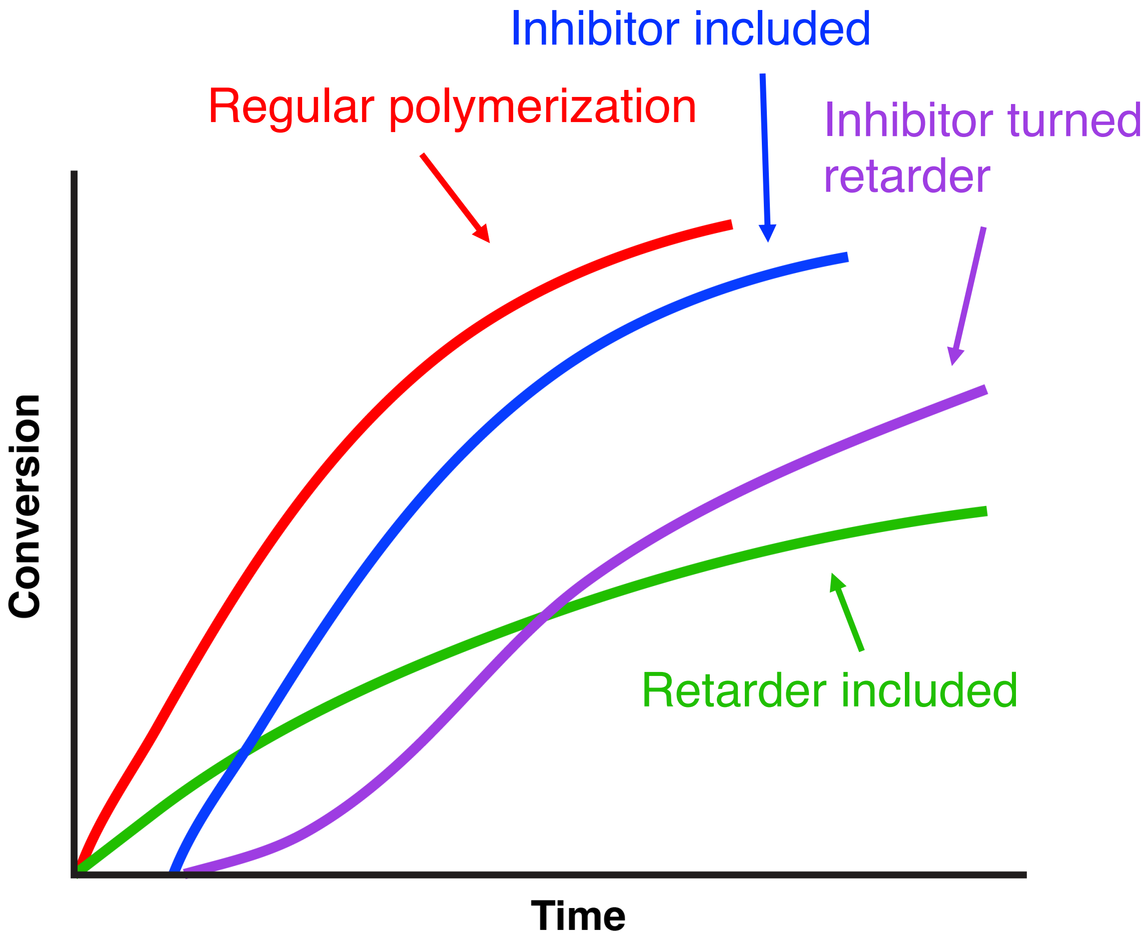
$$M_n^\bullet + Z \xrightarrow{k_z} M_n + Z^\bullet$$

Or adding to chain and forming less reactive radical

$$M_n^\bullet + Z \xrightarrow{k_z} M_n - Z^\bullet$$

Inhibitors: Reacts rapidly to produce radical that has little reactivity toward the monomer

Retarders: Reacts less rapidly to produce radical that reacts slower with monomer



Similar to Case 3 and 4: $k_a < k_p$

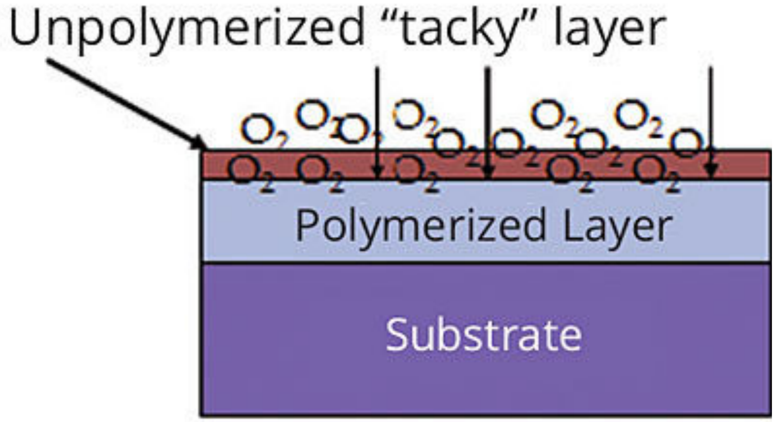
A Common Inhibitor: Oxygen

Depending on the system, oxygen can be a powerful inhibitor

$$M_n^{\bullet} + O_2 \longrightarrow M_n - \underline{OO^{\bullet}}$$

This radical (peroxy radical) is relatively unreactive!

Tacky surface layers



If you try and polymerize something in a mold, the air exposed face is polymerized less!

A more everyday example

A Common Inhibitor: Oxygen

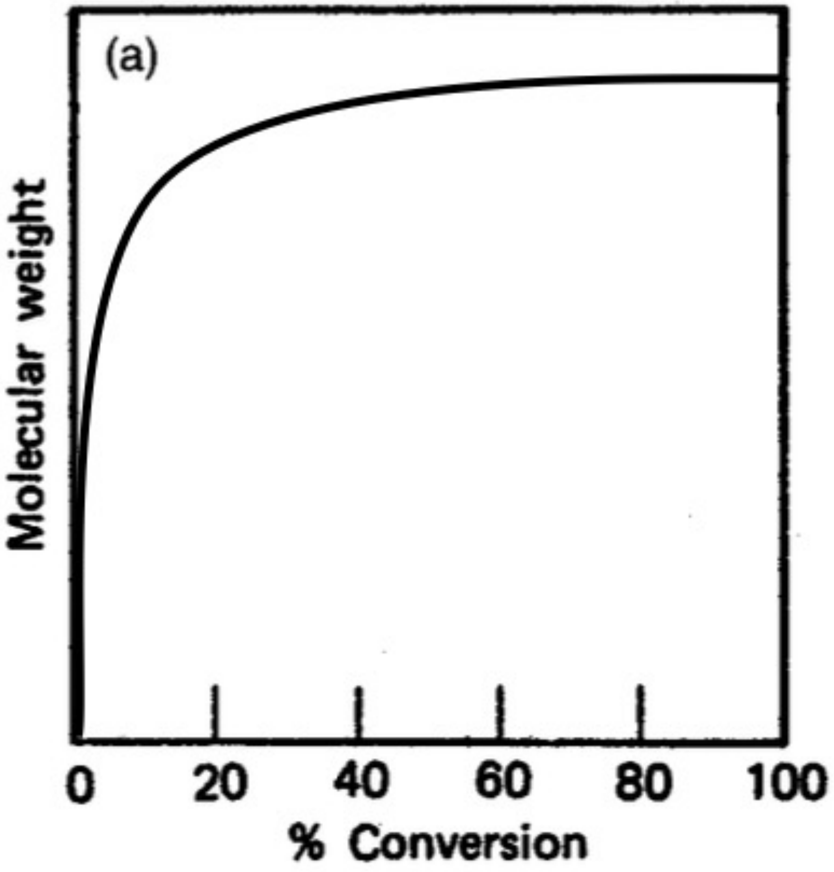
Oxygen inhibition can be a feature and not a bug

Rapid 3D printing (Carbon 3D)

Oxygen inhibition used to prevent sticking

Molecular Weight Evolution: Step growth Polymerization

Chain-growth Polymerization



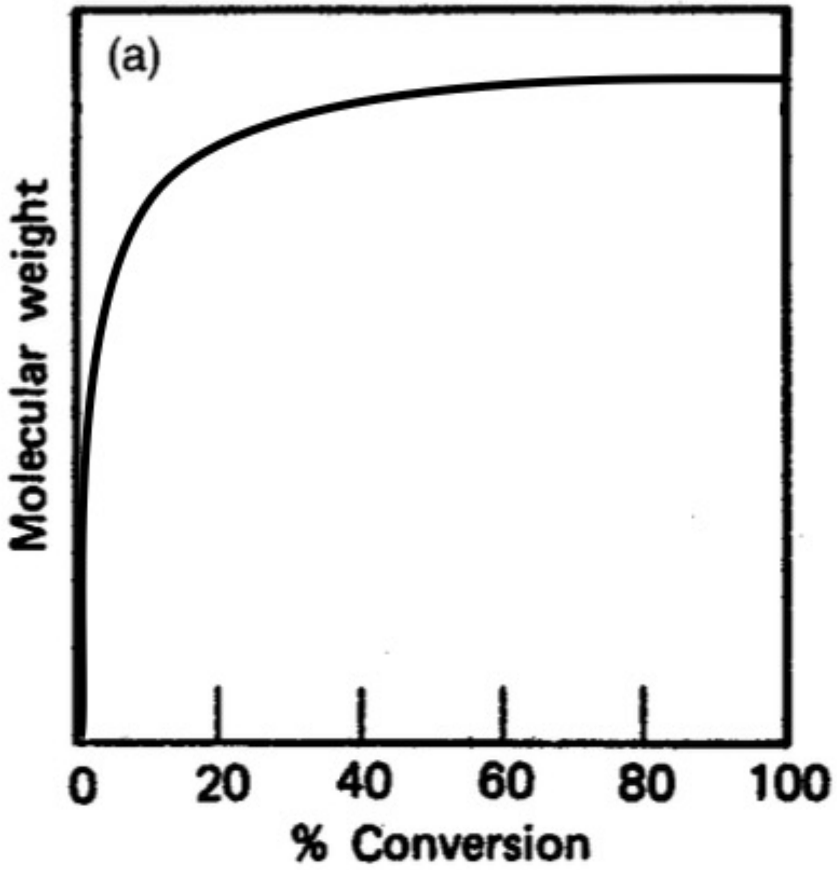
Molecular weight of polymer increases quickly and then tapers off.

At low conversions, the system contains some polymer with high molecular weight and monomers

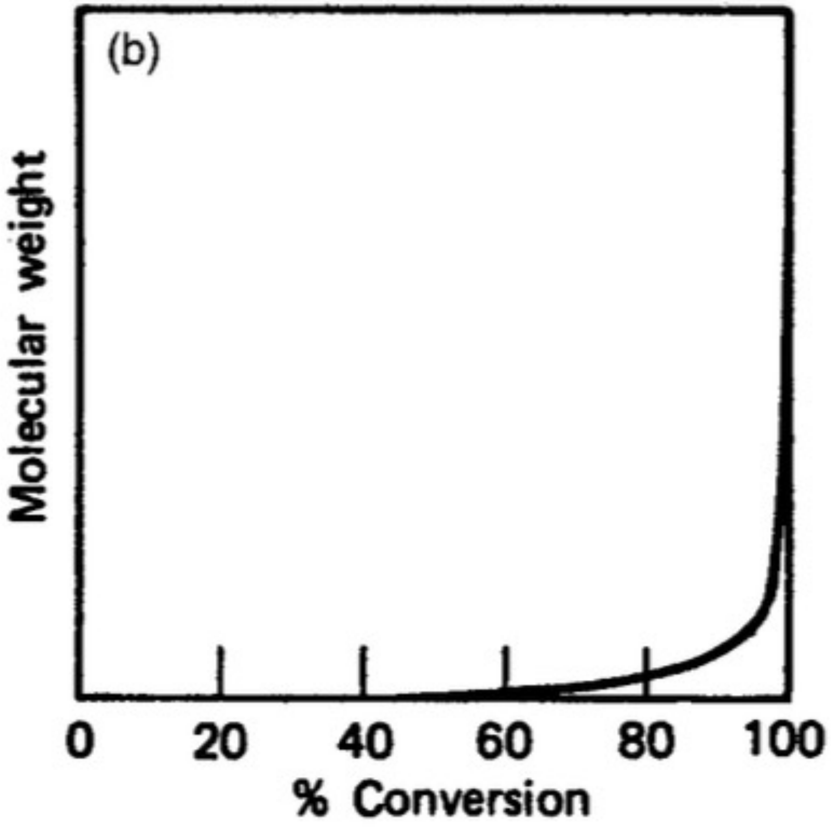
Increasing conversion does not increase molecular weight but increases the number of polymers in the system.

Molecular Weight Evolution: Step vs Chain

Chain-growth Polymerization



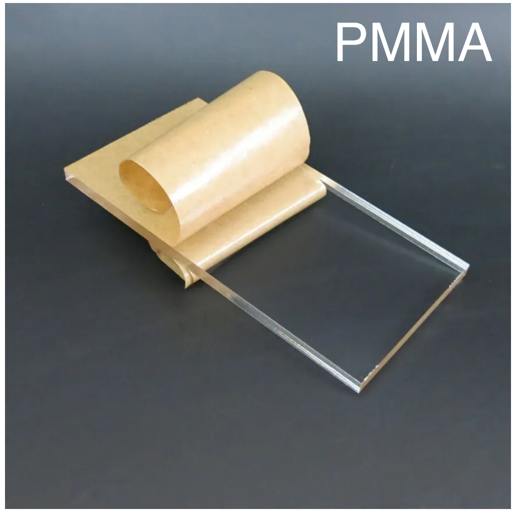
Step-growth Polymerization



Some Industrially Relevant Chain-Growth Polymers

- Polystyrene
- Polyethylene
- PVC (polyvinyl chloride)
- Poly(methyl methacrylate) (PMMA)
- Styrene-butadiene rubber (SBR)
- Neoprene (polychloroprene)
- “Superglue” (poly(ethyl cyanoacrylate))
- PTFE (polytetrafluoroethylene)

Note: Not all of these are made via radical chain growth. There is ionic, coordination, living, ring-opening, reversible-deactivation, and etc.


PMMA


SBR


Neoprene

Chain-growth Polymerization: What we did not cover

- Redox initiation, bulk monomer initiation, ionizing radiation initiation
- Multifunctional monomers
- Catalytic chain-transfer, autoinhibition
- Non-steady-state kinetics
- Energetics of chain-growth
- Autoacceleration
- Molecular weight distribution

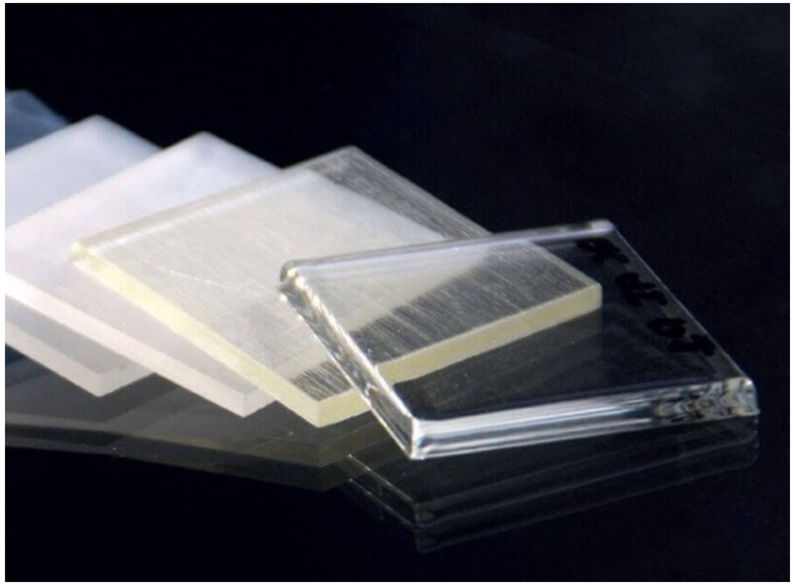
More advanced models that explains what you see in your day to day life but this isn't Polymer Chemistry 101

Key Takeaways

- Chain-growth polymerization only occurs at the active site of the polymer chain
- The three phases of chain-growth are initiation, propagation, and termination
- Large molecular weights occur at relatively low conversions
- Chain-transfer can be used to control molecular weight
- Inhibition and retardation can be used to control molecular weight

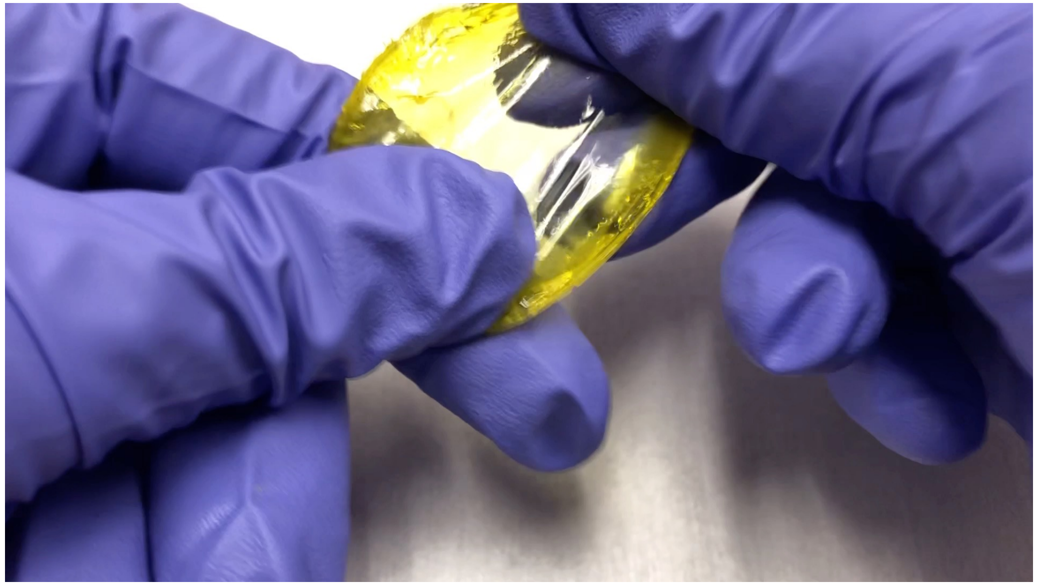
From Synthesis to Properties

Optical



Thermal

Mechanical

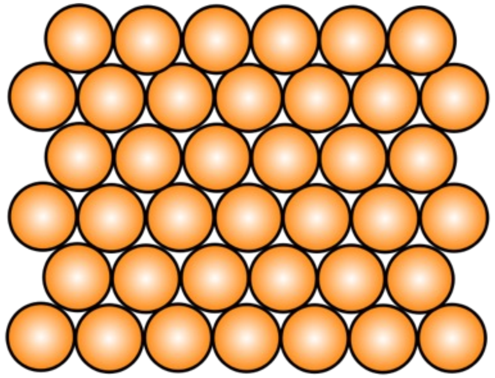


How can we understand the properties of polymers?

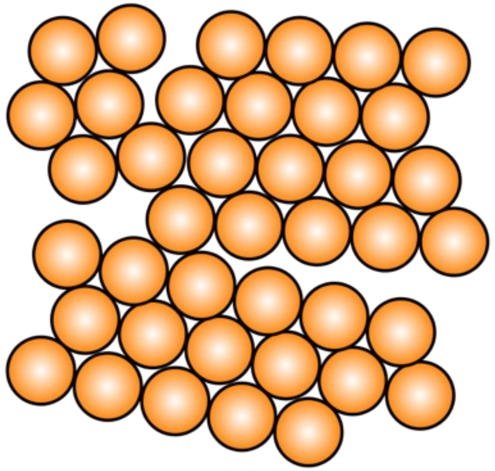
How does synthesis affect the properties?

Recall from MSE 101b: Crystalline vs Amorphous

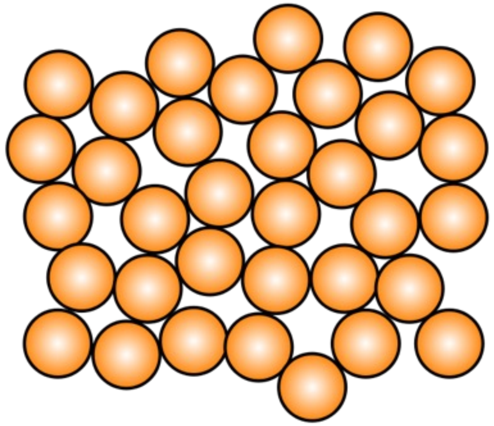
Crystalline



Polycrystalline



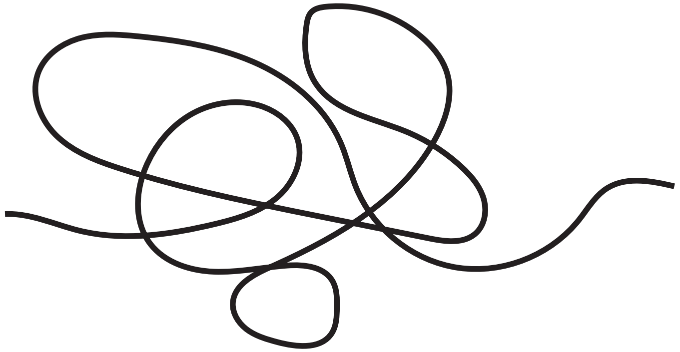
Amorphous



Simplest definition of cystallinity: Material whose constituents are arranged in a highly ordered manner

We've been representing polymers like this →

How do polymers crystallize?

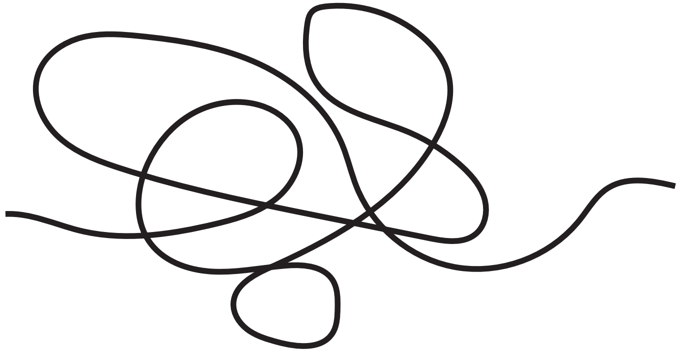


Single chain

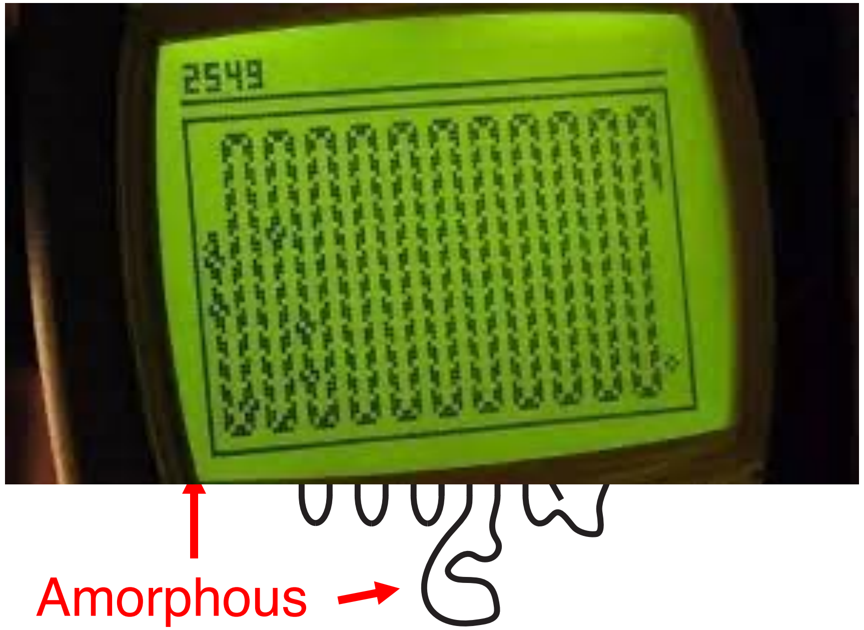
Multiple chains!

How do polymers crystallize?

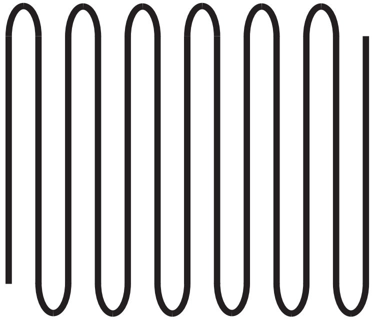
Amorphous



Basically a game of “snake”*



Crystalline



Crystallization is thermodynamically favorable!

Lowers energy state of the polymer

Polymers states:

Can be completely amorphous

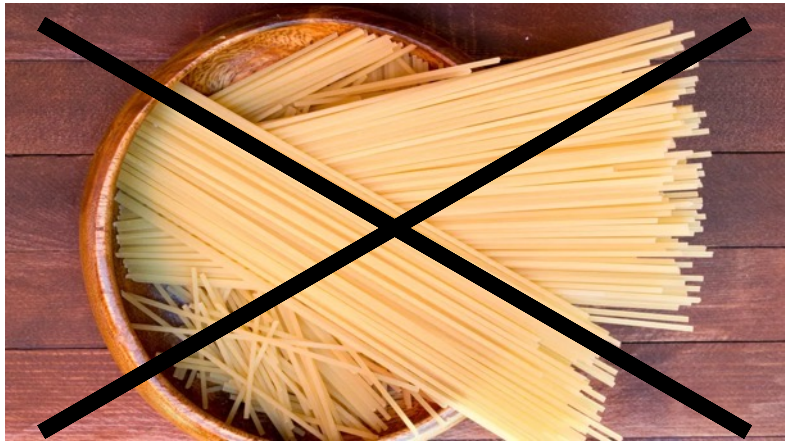
Can be semi-crystalline

Can never be 100% crystalline

*You might be too young for this…

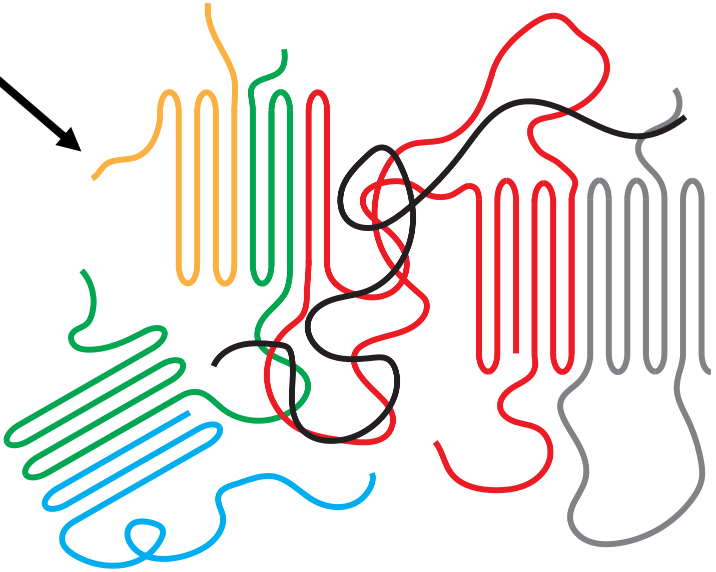
How do polymers crystallize?

For a system with multiple chains, how does crystallization happen?



Interactions between polymer chains prevent 100% crystallinity

Polymers that *can* crystallize only forms semi-crystalline polymers

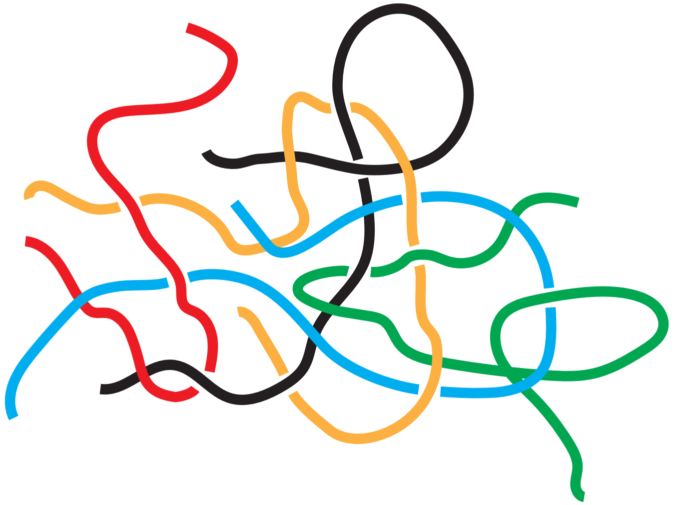


Polymer crystals surrounded by an amorphous matrix

A single chain can be involved in zero/one/multiple crystals

How do polymers crystallize?

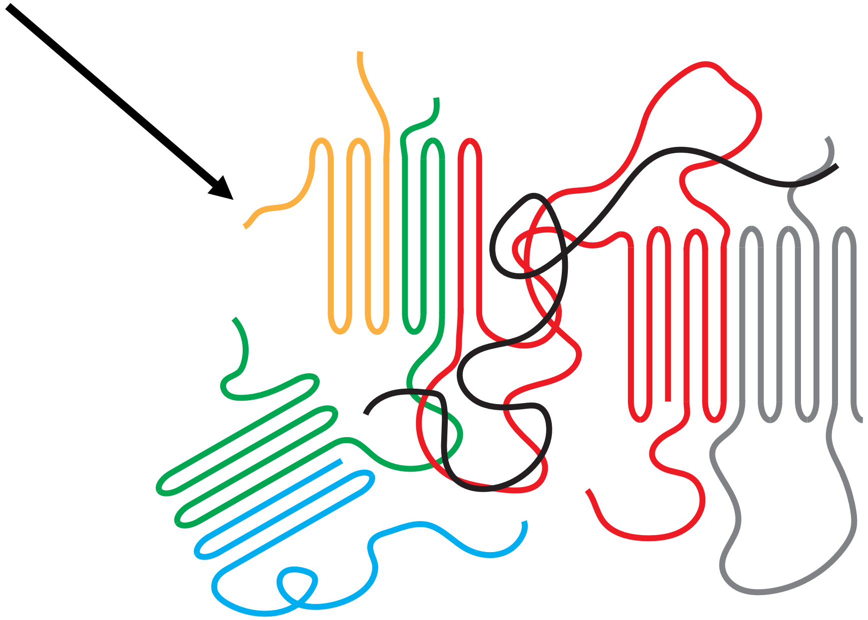
For a system with multiple chains, how does crystallization happen?



Long chains tend to get entangled and make crystallization difficult

Entanglements prevent 100% crystallinity and result in semi-crystallinity

Interactions between polymer chains prevent 100% crystallinity



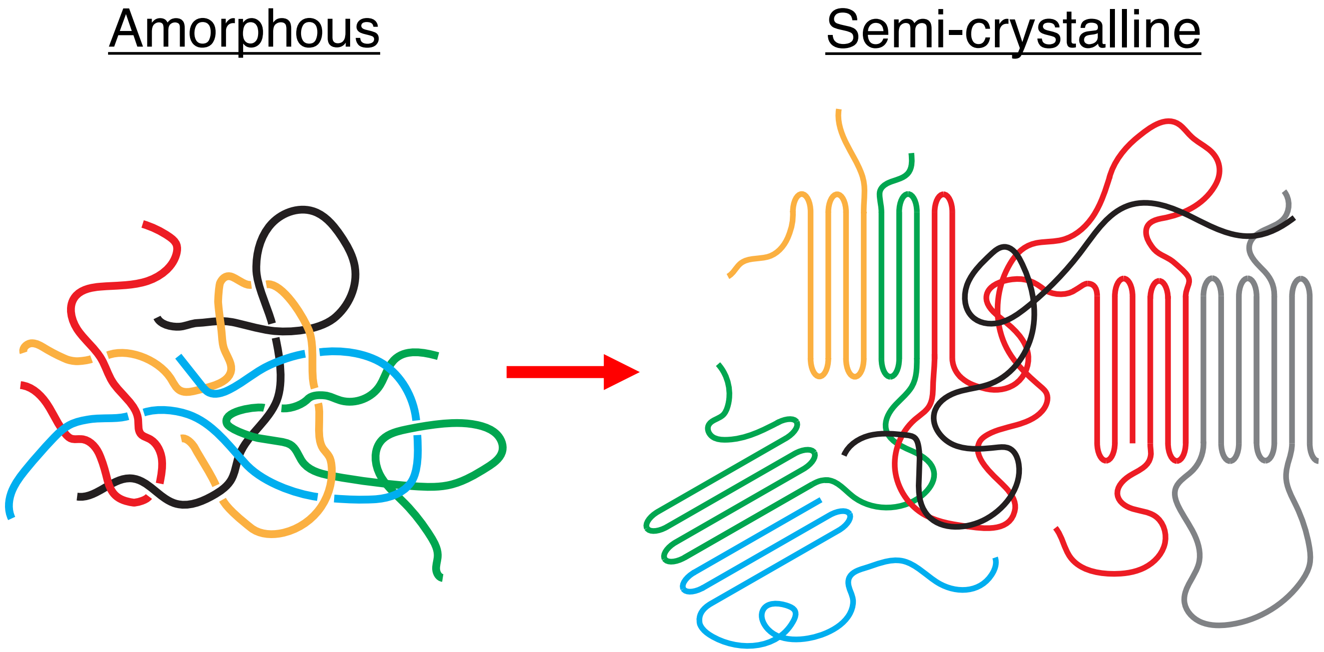
Polymers that *can* crystallize only forms <u>semi-crystalline</u> polymers

Polymer crystals surrounded by an amorphous matrix

A single chain can be involved in zero/one/multiple crystals

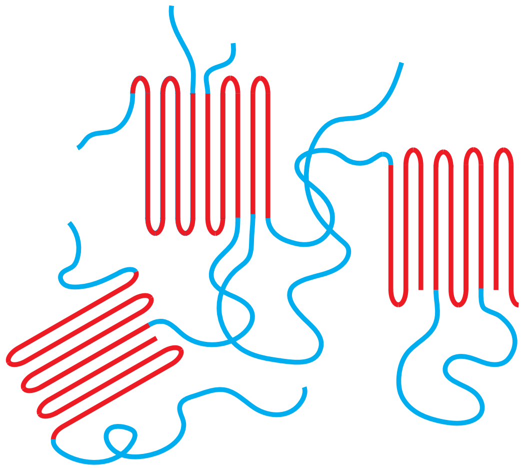
How do polymers crystallize?

For crystallization to happen, the polymer chains need to be able to get themselves into the right configurations



To understand crystallization, we first need to know about polymer phase transitions

Two key temperature transitions



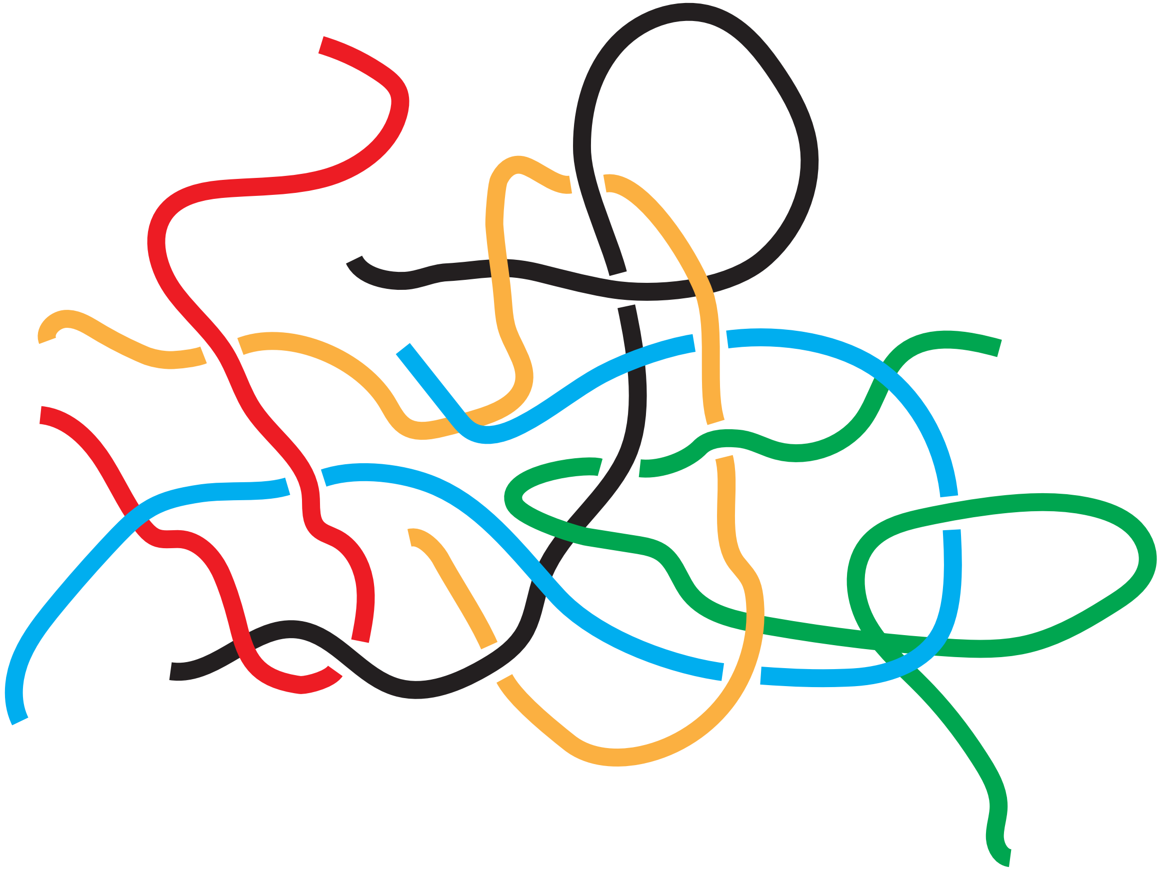
Glass transition temperature (T_g)

→ Temperature range where amorphous regions starts to move

Melting temperature (T_m)

→ Temperature range where crystalline regions starts to move

Glass Transition Temperature (T_g)



You can think of polymers as a mess of wires/cables/noodles

It’s hard for one chain to “escape” from the rest → Entangled with each other

Need to provide energy for the chains to be able to “move” out of the mess

The temperature where there starts to have enough energy is the glass transition temperature

Glass Transition Temperature (T_g)

Rubbery State
($T > T_g$)

Polymer chains have enough energy to move around and slide past each other quickly*

Freshly cooked hot spaghetti can flow easily!

Cooling
to T_g

Chains start to lose energy and move slower; hard to move them around

Spaghetti getting cold and clumpy

Glassy State
($T < T_g$)

Chains do not have energy to move around or move extremely slowly

Spaghetti frozen and stuck together!

---

*to be precise, polymer chains can undergo long range segmental motion

Glass Transition Temperature (T_g)

Can think of T_g as the temperature <u>range</u> where the polymer starts to soften

$T > T_g$ → Soft and deformable
$T < T_g$ → Brittle and hard

Depending on their design and processing history, the T_g of polymers can range from -100 to 200˚C

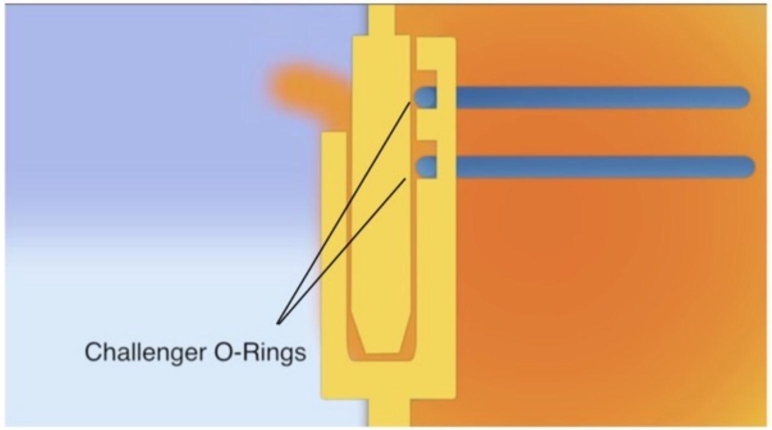
Temperatures easily accessible to humans and also within seasonal variations

Challenger Disaster

Cold day before launch

O-rings were in the glassy state and could not seal

don't launch = under the glass transition temperature



polymer chains are in a frozen state, locked in place; not flexible

Glass Transition Temperature (T_g)

Can think of T_g as the temperature range where the polymer starts to soften

$T > T_g$ → Soft and deformable
$T < T_g$ → Brittle and hard

Important to know the T_g so that the operating temperatures of the polymer can be established!

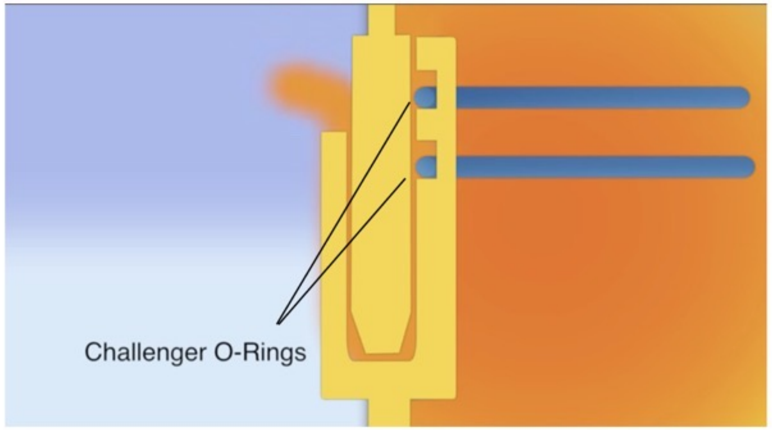
Critical for polymers used in critical applications or functions

Challenger Disaster

Cold day before launch

O-rings were in the glassy state and could not seal

don't launch = under the glass transition temperature



polymer chains are in a frozen state, locked in place; not flexible

States of Amorphous Polymers

$T < T_g$

Glassy state

- Polymer behaves like a stiff and brittle solid
- Polymer chains are effectively rigid
- Small scale motion*

$T > T_g$

Rubbery state

- Polymer behaves like a soft and easily deformed solid
- Polymer chains are mobile
- Long range motion*

$T >> T_g$

Fluid state

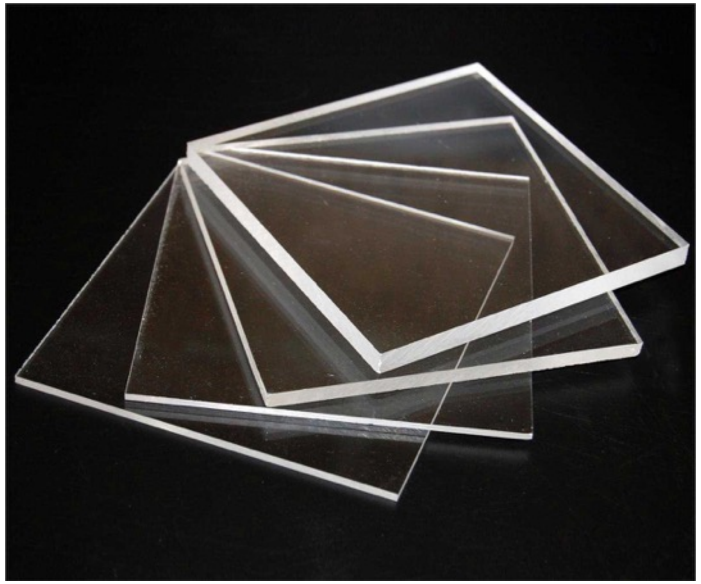
- Polymer behaves like a liquid

Polymers are often used based on how their glass transition temperature compares to room and operating temperature

*additional information

States of Amorphous Polymers

$T < T_g$
Glassy state



Plexiglass has
a T_g ~100˚C

$T > T_g$
Rubbery state

Low density polyethylene
has a T_g ~ –100˚C

$T >> T_g$
Fluid state*

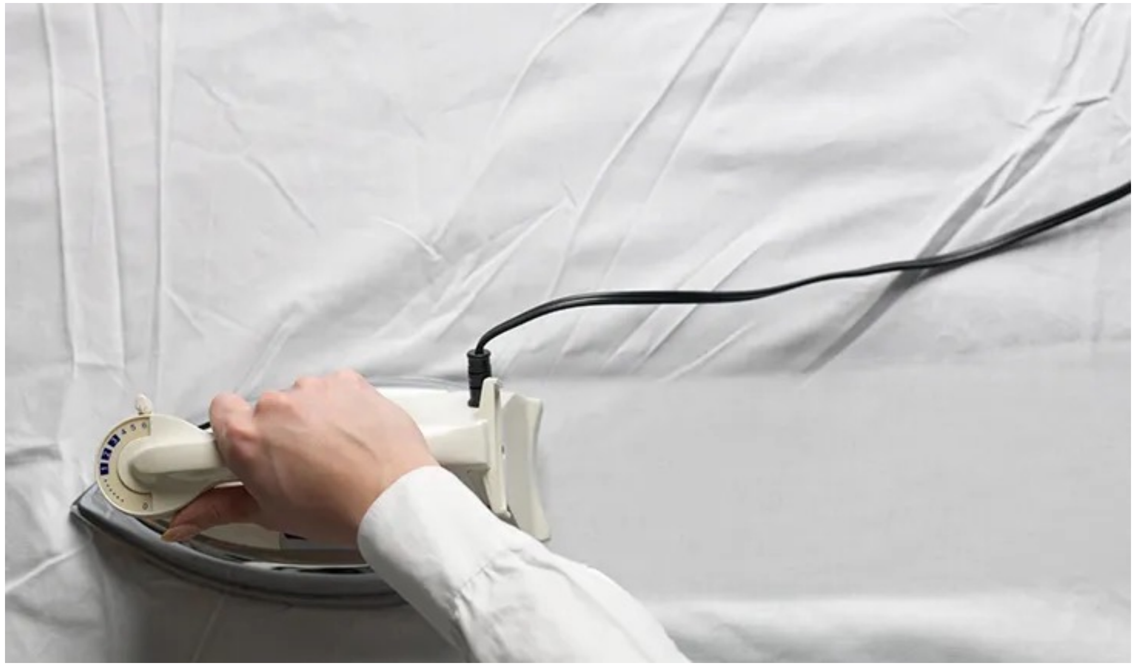
Polymers are often used based on how their glass transition temperature compares to room and operating temperature

*this is often referred to as a polymer melt…

Where have we used T_g in our daily lives before?

Shaping plexiglass/acrylics

Ironing



Heating a polymer past the glass transition allows us to manipulate its shape!

Week 3 Learning Objectives

- **Chain-growth Polymerization**
  - Terms: Chain polymerization, condensative chain polymerization, conversion, initiation, propagation, termination, chain transfer, inhibition, Mayo equation, kinetic chain length
- **Understand the molecular mechanisms of controlling molecular weight**
- **Understand the difference between amorphous and semi-crystalline polymers**
- **Understand what the glass transition temperature is**