Polymers: Essential Background and Definitions

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Please review the Instructor Document for detailed notes for each slide.

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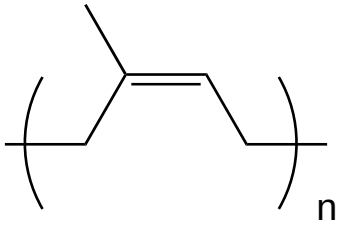
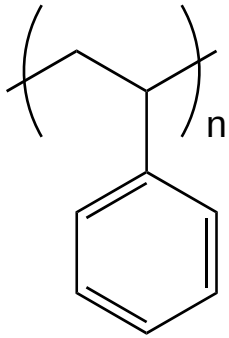
- Polymer properties (slides 9-11)
- Polymer topology (slides 12-13)
- Examples of uses/everyday polymers (14-18)

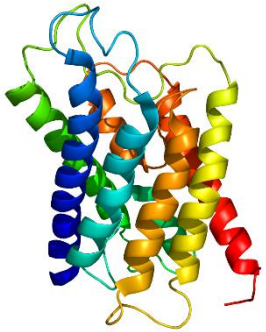
Polymers Compared to Small Molecules

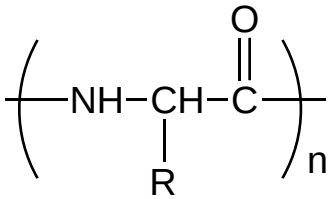


Rubber

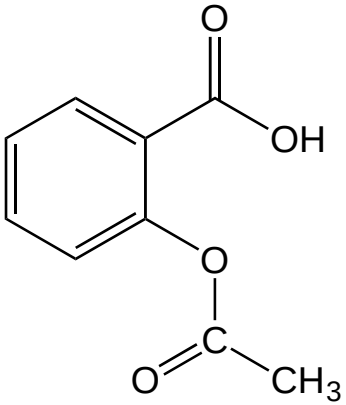


Styrofoam



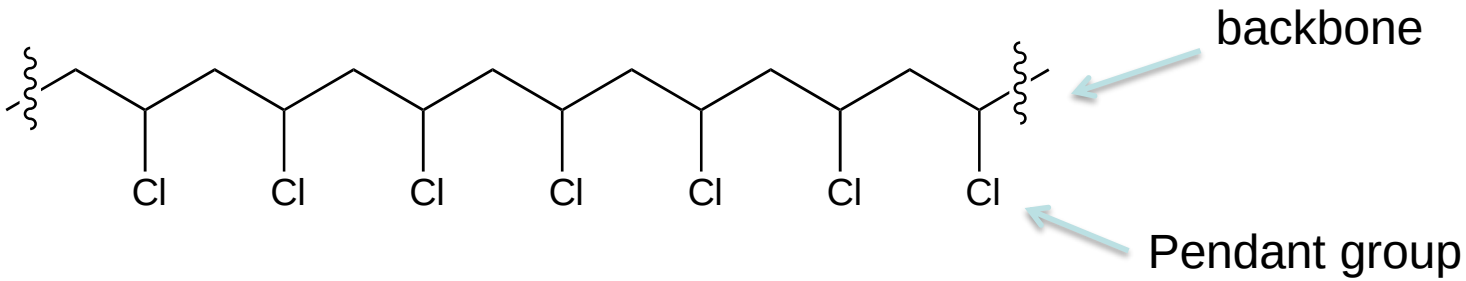


Polypeptide



Aspirin

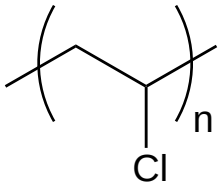
The Repeat Unit



Segment of poly(vinyl chloride)

Polymers may have hundreds to thousands of repeat units, making drawing the entire molecule an impossibility.

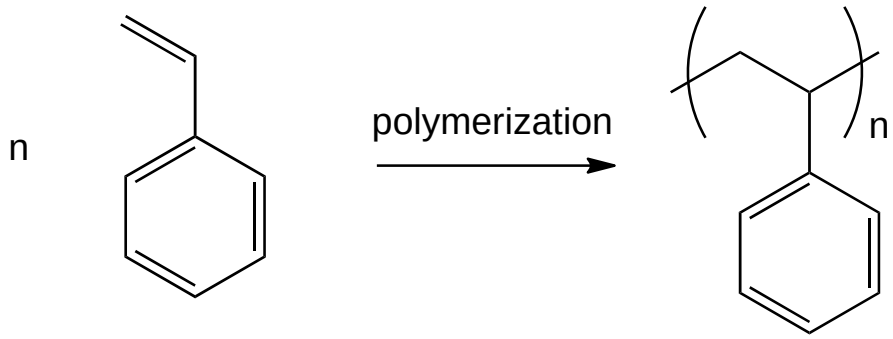
Polymer chemists take advantage of the repetitive structure, or repeat unit, and draw this:



Repeat unit of poly(vinyl chloride)

Note: End groups are usually omitted, and “n” is often used to show the non-uniformity of chain lengths

Major Classes of Polymers

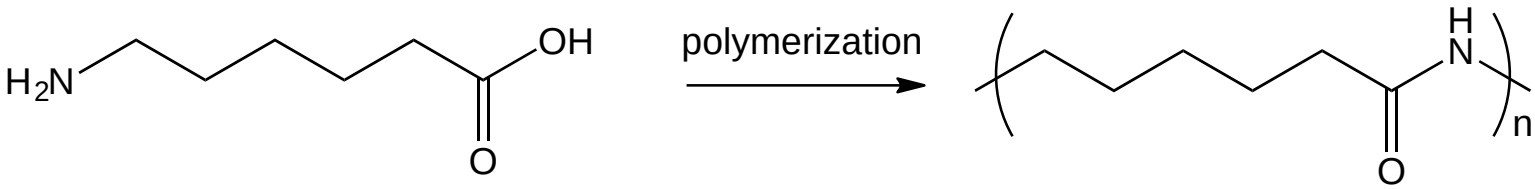


vinyl monomer

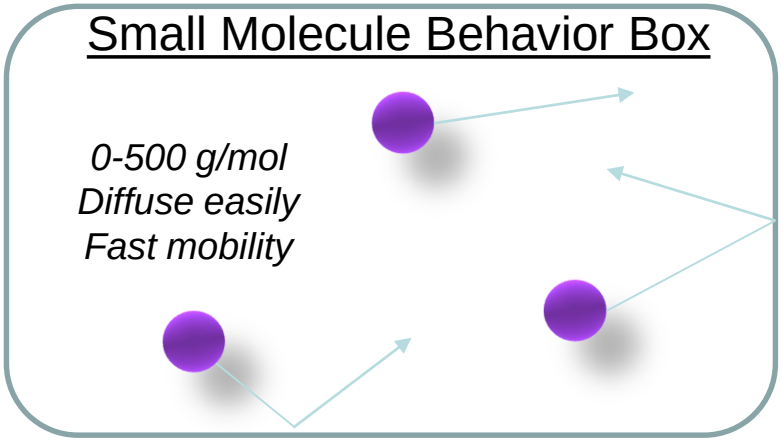
vinyl polymer

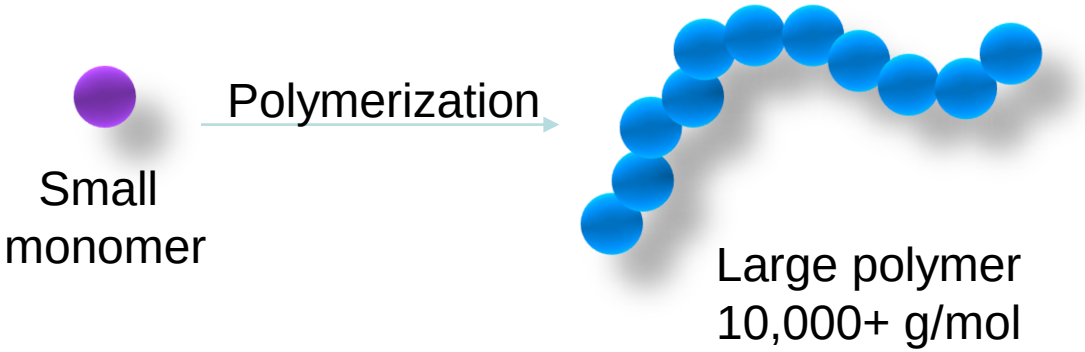
Vinyl polymers are commonly used plastics. High molecular weights are needed to achieve useful commercial properties

Condensation polymers are commonly used as fibers, for example in clothing. Functional groups in the backbone make these polymers more rigid and useful at lower molecular weights.

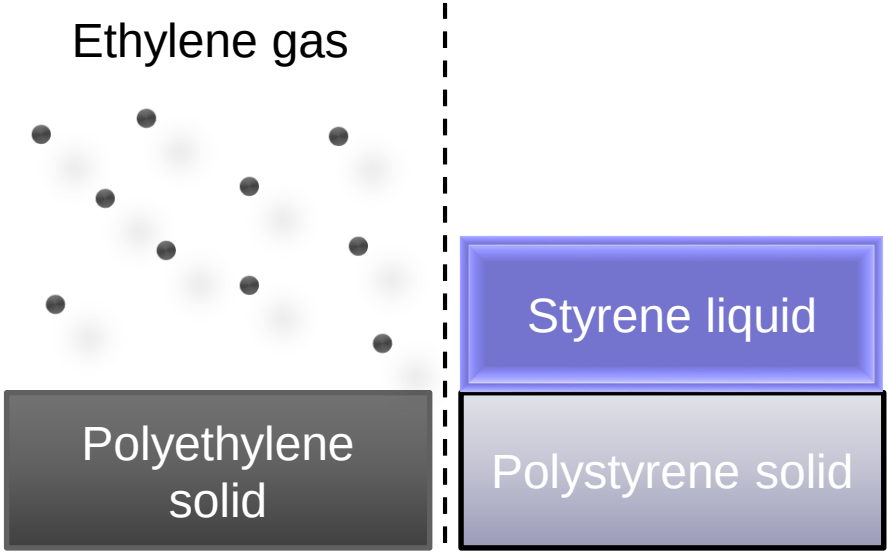


Polymers are large and slow



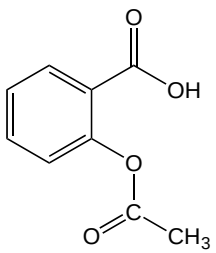


Under ambient conditions:

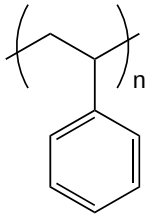


- Monomers can be liquids or gases
- Polymers tend to move slowly than small molecules
- Polymers dissolve more slowly in solvents
- Polymers possess “memory” of previous shapes

Molecular Weight



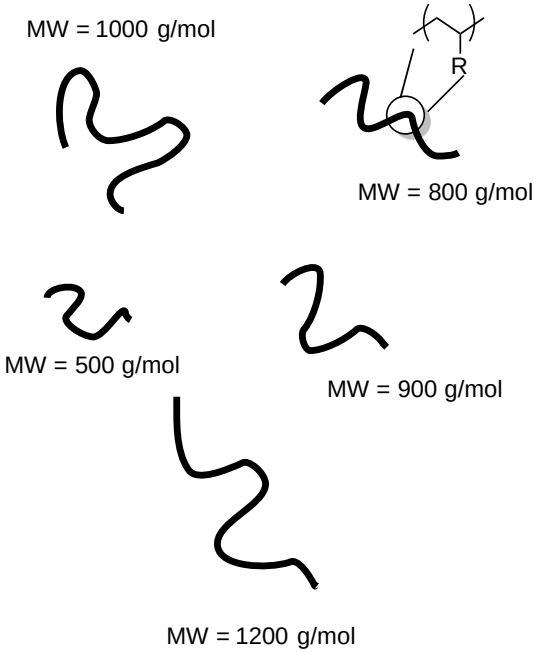
All molecules of aspirin (acetylsalicylic acid) have a molar mass of 180.157 g/mol. This is true regardless of how or where you synthesized the aspirin.



A sample of polystyrene is made up of molecules with a variety of molecular weights.

Key point: *There is no universal "molecular weight" that applies to all molecules of polystyrene or other synthetic polymers.*

Molecular Weight and Dispersity



A sample of polymer chains will have a variety of molecular weights. The molecular weight of the sample is expressed as an "average" molecular weight.

The <u>Dispersity</u> of a polymer sample is a measure of the extent of this variety.

<u>2 main ways to express the average molecular weight (MW):</u>

Number average MW (M_n) = $\frac{\Sigma N_x M_x}{\Sigma N_x}$

Weight average MW (M_w) = $\frac{\Sigma N_x M_x^2}{\Sigma N_x M_x}$

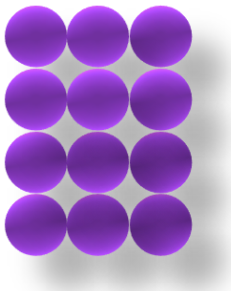
N_x = # of molecules having a mass of M_x

So, the sample of polymer chains above would have an M_n of 880 g/mol and an M_w of 941 g/mol .

The ratio of these two describes the dispersity of the sample: 1.07 (M_w / M_n)

Polymers may be *semi*crystalline

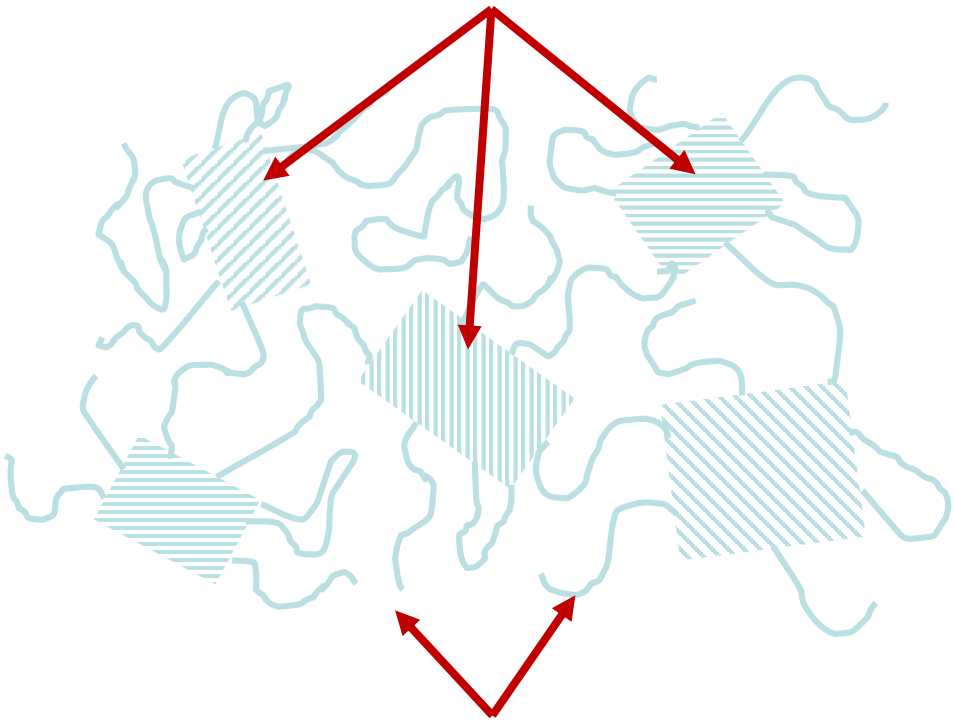
Small Molecule Behavior Box



Well-ordered, crystalline, solid

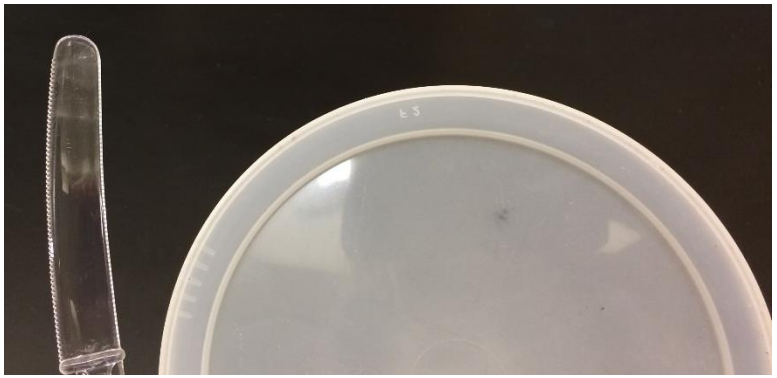
Polymers only *partially* crystallize in the solid state, resulting in polymer *crystallites* surrounded by *amorphous* solid polymer. Some polymers are entirely amorphous and do not crystallize.

Ordered polymer crystallites



Disordered amorphous polymer

Polymer crystals scatter light, making crystalline polymers appear opaque (right) and amorphous polymers appear transparent (left).



The Glass Transition (T_g)

Small Molecule Behavior Box

Ordered crystalline solid melts and freezes

H_2O *(s)* ↔ H_2O *(l)*

T_g applies to the *amorphous portion* of the solid polymer.

Polymer *(s, glass)* ↔ Polymer *(s, rubber)*

Each polymer has its own T_g, just like each small molecule has its own T_m.

Temperature

Above T_g: Polymer is soft and rubbery

T_g

Below T_g: Polymer is hard, brittle, and glassy

Polymer	T_g (°C)	At 25 °C:
Rayon™	157	glassy
Polystyrene	100	glassy
PET soda bottle	69	glassy
Teflon™	-113	rubbery
Silicone rubber	-123	rubbery
Plastic trash bag	-125	rubbery

Polymers are *viscoelastic*

Small Molecule Behavior Box

Under shear (sliding force), a solid stretches like a spring, and a liquid flows. All matter is either solid or liquid, never both.

Polymers are *large* and therefore *slow*, so depending on time scale and temperature they may behave -
more like a solid or *more like a liquid*.

Visco-elastic

"liquid-like" "solid-like"

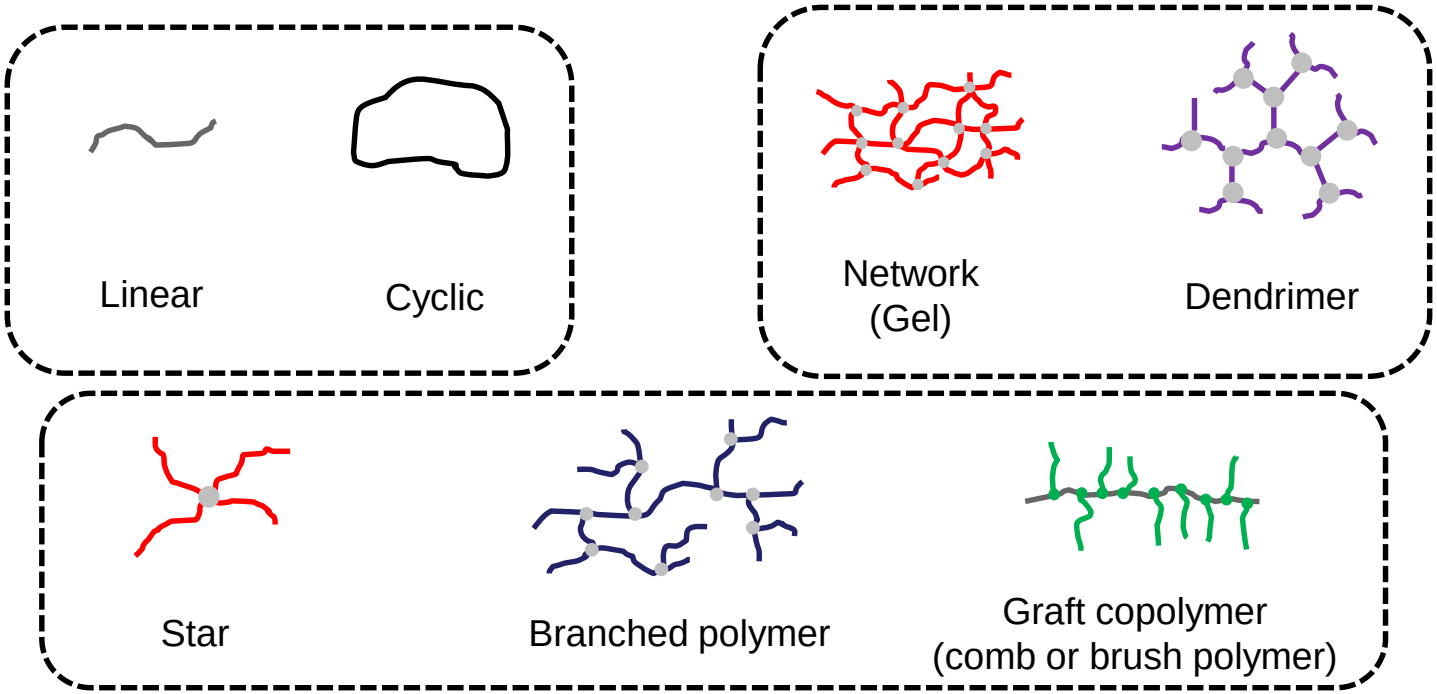
Fast Deformation or Low Temperature	Slow Deformation or High Temperature

• Reduced chain mobility
  • Fast deformation doesn't give chains time to relax and flow
  • Low temperatures freeze chains in place
• Polymer acts more "solid-like"
	• Increased chain mobility
	  • Slow deformation allows chains time to relax and flow
	  • High temperatures soften chains, letting them move
	• Polymer acts more "liquid-like"

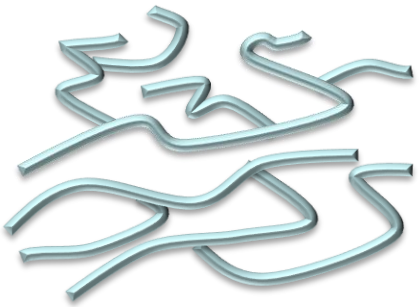
Topology of Polymers

The properties of synthetic polymers depend not only on their chemical composition, but also on their 3D architecture, or topology. Because polymers are long-chain molecules they can adopt a multitude of conformations which result in different properties.

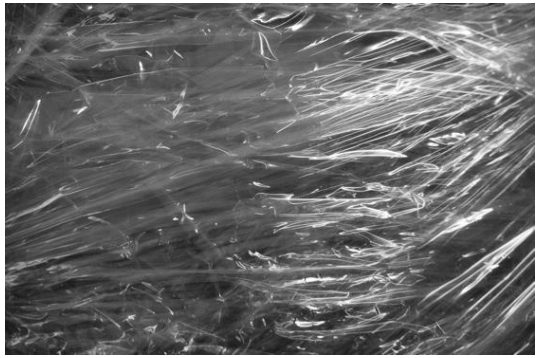
Examples of polymer topologies are:

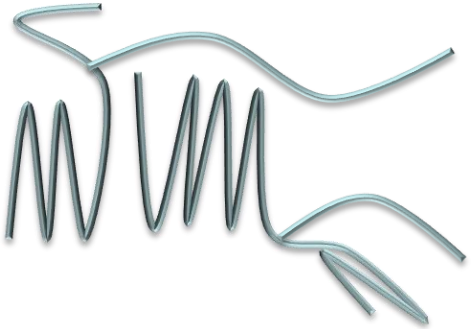


Topology

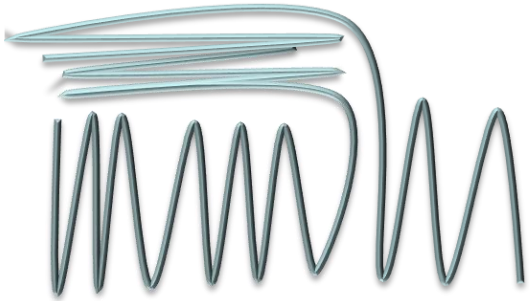


Low Density PE-Branched
Plastic wrap, 6 pack rings etc.



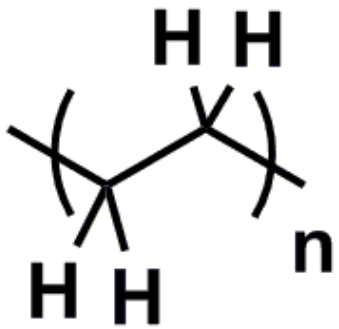


High Density PE (mostly linear)
Bottle Caps, folding chairs etc.

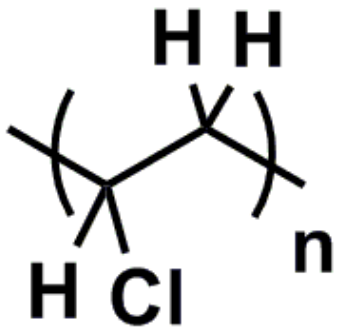


Ultra Molecular weight PE (long chain)
Parachute cords, body armor, etc

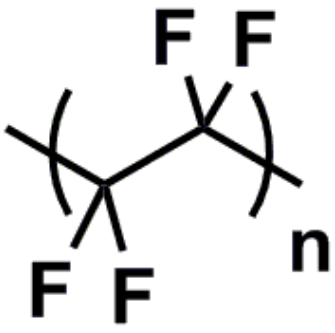
Familiar Polymers in Everyday Life



Poly(ethylene) (PE)



Poly(vinyl chloride (PVC)

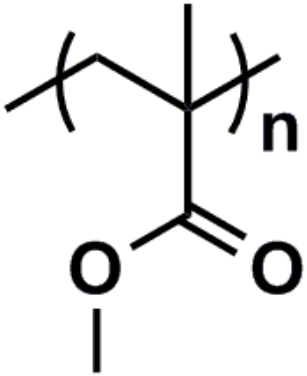


Poly(tetrafluoroethylene)
”Teflon”

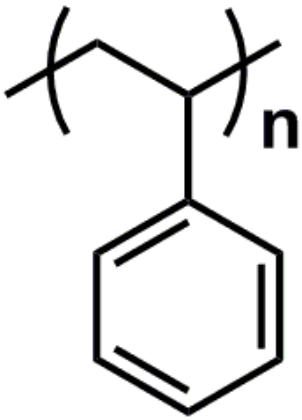
Simple changes to the backbone result in major changes in the properties

- PE : plastic grocery bags
- PVC : pipes to chewing gum (plasticizer)
- Teflon : non-stick coating

Multi-purpose



Poly(methyl methacrylate) (PMMA)

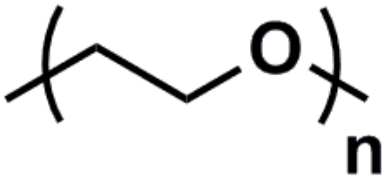


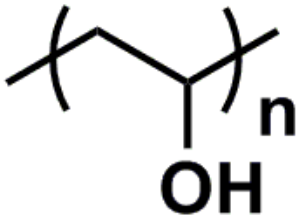
Poly(styrene) PS

- Windshields (Plexiglass)
- Hard contact lens
- Cavity fillings

- Red “Solo” cups
- “Styrofoam”

Polymers in Personal Care

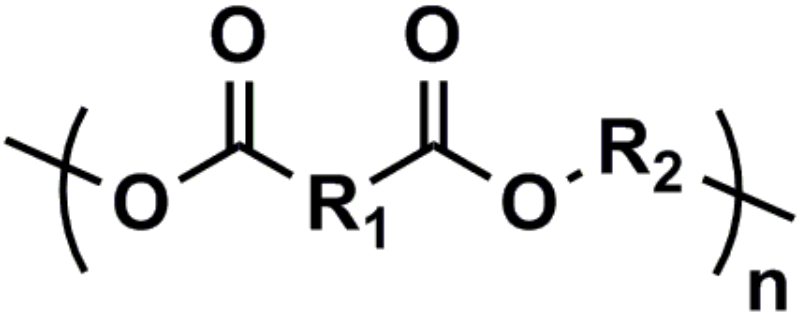




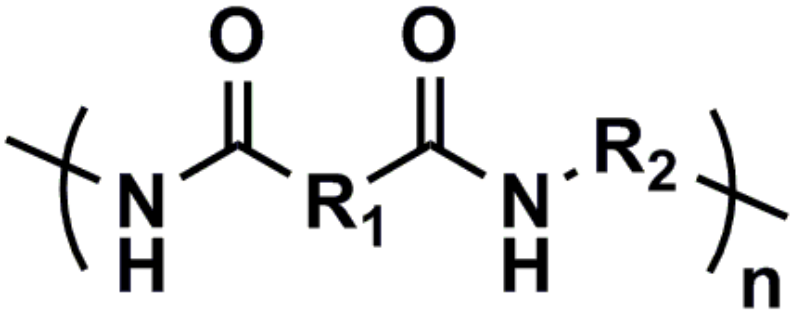
- Poly(ethylene oxide) (PEO)
- Poly(ethylene glycol) (PEG)
- Poly(vinyl alcohol) (PVA)

Students : what polymers can you find in your shampoo?
(not the bottle, but the actual ingredients)
Look for :
PVA###
PEG###

Polymers in Clothing



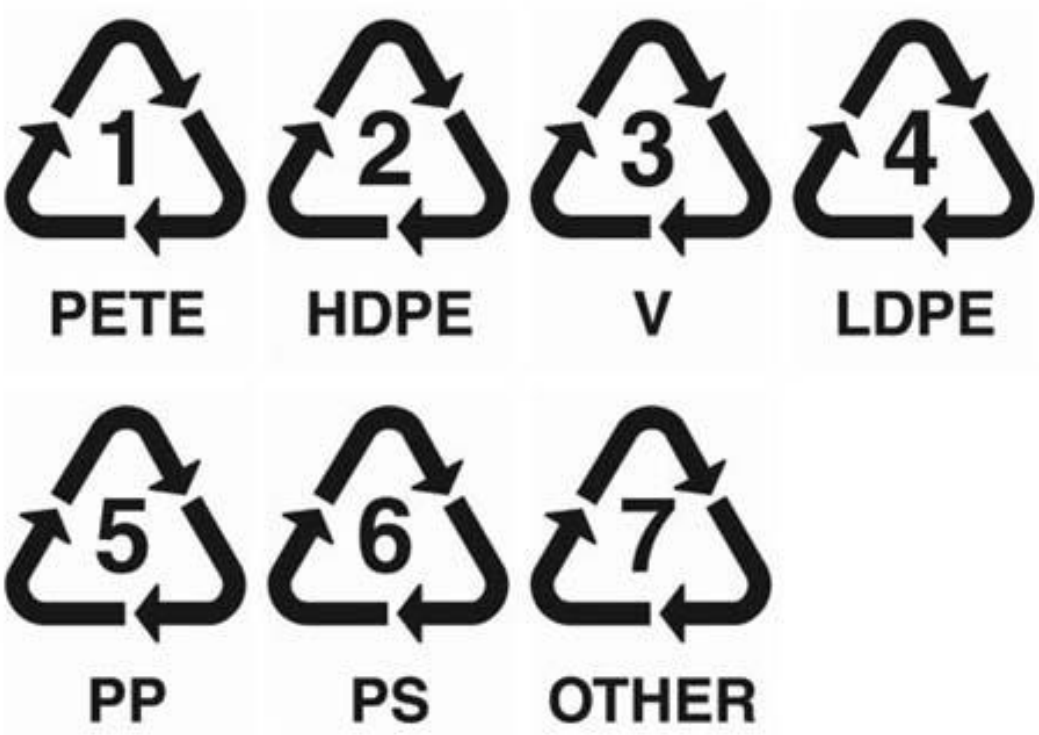
Poly(ester)



Poly(amide)

- Vary the R group to control properties
- Rayon
- Nylon

Recycling of Synthetic Polymers



1) *Poly(ethylene terephthalate) (PET)*
2) *High Density Poly(Ethylene) (HDPE)*
3) *Poly(vinyl chloride) (PVC)*
4) *Low Density Poly(Ethylene) (LDPE)*
5) *Poly(propylene) (PP)*
6) *Poly(styrene) (PS)*