Office Hours

Section 166	Section 133	Section 177
Time: Tue/Thu 11:00-12:20	**Time**: Tue/Thu 15:30-16:50	**Time**: Tue/Thu 12:30-13:50
Location: CHEM B250	**Location**: HEBB 100	**Location**: **CIRS 1250**
Instructor: Amani Hariri	**Instructor**: Dan Bizzotto	**Instructor**: Keng Chou
Office: CHEM A127	**Office**: AMPEL 318	**Office**: CHEM D348
Email: amaniah@chem.ubc.ca	**Email**: bizzotto@chem.ubc.ca	**Email**: kcchou@chem.ubc.ca
Office Hours	*Office Hours*	*Office Hours*
Wed 5:00 - 6:00 pm in A127	Mondays 4:30-5:30 pm in AMPEL 318	Tuesdays 2:00 - 3:00 pm in D348
(also by appointment)	(also by appointment)	(also by appointment)
Lecture TA: Albert Li	**Lecture TA**: Daina Baker	**Lecture TA**: Weiming Song
Office Hours: Mon 6:00-7:00pm in C126 (Chem)	**Office Hours**: 10:00 to 11:00 am in AMPEL 342	**Office Hours**: Thurs 6:00-7:00pm in MCLD 2012

- You may attend any office hours, regardless of your section.

Unit 5
Polymers II

Slide Color Codes

All Lectures

Section Only

Required

Required

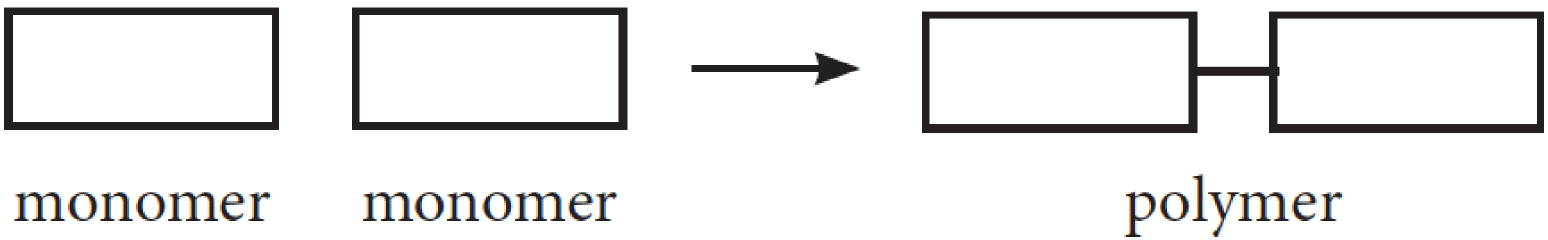
OK to Skip

Useful

Not Examable

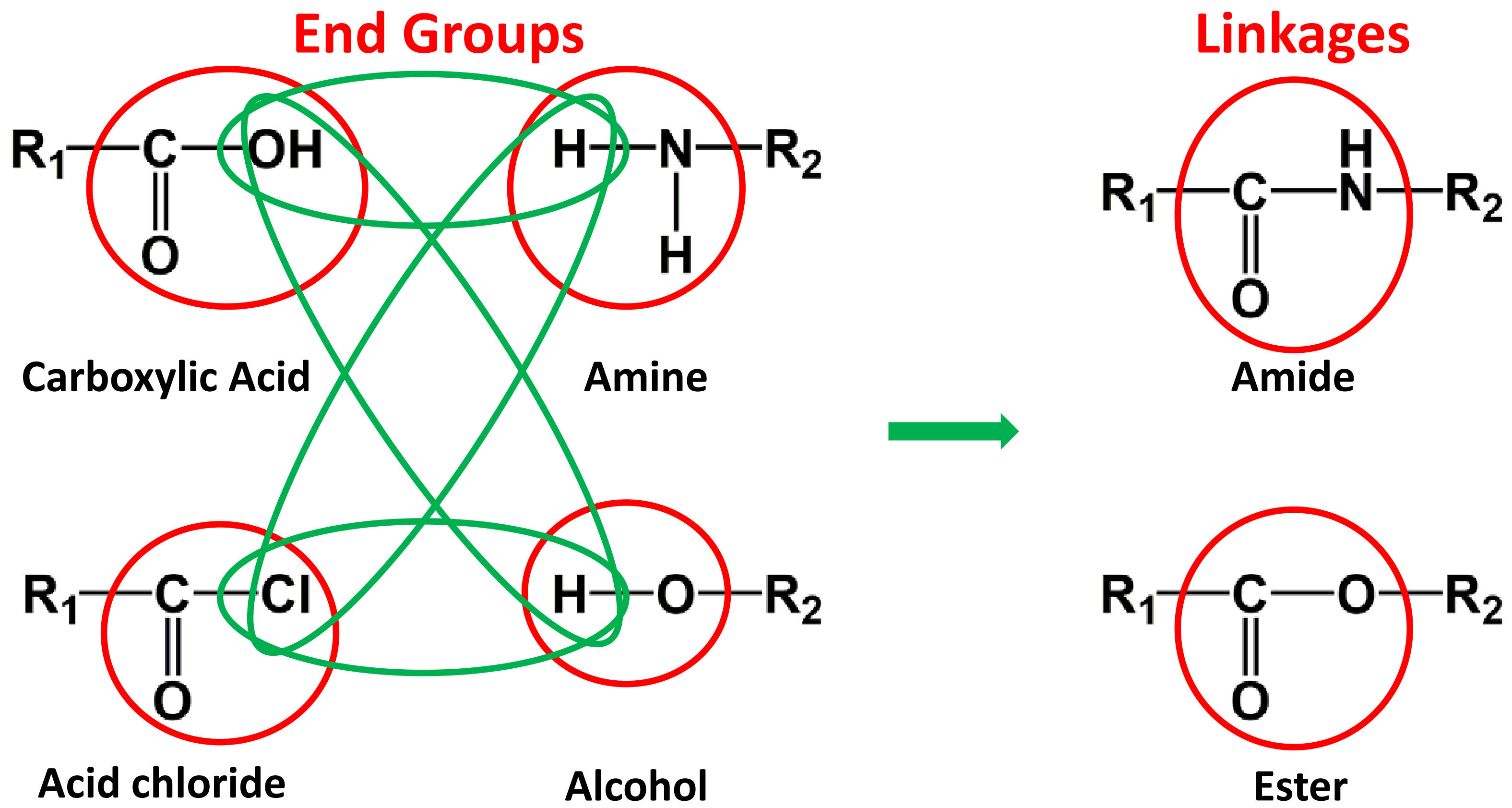
Polymers

- A **polymer** is a macromolecule constructed by a sequential stringing together of smaller molecules called monomers.



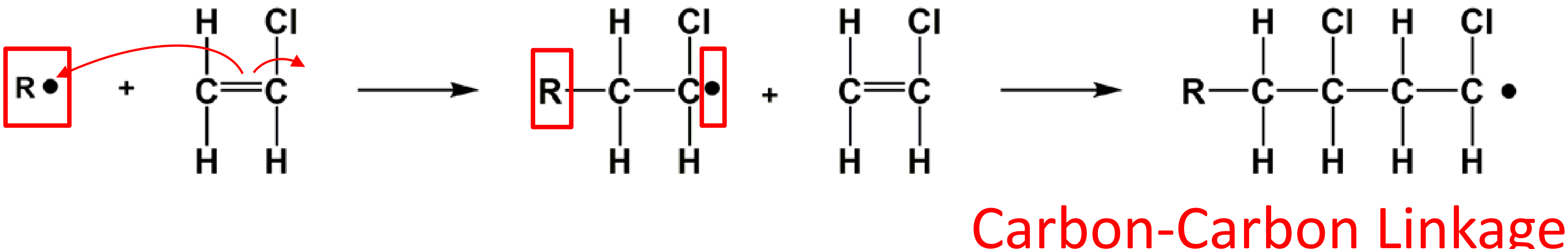
- We'll discuss two types of polymers:
  - **Condensation polymers**
  - **Addition polymers**

Condensation



Addition Polymers

- **Addition reactions** occur when two or more molecules join to form a larger molecule *without* the loss of any atoms / small molecules.
- 'R·' is an abbreviation for a molecule that initiates the polymerization process.
- **Dot (•):** The dot signifies the presence of an **unpaired valence electron,** , which makes the species a **free radical.**



Polymerization steps

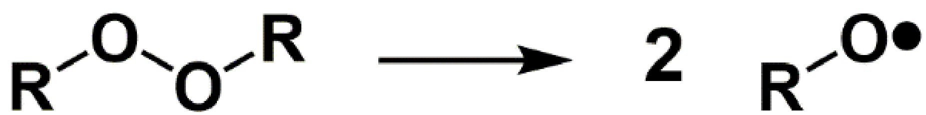
Addition polymerization occurs in three key stages:

1) **Initiation.** Number of radicals increases.
2) **Propagation.** Number of radicals remains constant.
3) **Termination.** Number of radicals decreases.

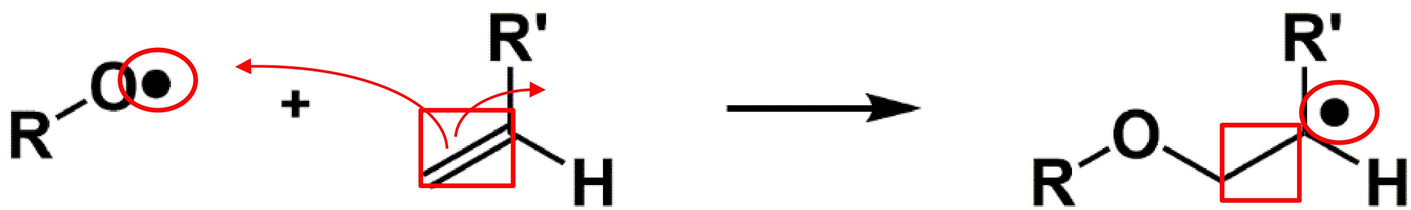
Initiation

- A polymerization reaction starts by the formation of a reactive species such as a free radical.
- Radicals are very reactive species with an odd number of electrons. Radicals are generally abbreviated as R·, where the dot represents the unpaired electron.

(1) Bond cleavage:



(2) Addition:

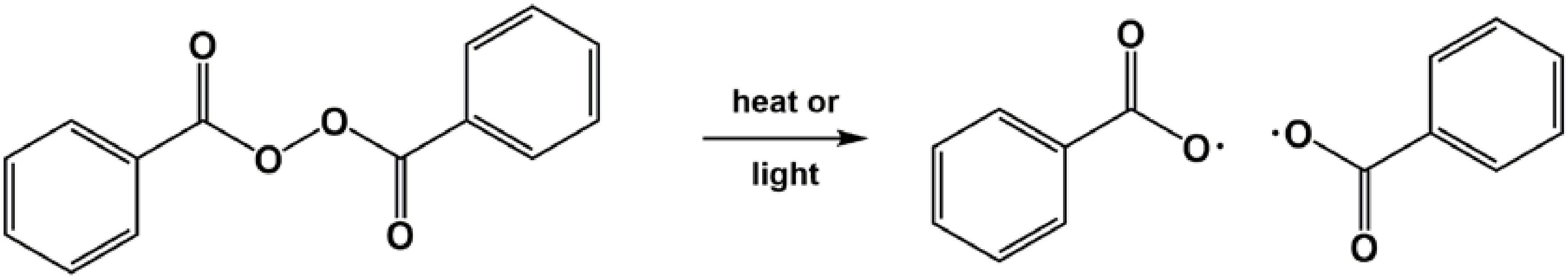


In general: **RO·** Is just notated as **R·**

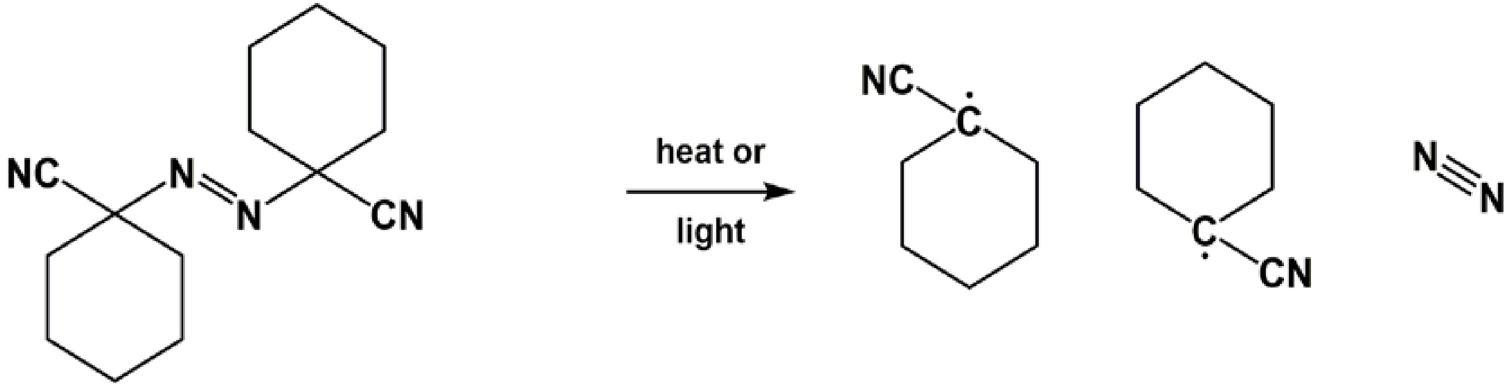
Initiators

- A common radical initiator. Peroxides may be explosive.

(1) Benzoyl peroxide:

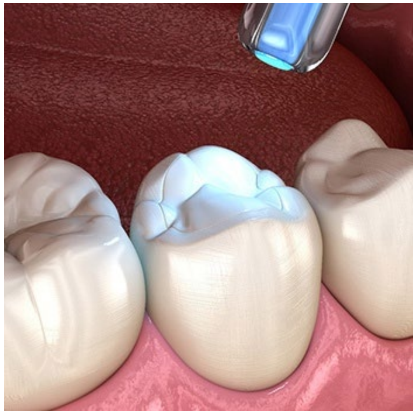


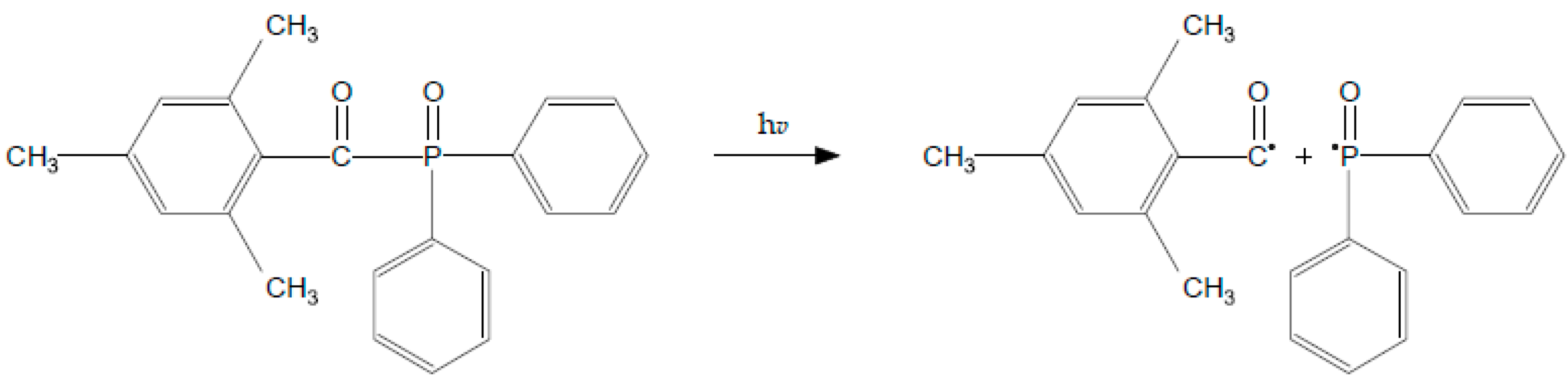
(2) Azobisisobutyronitrile (AIBN):



You do NOT need to memorize these structures

Photoinitiators Used in Dental Composite





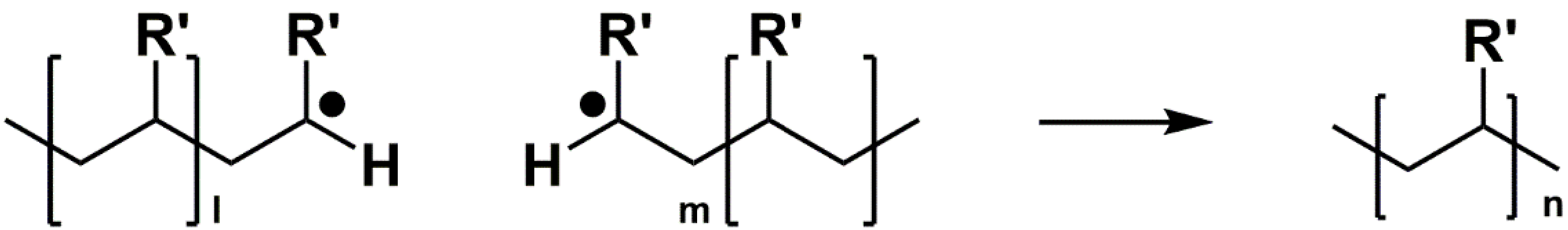
Propagation

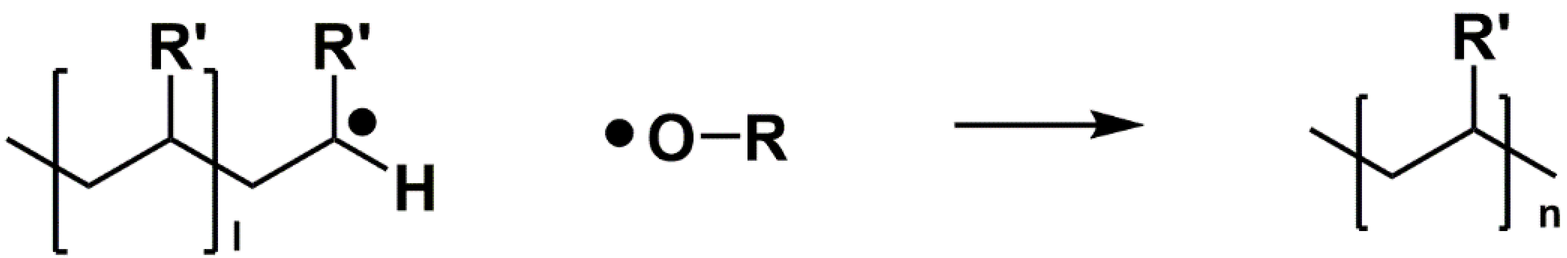
- A growing polymer chain reacts with a monomeric unit, extending the length of the polymer.
- No overall change in number of radical species.

(Radical + monomer → Radical)

Termination

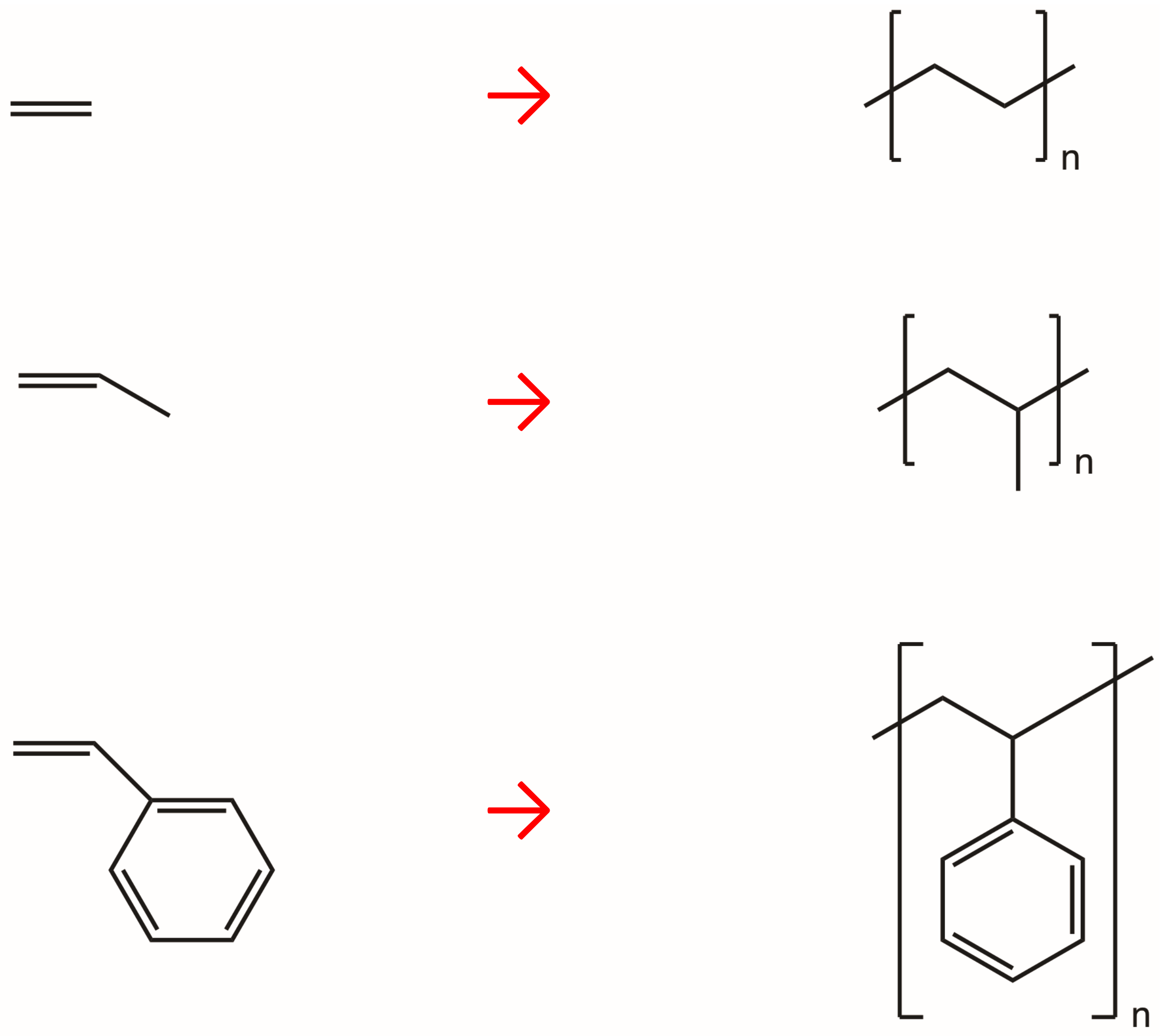
- Reaction between a growing chain and another radical species (another growing chain, or an initiator).



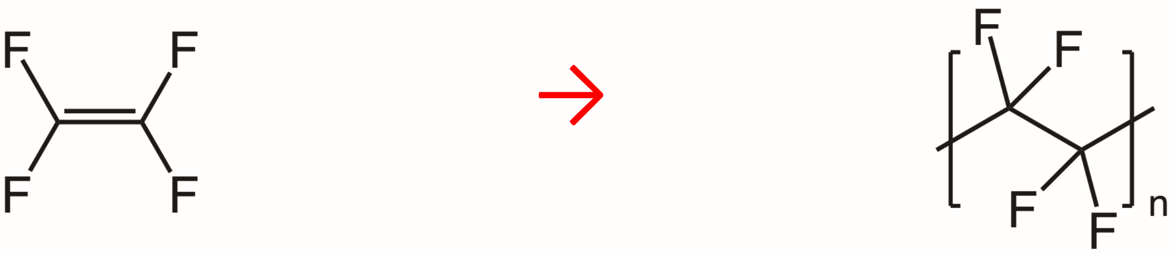


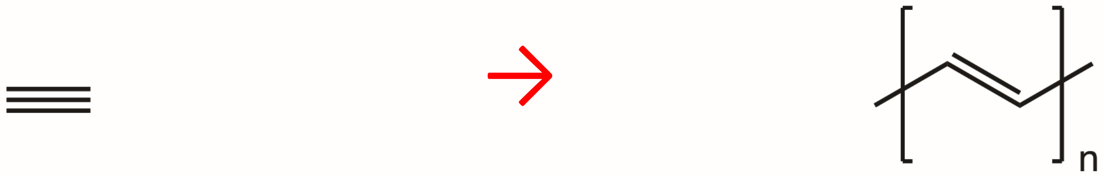
(Radical + Radical → Polymer)

Examples of addition polymers

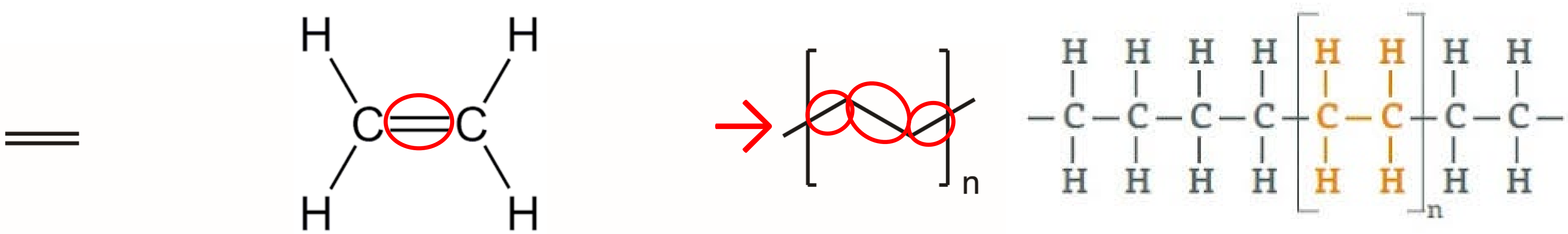


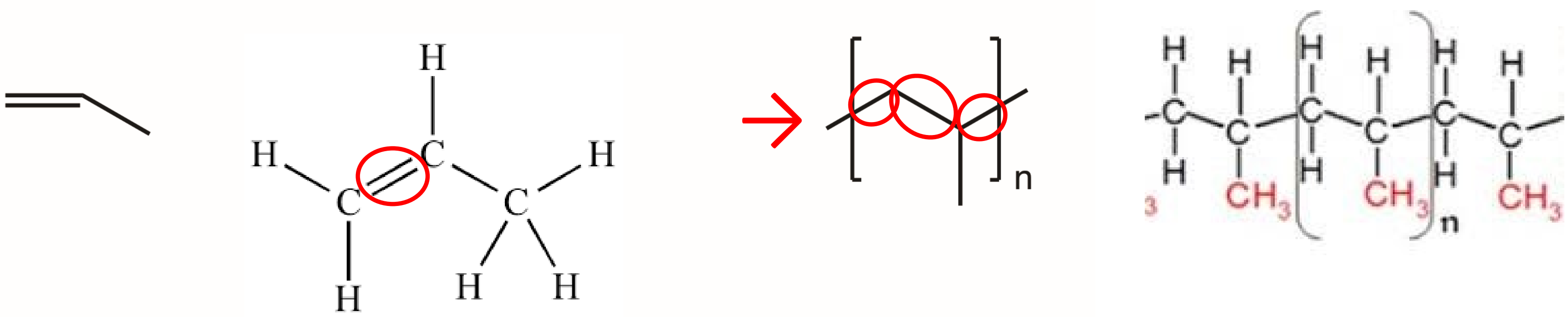
Examples of addition polymers

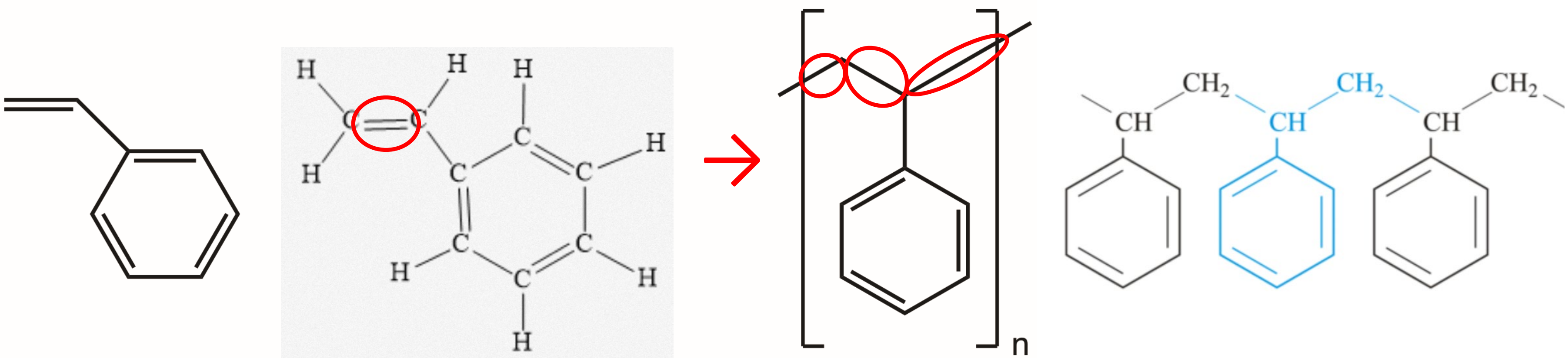




Examples of addition polymers





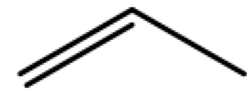


Worksheet Question #7-8

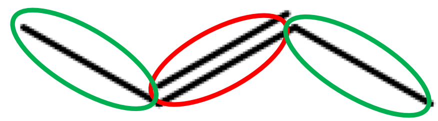
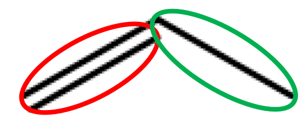
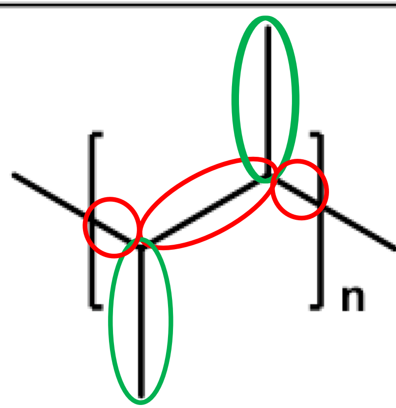
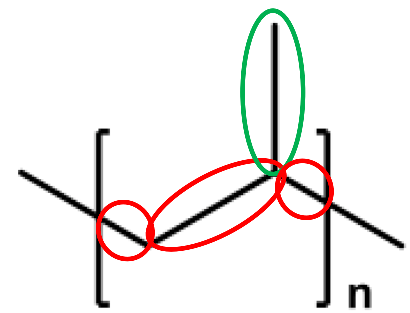
Fill in the blanks in the table below by drawing the polymer or smallest possible monomer. Classify each polymer as condensation or addition polymer by circling the correct option. Name the type of linkage.

If you find these concepts difficult, please view the videos posted on Canvas that go through these type of problems in detail.

Review Clicker Question

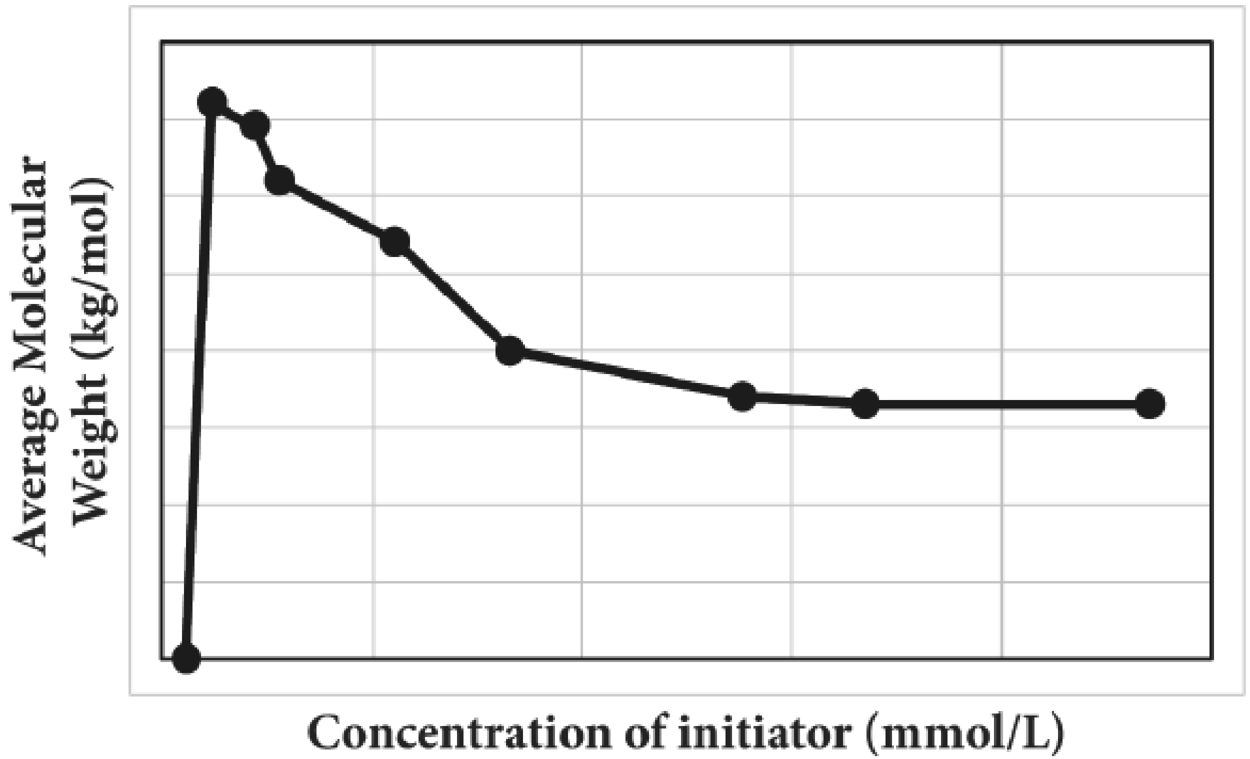
Monomer		
Polymer		

Review Clicker Question

Monomer		
Polymer		

Worksheet Question #6 – GOOD QUESTION

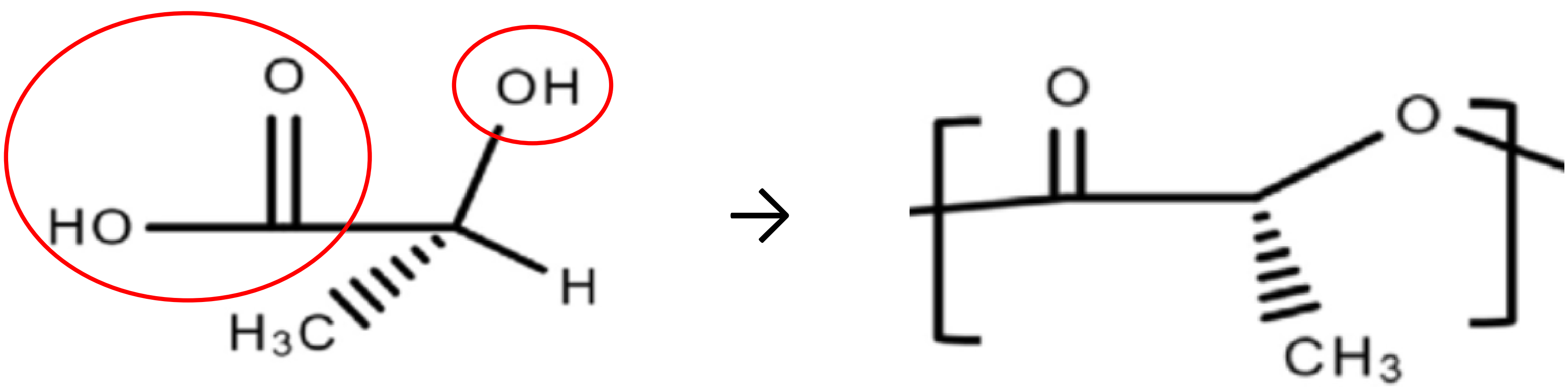
Provide a valid explanation for the trend in polymer molecular weight of **poly(methyl methacrylate)** shown below.



- When the number of radicals is small, the termination step is less likely to occur so the polymers continue to grow longer.

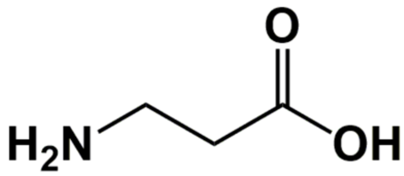
Direct condensation polymerization

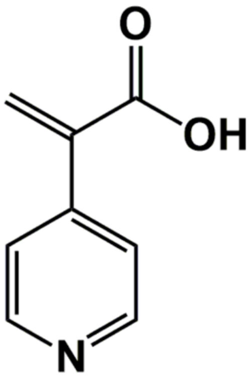
- Monomers with two or more functional groups, such as –COOH, –OH, –NH_2, react directly to form polymers.
- No prior chemical modifications needed.
- Example:

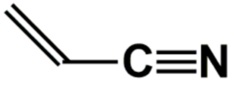


Clicker review: worksheet question 7

Which of the monomers below directly lead to condensation polymerization reactions?

A


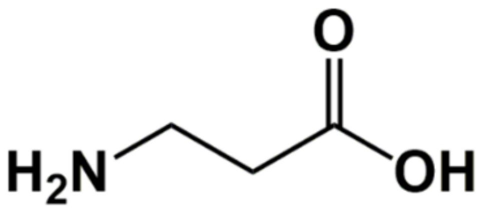
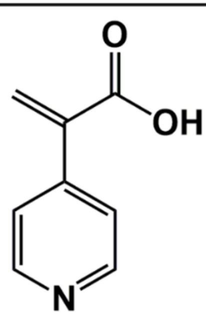
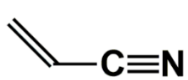
B


C


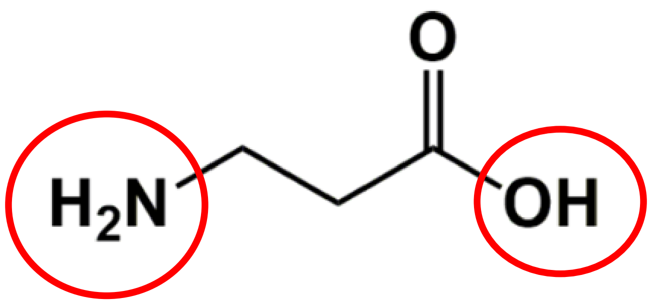
D. Molecules A + B

E. Molecules B + C

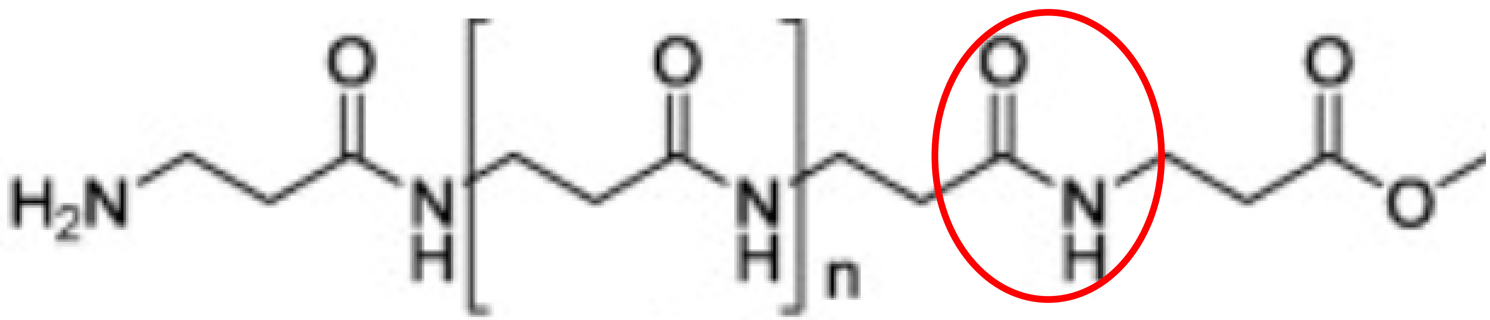
Worksheet Question 7

Monomer(s)	**Polymer**
	Addition Condensation
	If condensation, type of linkage:
	Addition Condensation
	If condensation, type of linkage:
	Addition Condensation
	If condensation, type of linkage:

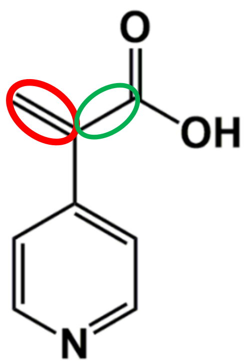
Worksheet Question 7

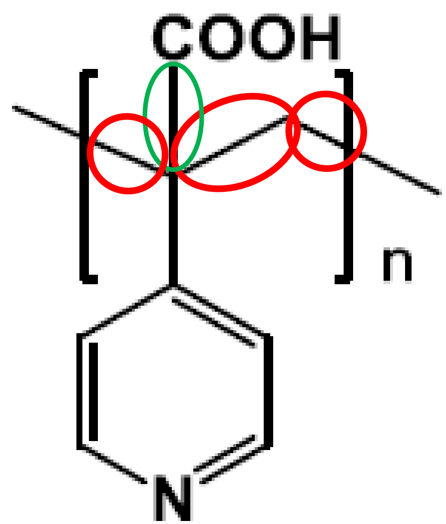
Monomer(s)	Polymer
	Addition Condensation
	If condensation, type of linkage:

Amide

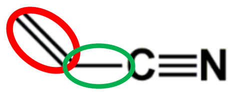


Worksheet Question 7

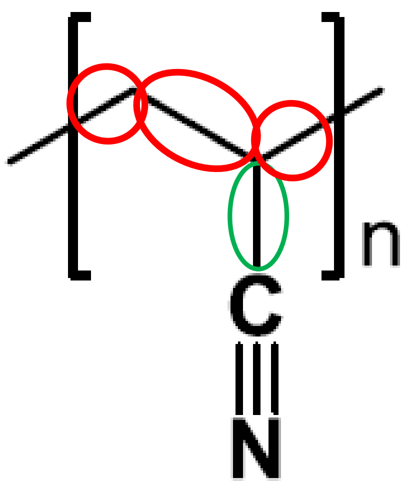
	Addition ✓ Condensation
	If condensation, type of linkage: Carbon-Carbon



Worksheet Question 7

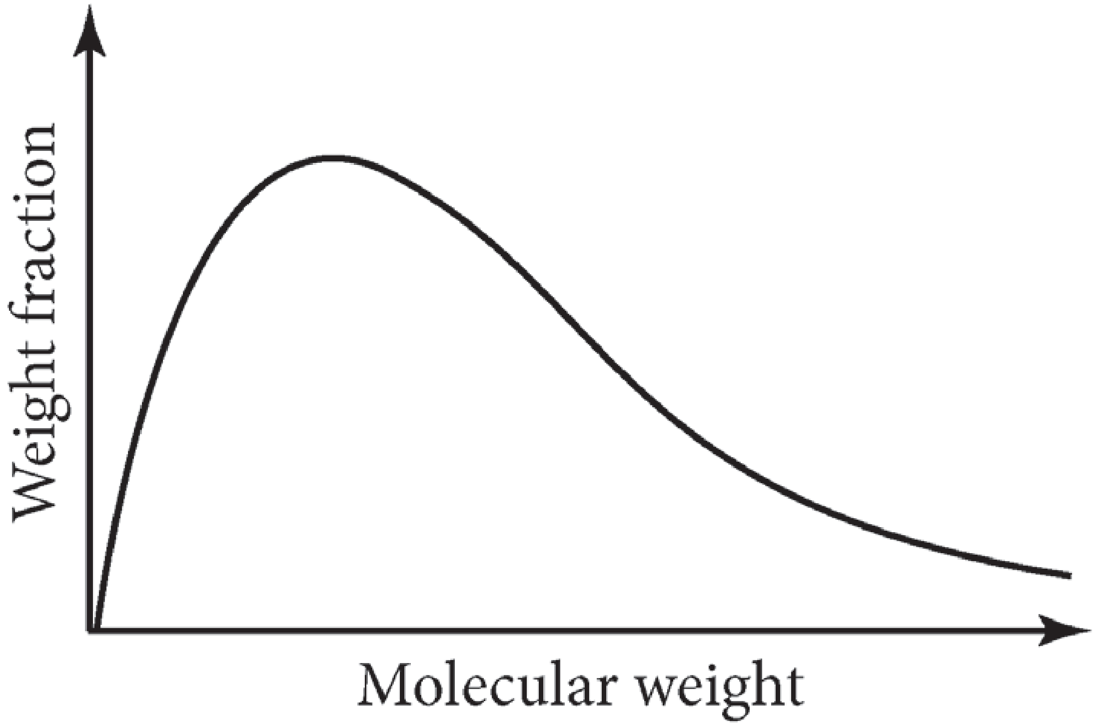
	Addition ✓ Condensation
	If condensation, type of linkage:

Carbon-Carbon



Molecular weight (MW) distributions

- A synthetic polymer will have a range of chain lengths of differing molecular mass, or a *mass distribution*.
- Differences in molecular weight affect solubility, strength, viscosity, among other properties.

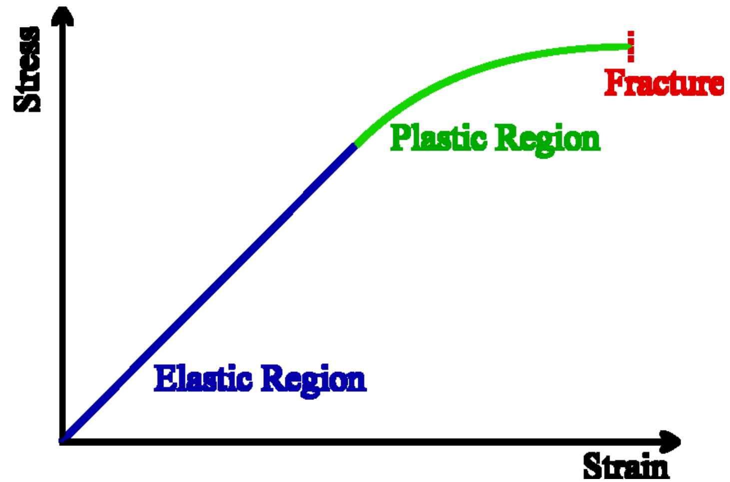


Factors affecting polymer properties

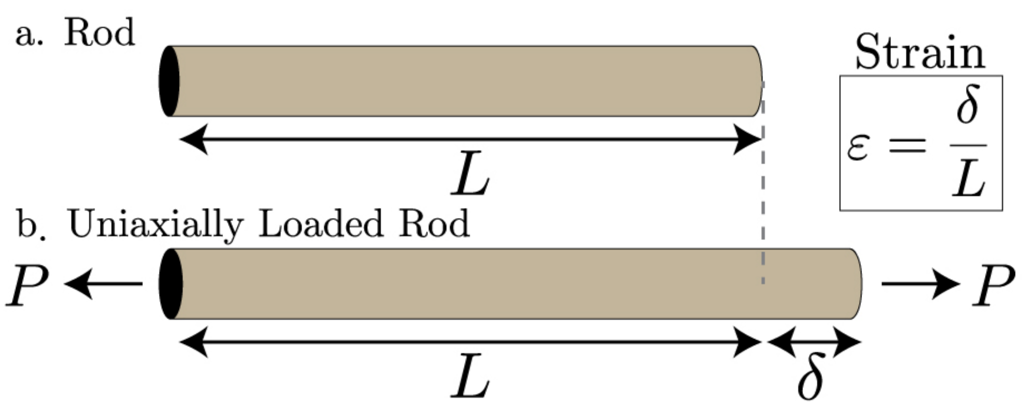
- Polymers are versatile materials because their properties can be tailored in a number of ways.
- For instance, <u>molecular weight</u>, <u>architecture</u>, <u>crosslinking</u>, and <u>composition</u> are some of the factors that can be modified to produce materials with different properties.

Mechanical strength

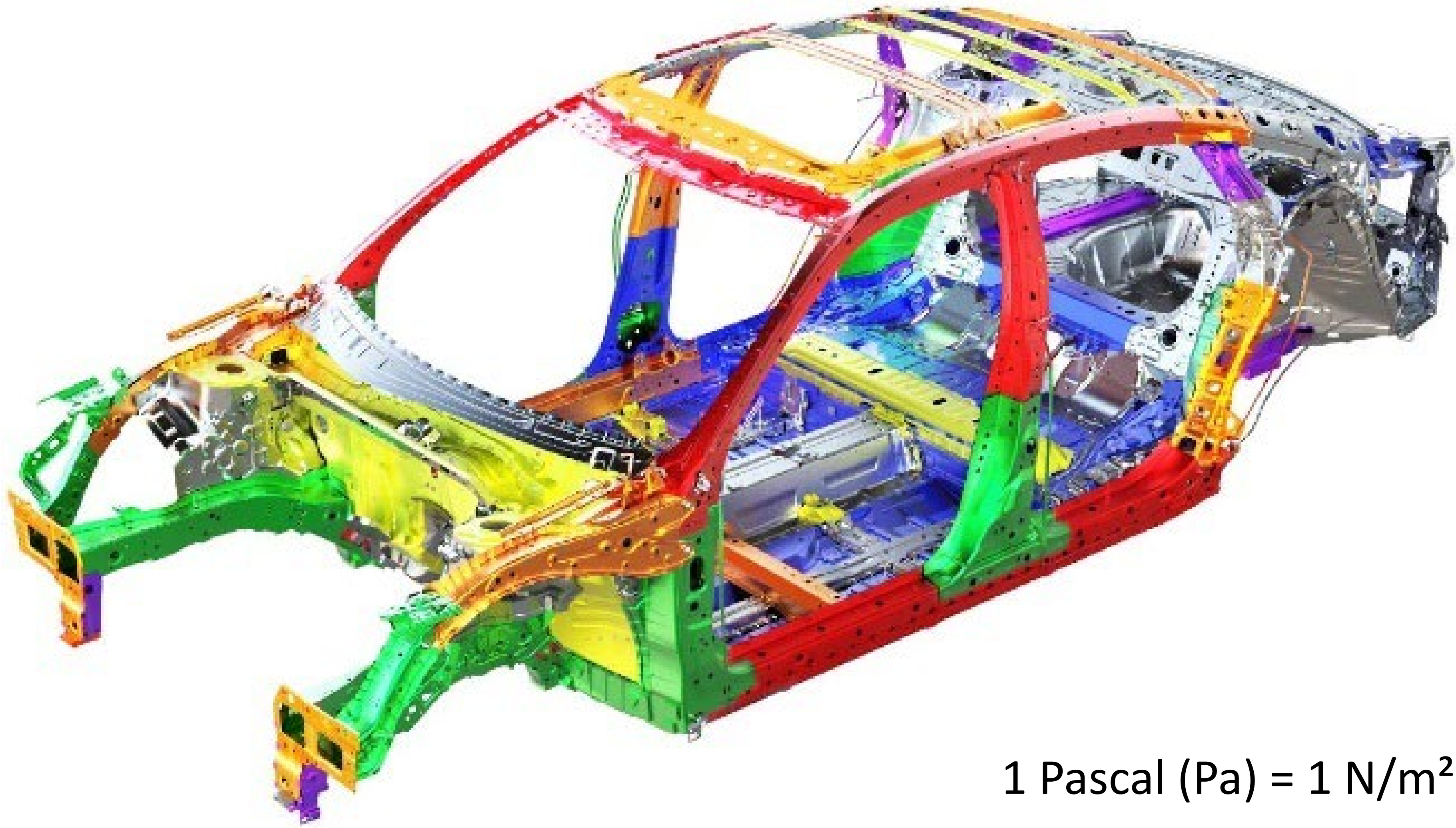
- Definition – the strength of a material is its ability to withstand an applied load <u>without plastic deformation</u>.



- Stress: force per unit area
- Strain: the ratio of the change in length to the original length



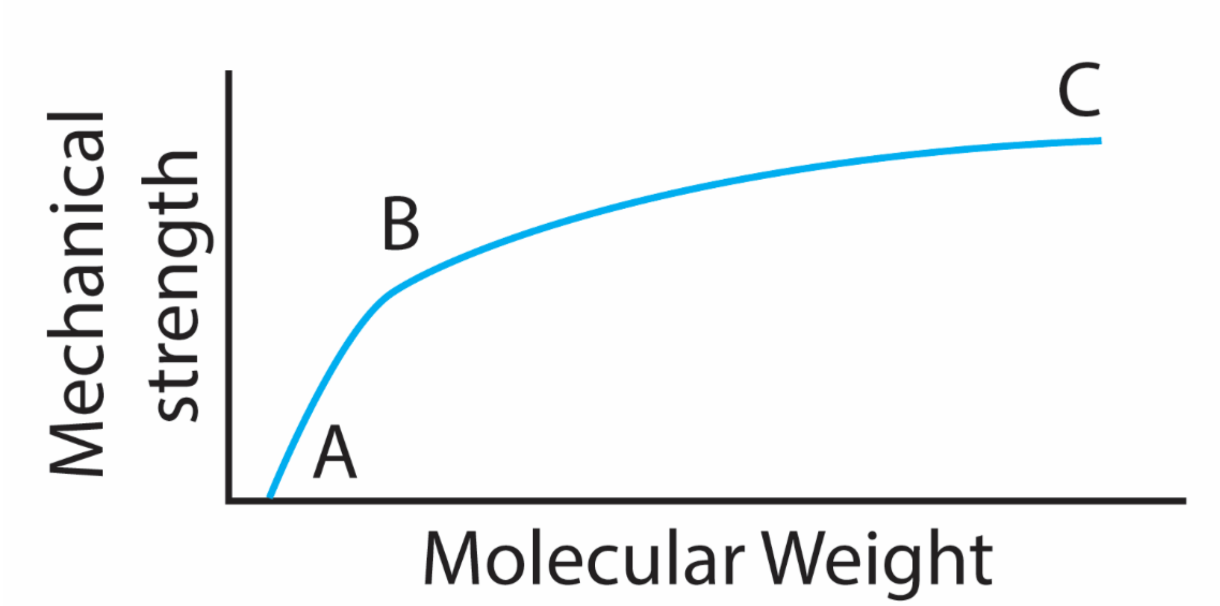
Steel Strength Used in Cars



$$1 \text{ Pascal (Pa)} = 1 \text{ N/m}^2$$

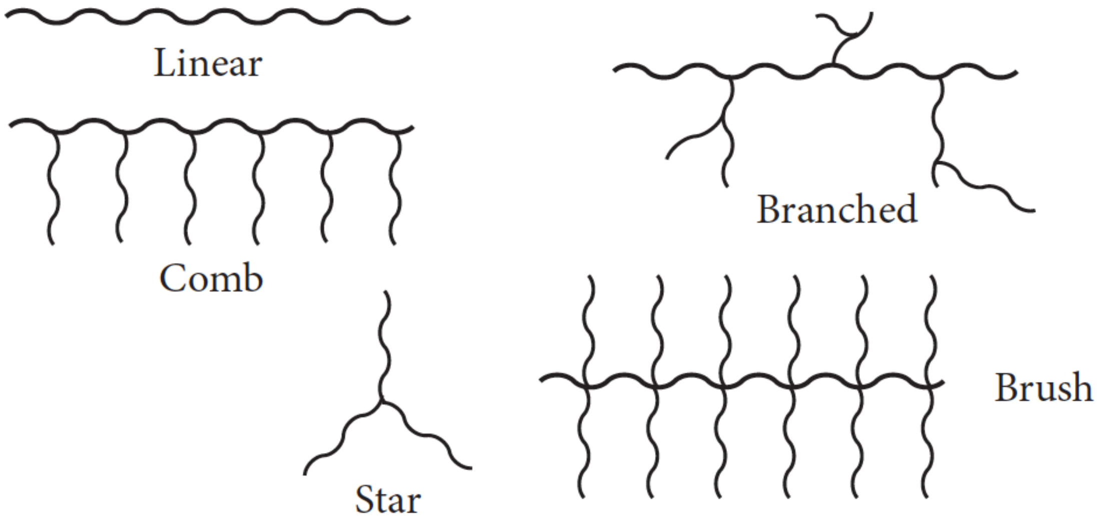
Molecular weight and mechanical strength

- When MW is below a certain point, the polymer has no mechanical strength.
- As MW increases beyond that point, mechanical strength increases rapidly (A-B).
- At a given chain length, the increase in MW does not significantly change the mechanical strength of the material.



Architecture

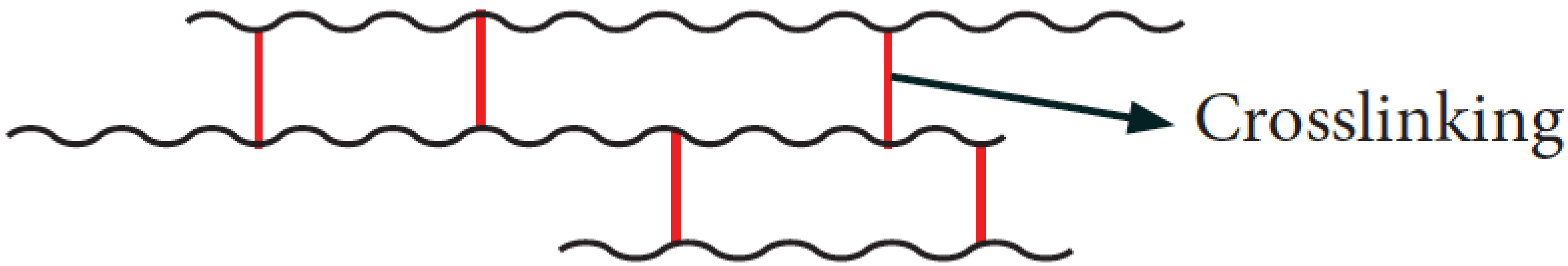
- Polymers are <u>not always linear</u>, they can also be branched.
- Branched polymers can have several architectures: star, comb or brush to name a few.



- Architecture can have significant effects on polymer properties.
- For instance, <u>branching</u> can enhance chain entanglement that leads to <u>increased viscosity</u>. A polymer's viscosity is important for polymer processing.

Crosslinking

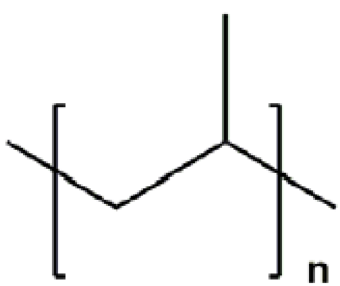
- When two or more polymer chains are connected via covalent bonds the chains are said to be crosslinked.
- The molecular weight of a cross-linked polymer is very high.



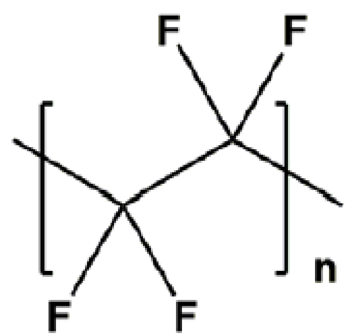
- Crosslinking has marked effects on a polymer’s properties. It improves mechanical strength and increases thermal stability.
- The reversibility of **elastomers** is due to “light” (occasional) crosslinking between the polymer chains.

Composition

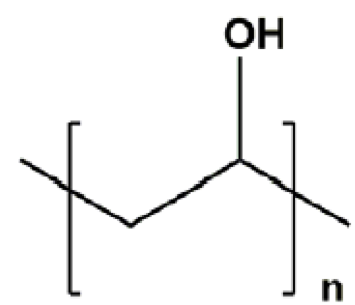
- The identity of the monomer will also greatly impact the properties of the polymer.
- For example, polymers with CH_3 or F side chains are hydrophobic whereas polymers with OH groups are hydrophilic.



Polypropylene
(Hydrophobic)

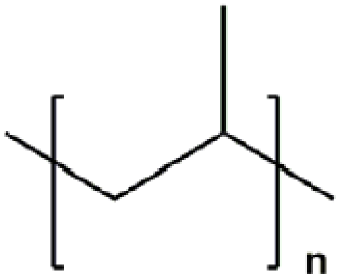


Teflon
(Hydrophobic)

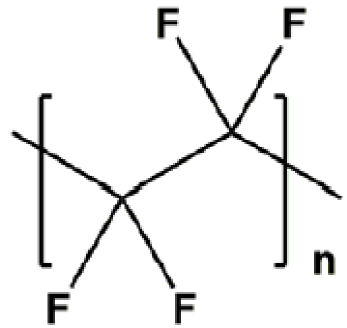


Poly(vinyl alcohol)
(Hydrophilic)

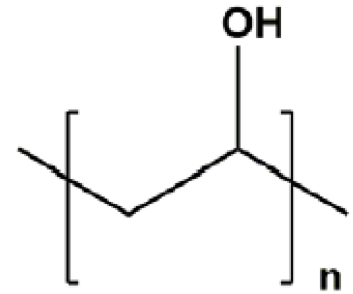
Composition



Polypropylene
(Hydrophobic)



Teflon
(Hydrophobic)



Poly(vinyl alcohol)
(Hydrophilic)

- heat-resistant
- resistant to acids
- high strength

water-soluble

Detergent pods

Entropic elasticity

- Glass transition- a physical transformation at its glass transition temperature (T_g), where the polymer change from a hard, rigid, glassy state to a softer, more flexible, rubbery state, or vice versa.

T_g (glass transition)

Change in physical properties but not a true phase transition

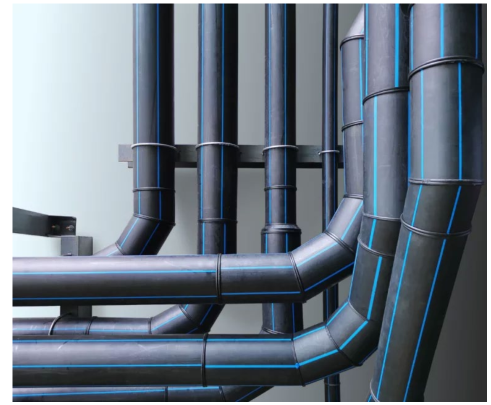
$T<T_g$	$T>T_g$
hard, brittle (but amorphous) state	soft, gummy, elastic (but still solid) state
eg. Lexan, HDPE, hard candy	eg. rubber band, gummy worm
High degree of structural order (eg. crystalline domains) or extensive cross-linking: strong & stiff	Low degree of order…

Examples of Glass Transition

- **Summer Tires**: Have a T_g around 5-10 °C, making them suitable for warmer weather but performing poorly in cold conditions.
- **Winter Tires**: Are engineered with a much lower T_g, around -50 °C, staying flexible and maintain grip in the winter.

HDPE vs LDPE

- HDPE (high-density polyethylene)



- LDPE (Low-density polyethylene)


HDPE vs. LDPE

	HDPE (#2 plastic)	LDPE (#4 plastic)
Structure	Linear	Branched
Uses	Hard hats, bottle caps, Nalgene bottles (semi-opaque)	Plastic wrap, snap-on lids, 6-pack rings
Young's modulus	600-1400 MPa	200-400 MPa
Chemical formula	$(CH_2)_n$	$(CH_2)_n$
Synthetic method	Metal catalyst (e.g. Ziegler-Natta)	Radical/addition polymerization

HDPE: high-density polyethylene

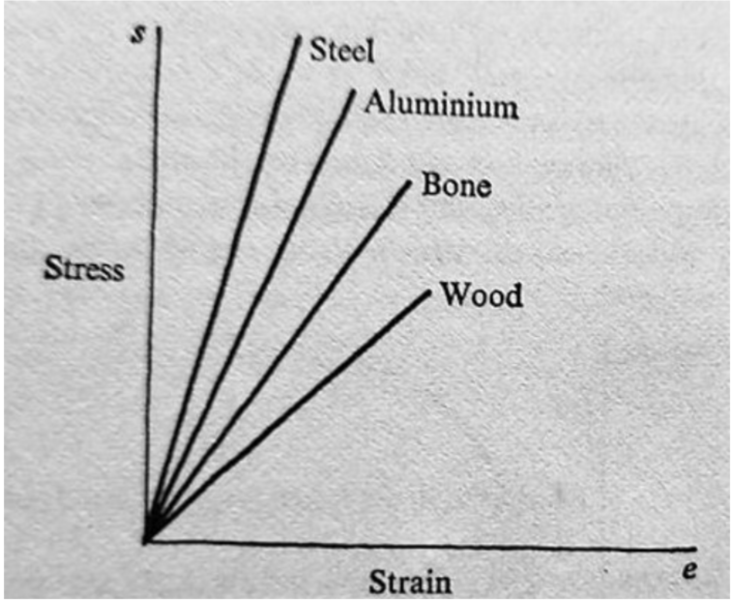
Young's modulus

- Definition:

$$E = \frac{\sigma}{\epsilon}$$

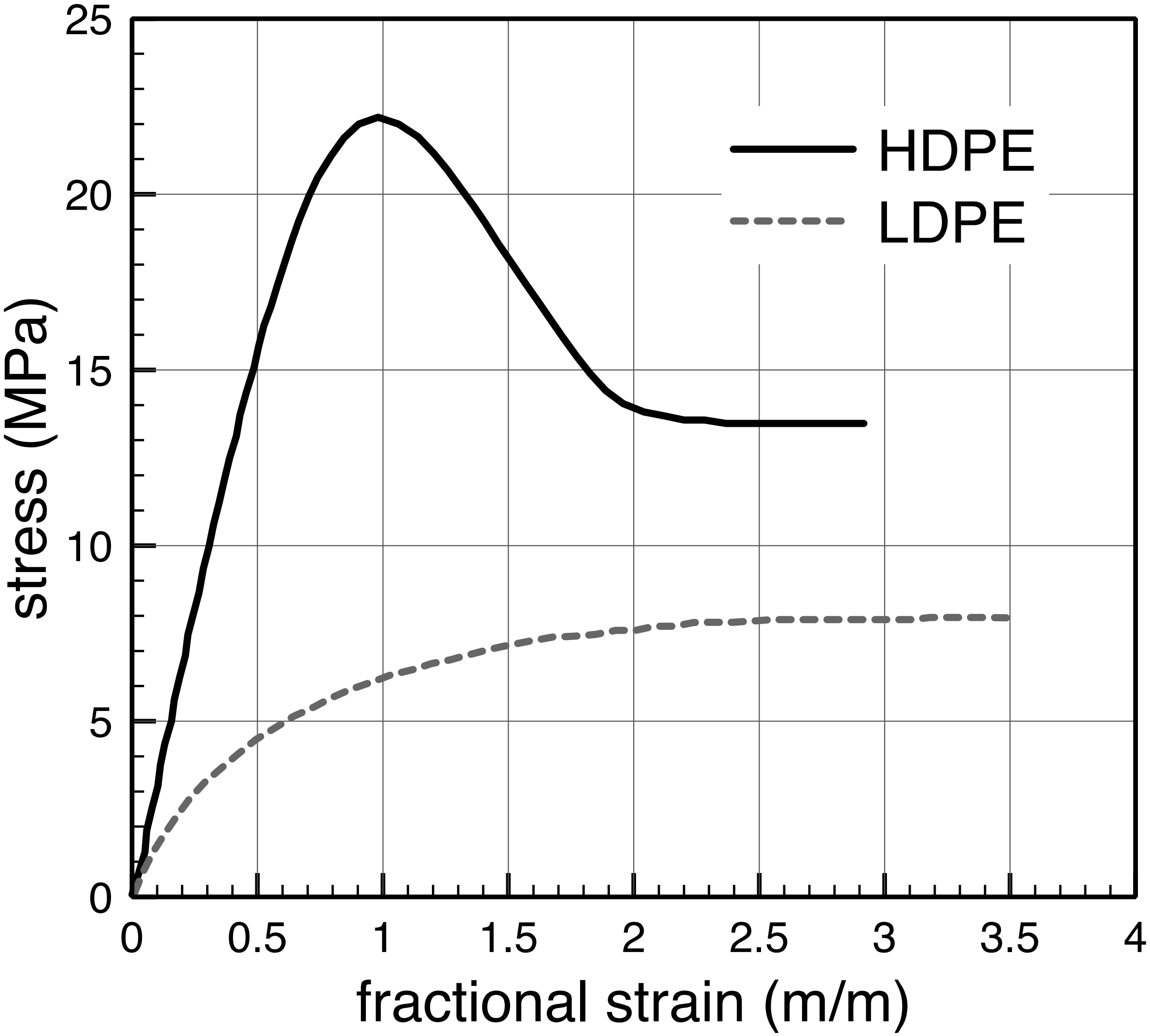
σ is stress (force per unit area)

ϵ is strain (proportional deformation)



	Young's Modulus ($\times 10^9$ Pa)
cotton	5
leather	0.22
brass	110
copper	130
lead	14
nylon	1.8
Brick	28
Concrete	24
Diamond	11,000
Pine	13, 1.2
natural rubber	0.0019

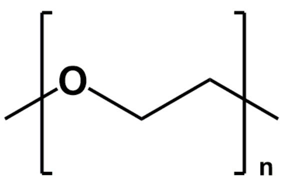
HDPE vs. LDPE



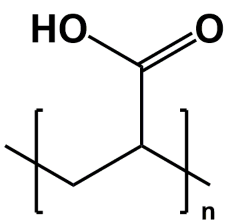
HDPE
LDPE
stress (MPa)
fractional strain (m/m)
0
5
10
15
20
25
0
0.5
1
1.5
2
2.5
3
3.5
4

Worksheet Question #9 – GOOD QUESTION

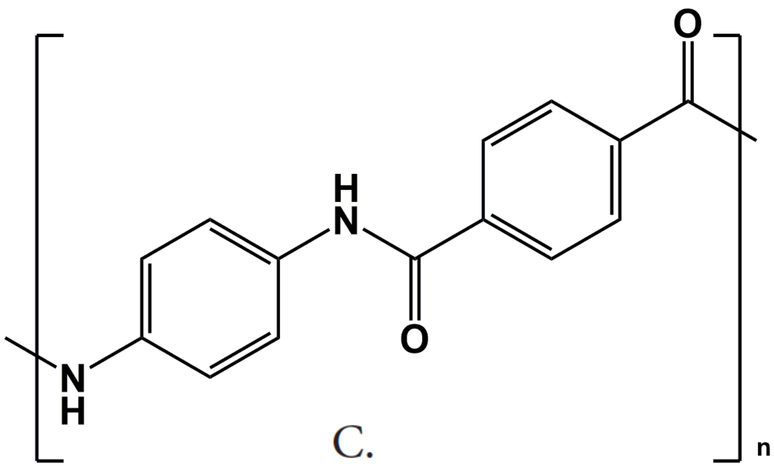
Rank the following polymers in terms of <u>increasing flexibility</u>. Explain your reasoning.



A.
polyethylene glycol
(PEG)



B.
polyacrylic acid
(PAA)



C.
Kevlar

A) A < B < C

B) A < C < B

C) B < A < C

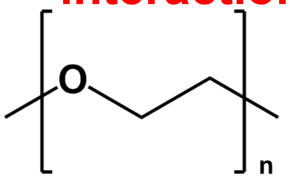
D) C < A < B

E) C < B < A

Worksheet Question #9 – GOOD QUESTION

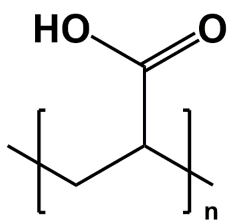
Rank the following polymers in terms of <u>increasing flexibility</u>. Explain your reasoning.

London dispersion interactions



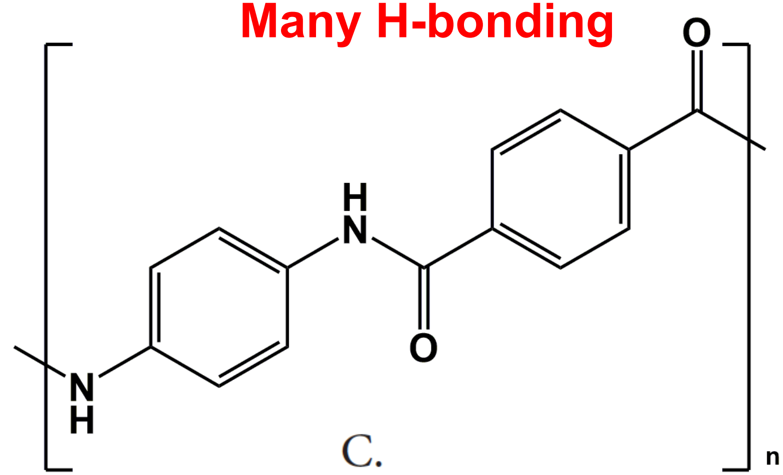
A.
polyethylene glycol
(PEG)

H-bonding



B.
polyacrylic acid
(PAA)

Many H-bonding



C.
Kevlar

A) A < B < C

B) A < C < B

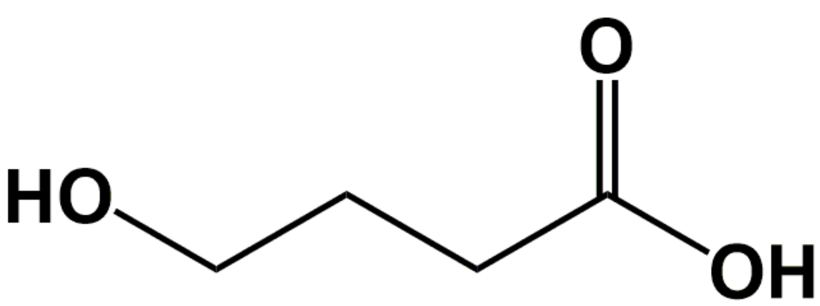
C) B < A < C

D) C < A < B

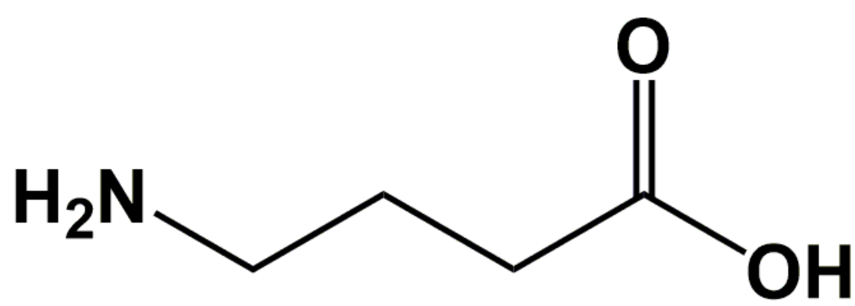
E) C < B < A

Worksheet Question #10 – GOOD QUESTION

Which of the following monomers (A or B) produces a polymer with the highest melting point? Briefly explain your reasoning. Assume the molecular weight of the resulting polymer is the same.



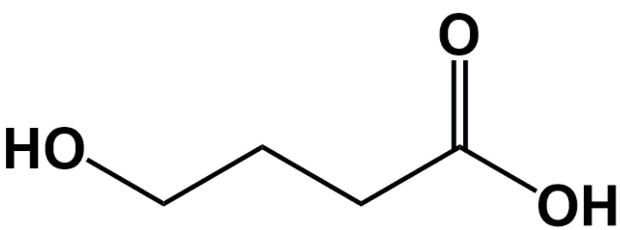
A.



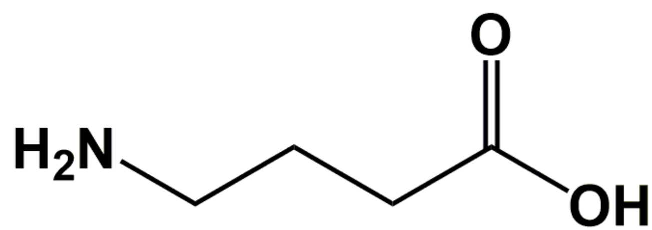
B.

Worksheet Question #10 – GOOD QUESTION

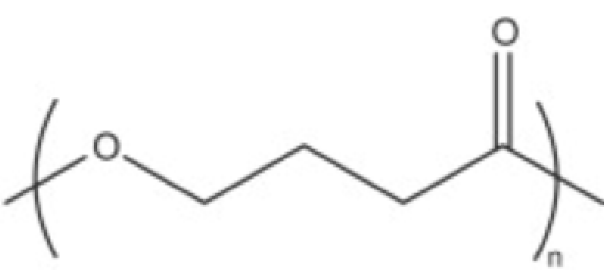
Which of the following monomers (A or B) produces a polymer with the highest melting point? Briefly explain your reasoning. Assume the molecular weight of the resulting polymer is the same.



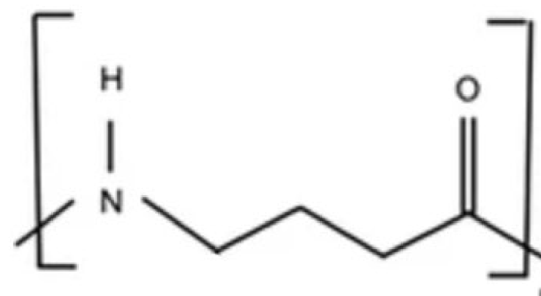
A.



B.



ester linkage

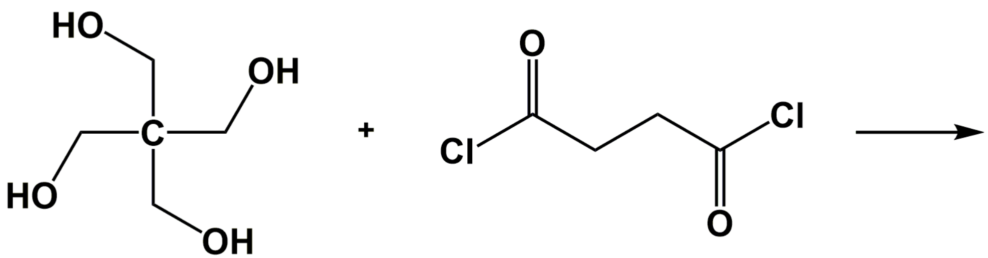


amide linkage (form H-bonds)

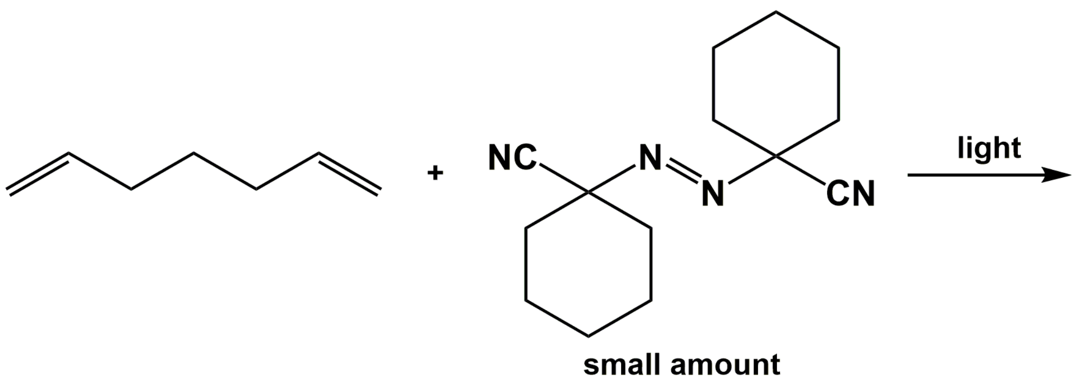
Worksheet Question #11 – GOOD QUESTION

Which of the following reactions produces a branched polymer?

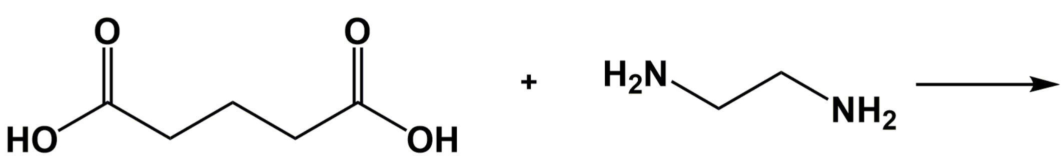
A.



B.



C.



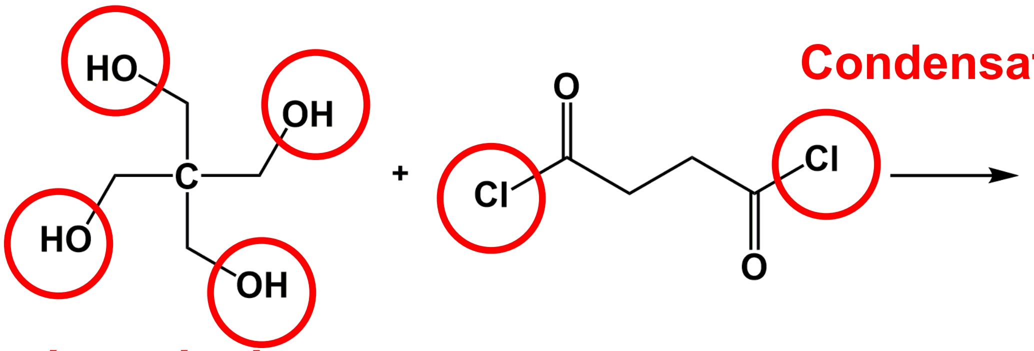
D. Both A + B

E. Both A + C

Worksheet Question #11 – GOOD QUESTION

Which of the following reactions produces a branched polymer?

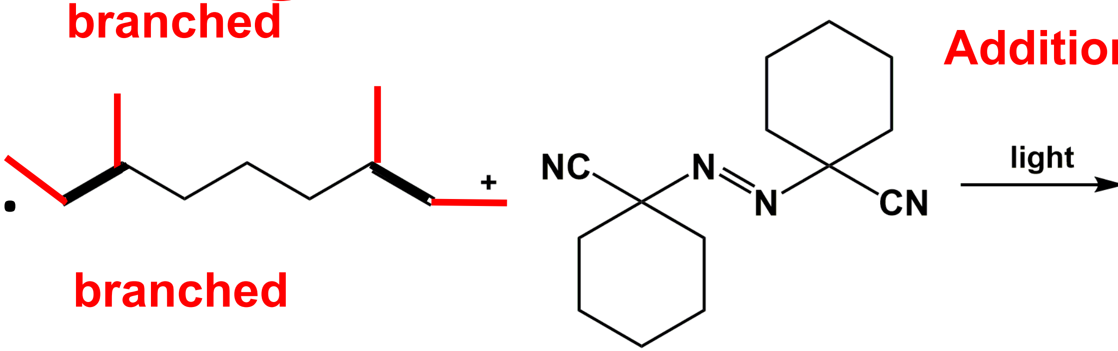
Condensation

A. 

branched

D. Both A + B

Addition

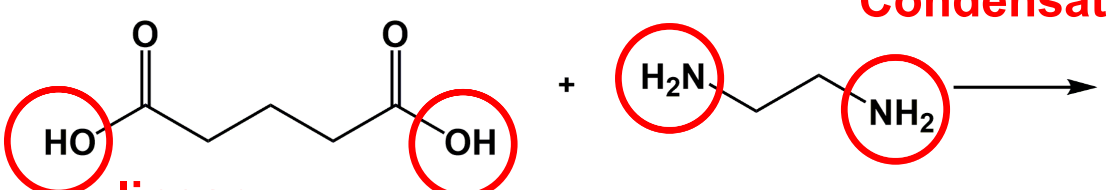
B. 

small amount

branched

E. Both A + C

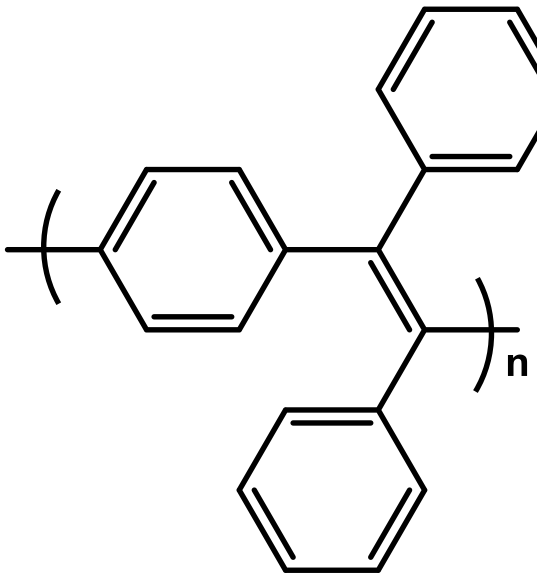
Condensation

C. 

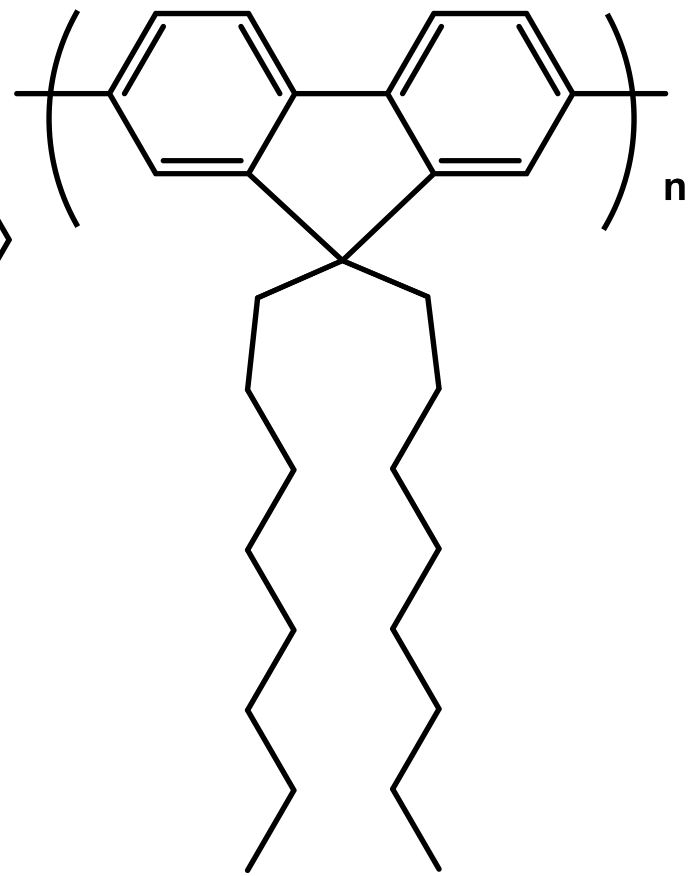
linear

Special monomer properties

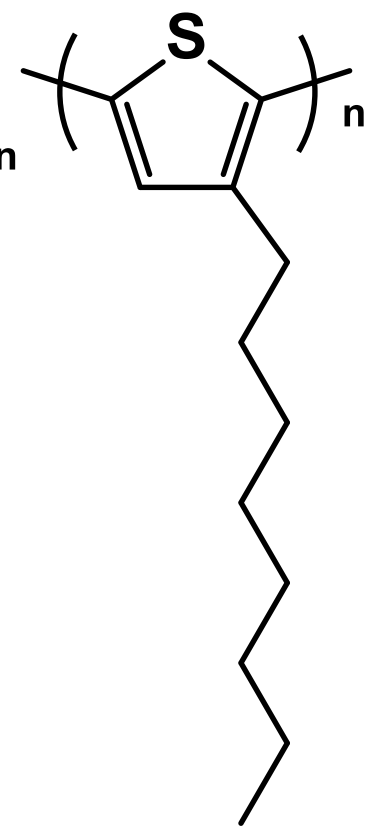
Polymer light emitting diodes (PLEDs) can be used for bendable screens.



Green



Blue



Red

Blueprint question

LDPE

HDPE

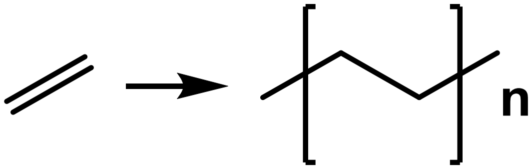
Kevlar

Nylon

What factors need to be considered when designing polymers for various applications?

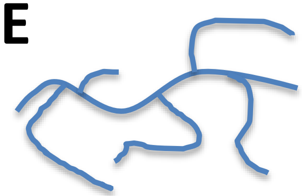
http://toyworth.com/browse/action/figure/Star/Wars/89/1979/Accessories/Millennium/Falcon.html
https://www.boiseweekly.com/CityDesk/archives/2015/03/24/video-north-idaho-pranksters-stretching-saran-wrap-across-highway
https://www.acparadise.com/acp/display.php?c=71400 https://sites.google.com/site/carloswilson291126/kevlar
http://www.jotun.com/ww/en/b2b/paintsandcoatings/chemical-plants/

Blueprint question

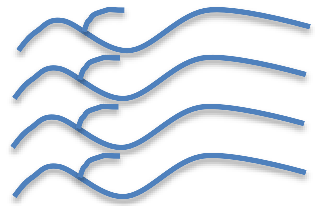


Same monomer,
different properties

Low- density polyethylene
LDPE



High-density polyethylene
HDPE



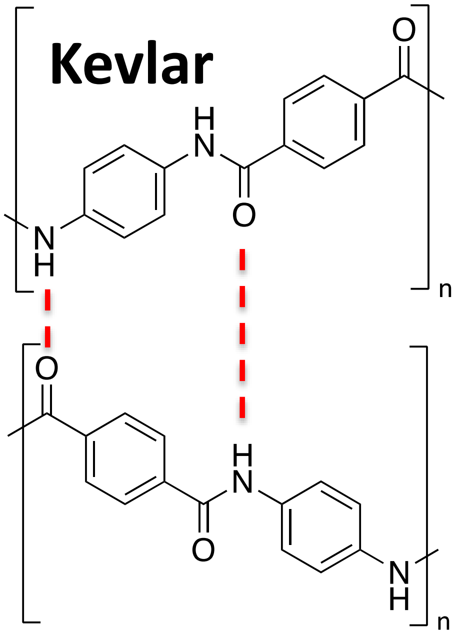
Branched structure
- Inefficient packing
- Flexible

Linear structure
- Efficient packing
- Strong but less flexible (LDFs)

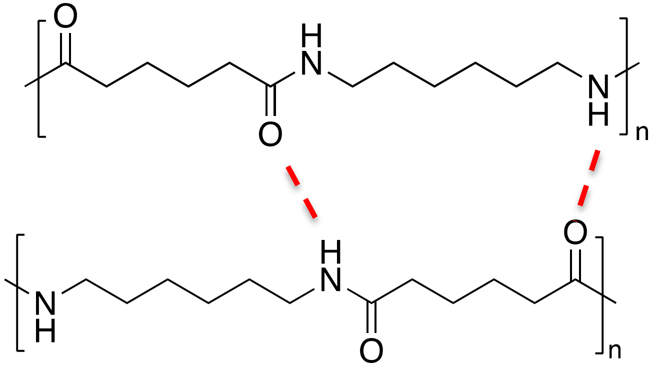
Thermoplastics, processed using injection molding or thermoforming

Blueprint question

Kevlar



Nylon



Not bulletproof

Kevlar has high strength but less elasticity → More H-bonding interactions and LDFs.

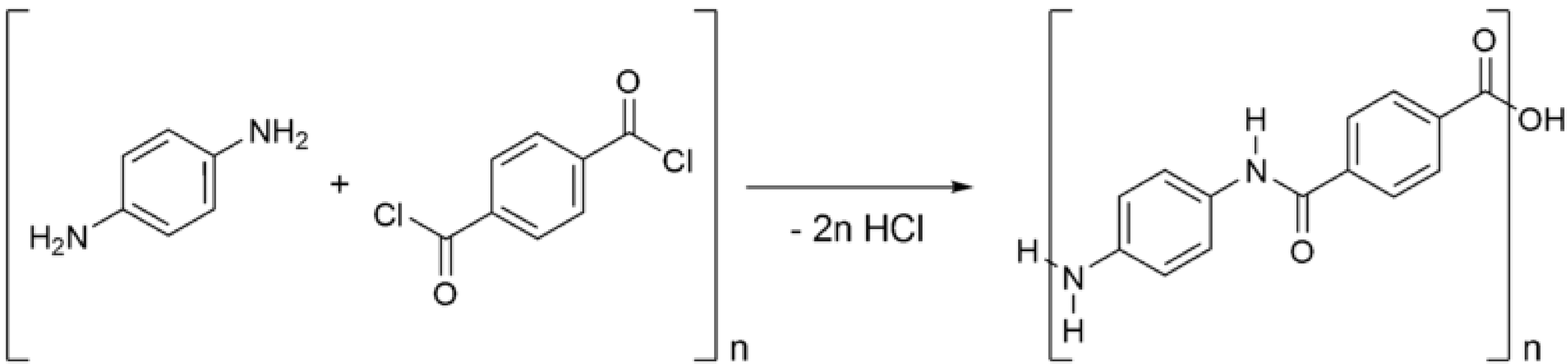
Both Nylon and Kevlar are spun into fibres that are woven into fabrics

Kevlar synthesis

condensation reaction:

poly paraphenylene terephthalamide
a.k.a Kevlar

terephthaloyl chloride

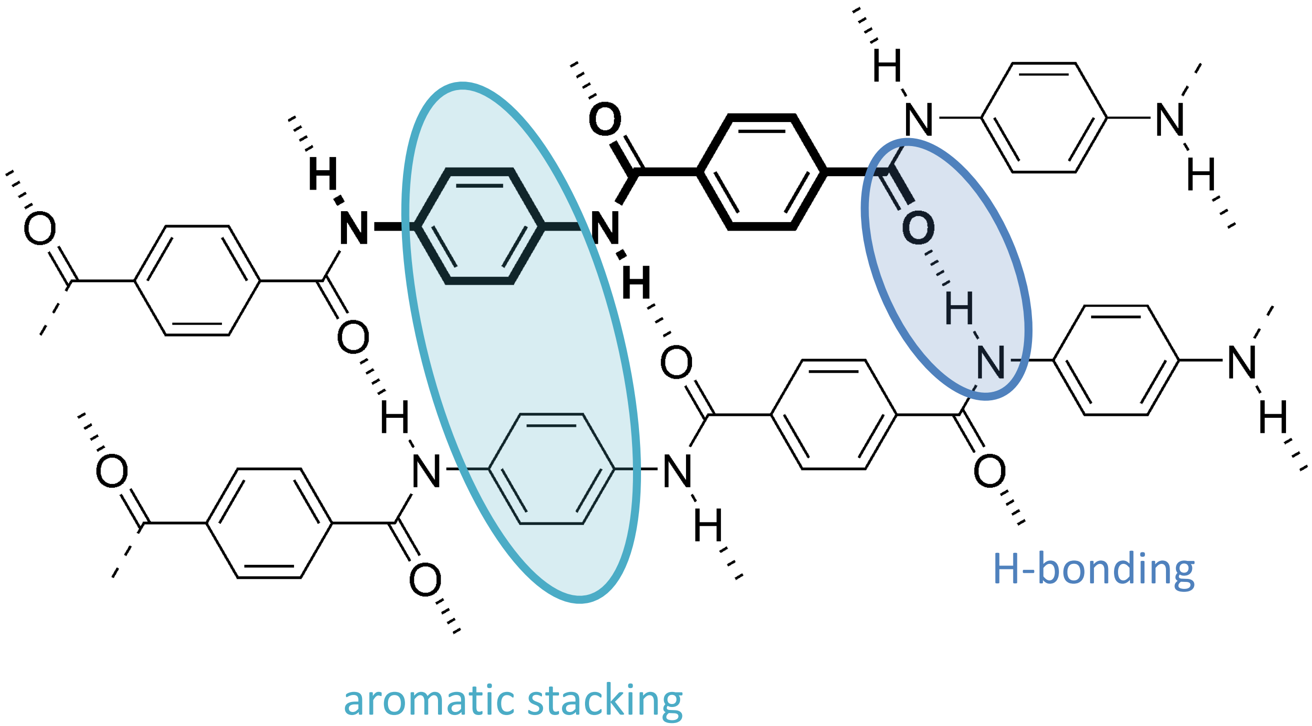


1,4-phenylene-diamine (para-phenylenediamine)

soluble in sulfuric acid

Kevlar (para-aramid synthetic fiber)

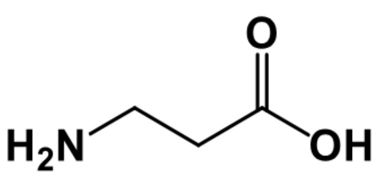
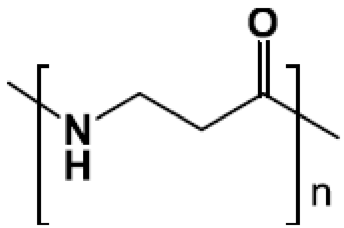
Strength from many interchain bonds…



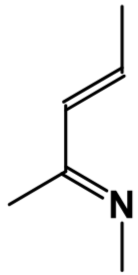
polymer strands are oriented along fiber direction during spinning

Worksheet Question #7

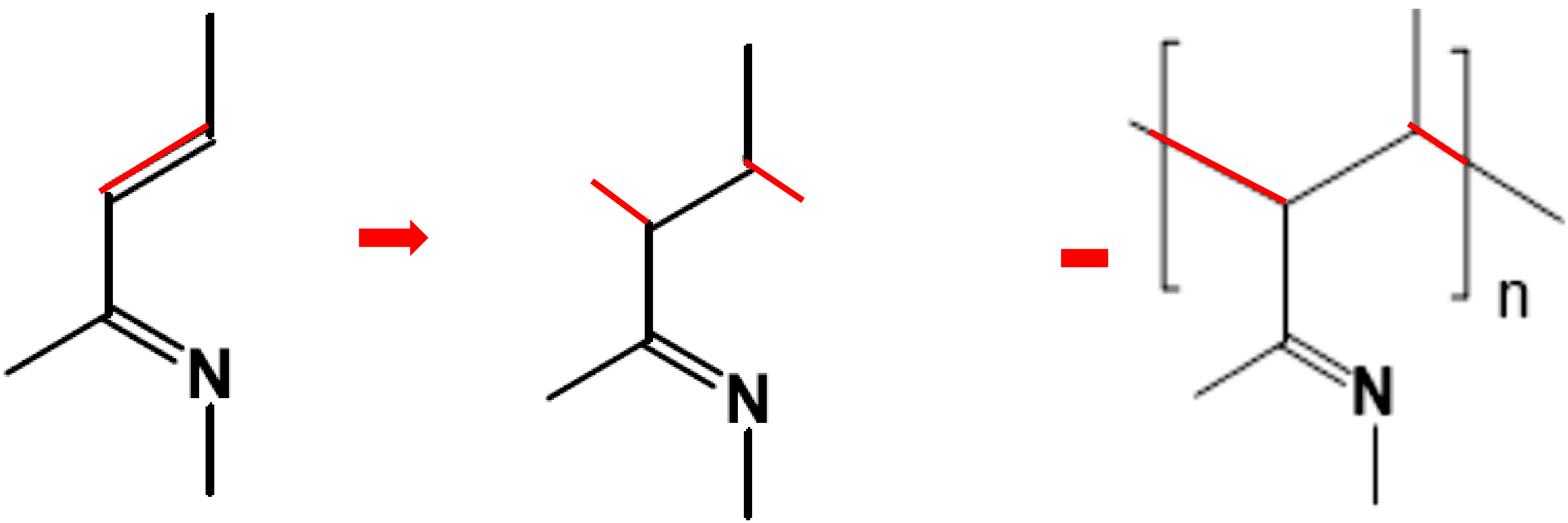
- Fill in the blanks in the table below by drawing the polymer or smallest possible monomer.
- Classify each polymer as a condensation or addition polymer by circling the correct option.
- Name the type of linkage.

Monomer	Polymer	Type of Polymerization
		Addition Condensation
		Type of linkage:

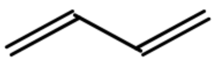
Worksheet Question #7

Monomer	Polymer	Type of Polymerization
		Addition Condensation
		Type of linkage:

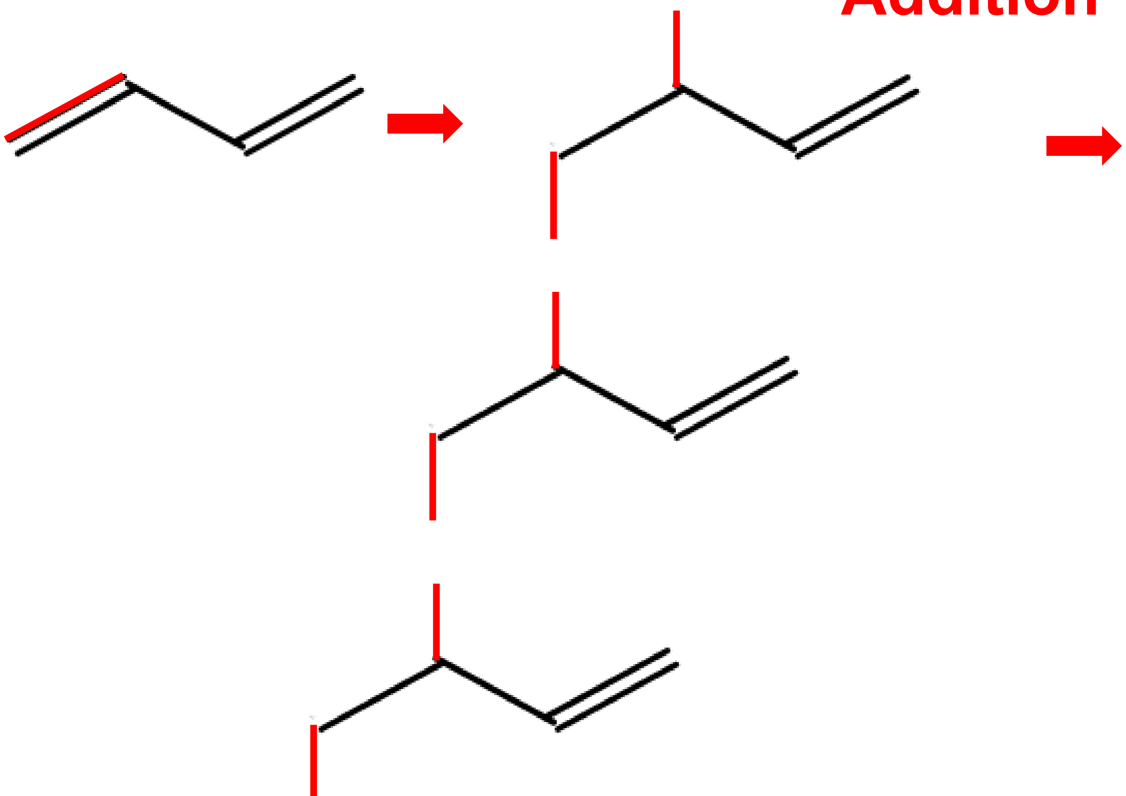
Addition carbon-carbon



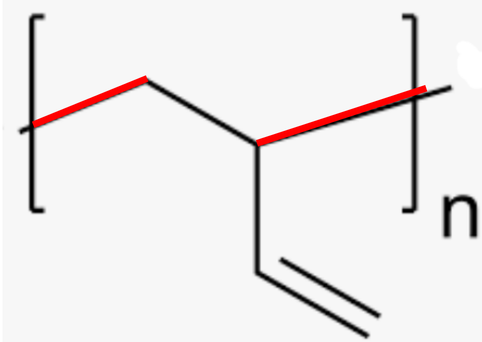
Worksheet Question #7

Monomer(s)	Polymer	Type of Polymerization
Challenge: 		Addition Condensation Type of linkage:

Addition

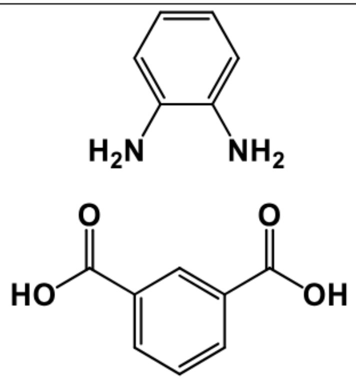


carbon-carbon



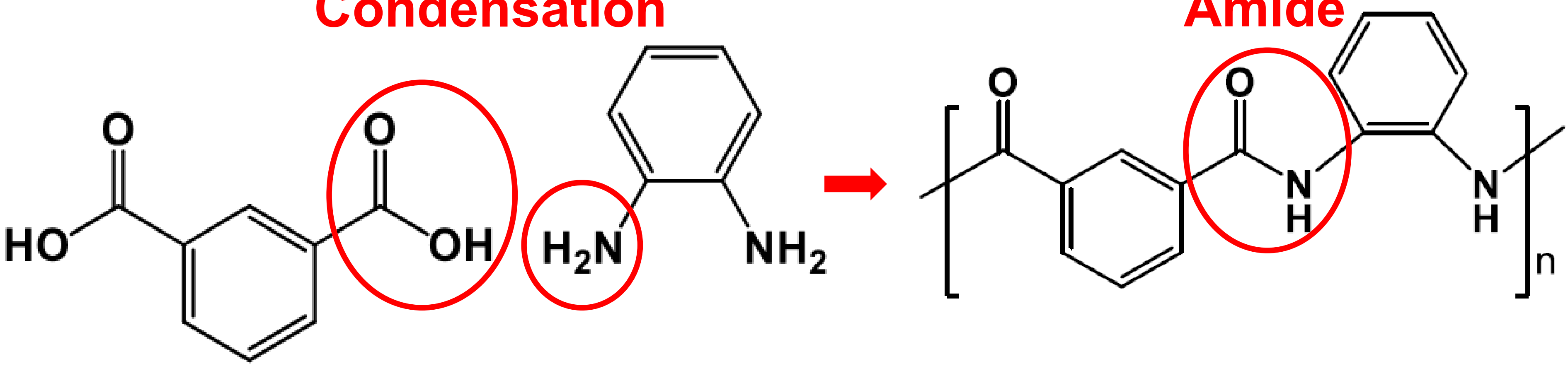
and more possibilities!

Worksheet Question #7

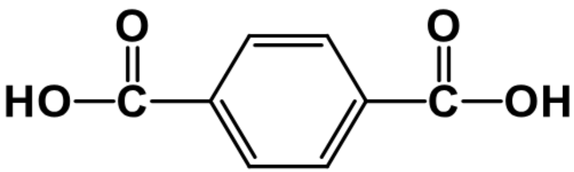
Monomer(s)	Polymer	Type of Polymerization
		Addition Condensation Type of linkage:

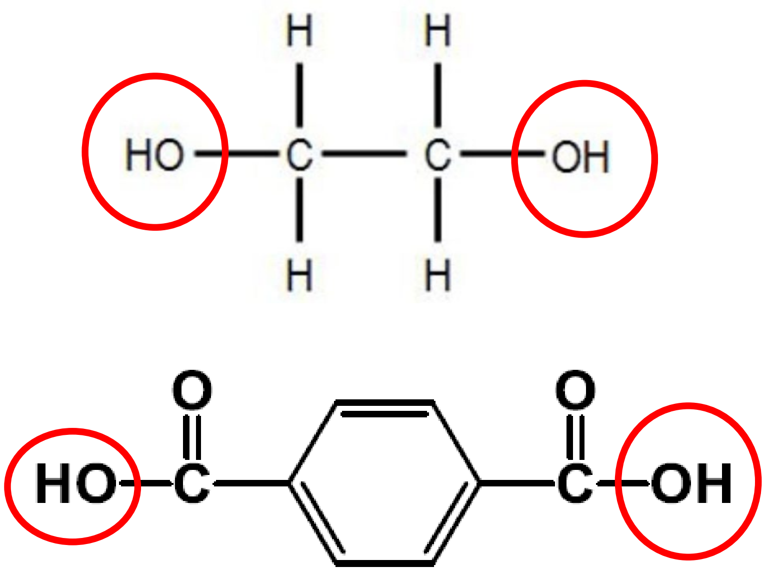
Condensation

Amide



Worksheet Question #7

Monomer(s)	Polymer	Type of Polymerization
$HOCH_2CH_2OH$ 		Addition Condensation Type of linkage:



Condensation

Ester