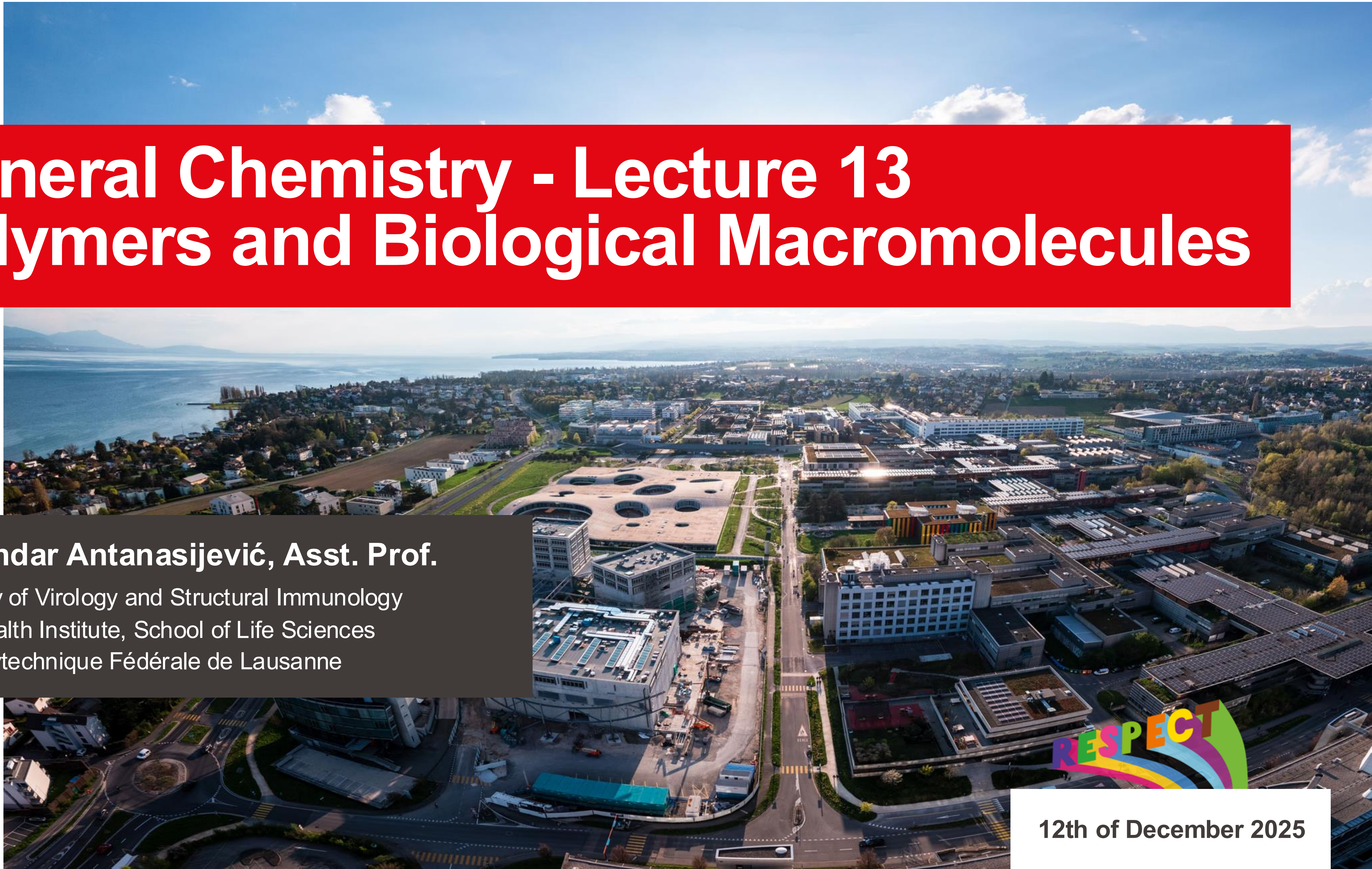
EPFL

General Chemistry - Lecture 13
Polymers and Biological Macromolecules



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RESPECT

12th of December 2025

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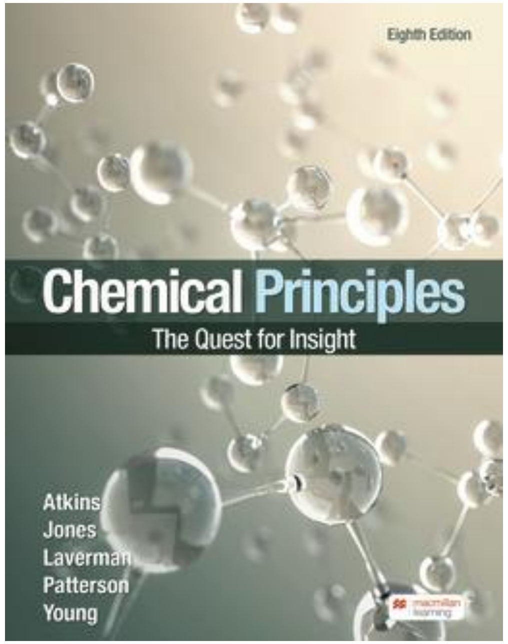
Learning Objectives

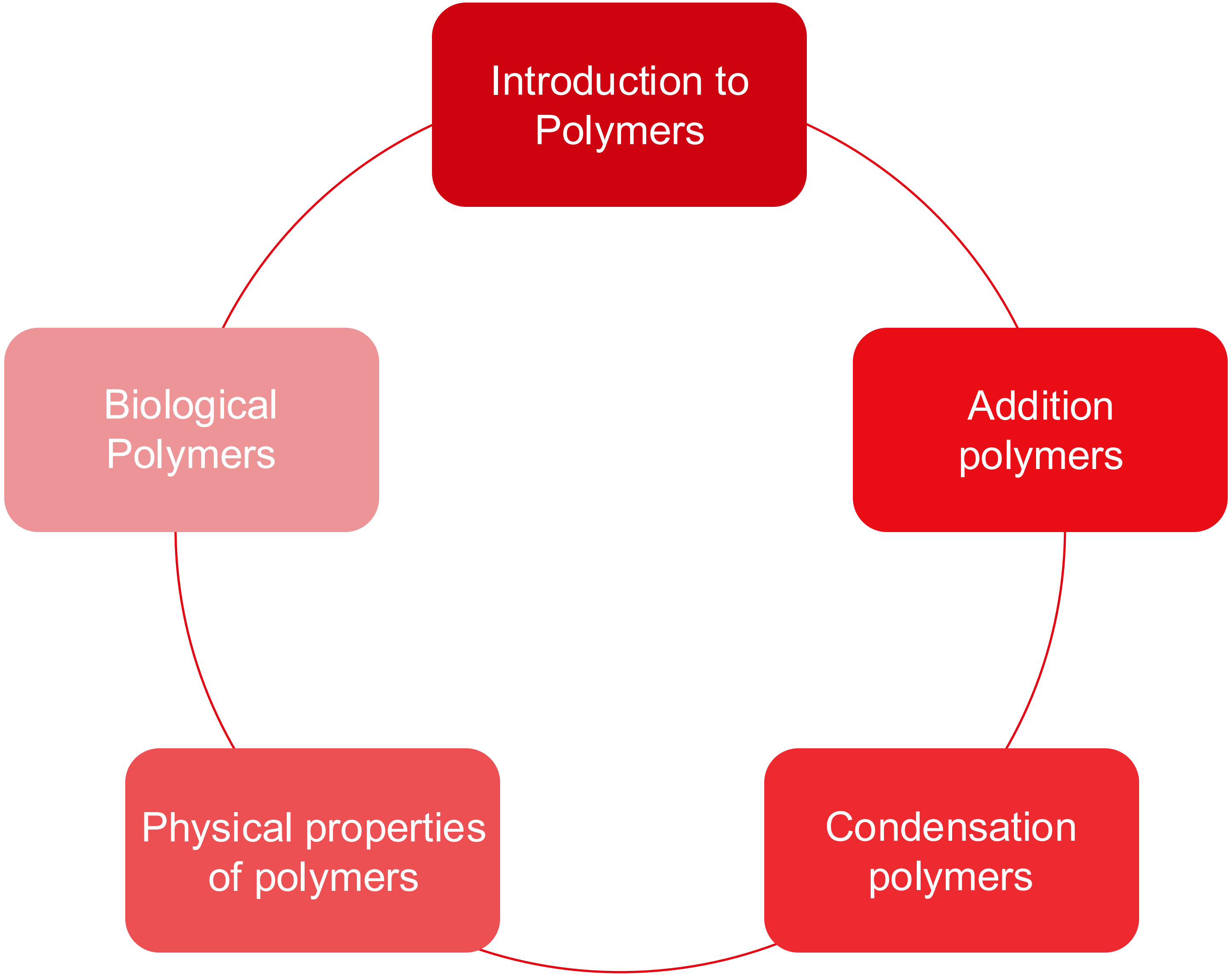
- Understating different classes of polymerization reactions
- Learning about synthetic polymers and copolymers
- Connecting composition to physical and chemical properties
- The basics of biological polymerization

Reading suggestions

- Chemical Principles: The Quest of Insight
  - Chapter 10E



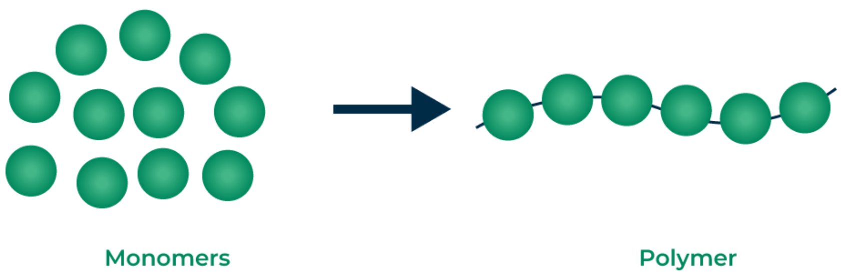
Plan


Introduction to Polymers
Addition polymers
Condensation polymers
Physical properties of polymers
Biological Polymers

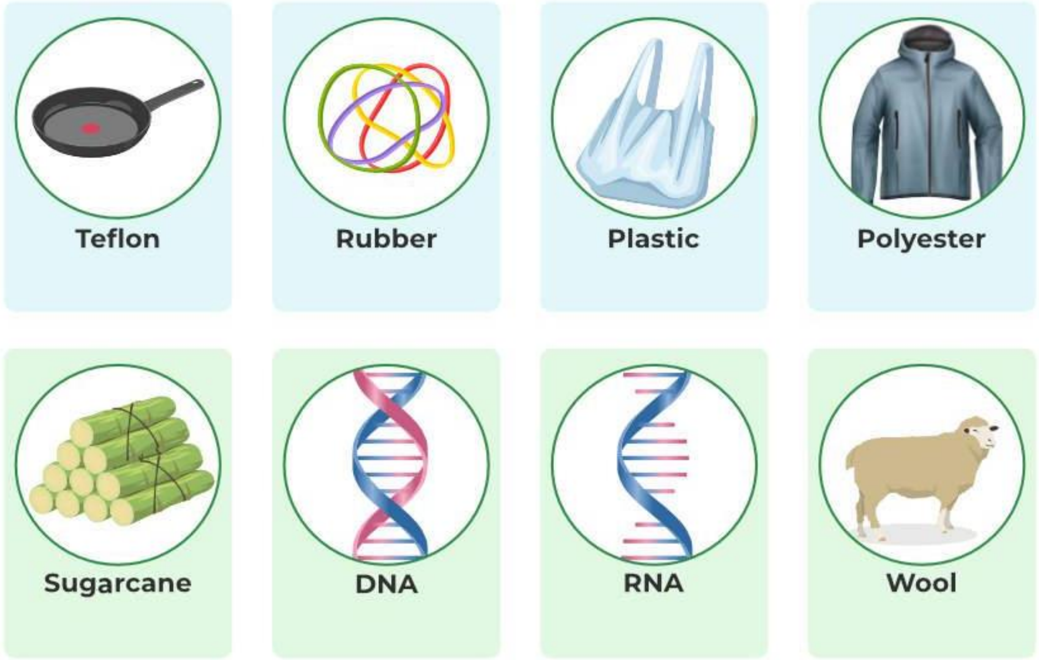
What are polymers?

- A **polymer** is a large molecule made up of many repeating smaller units called **monomers**, which are chemically bonded together in long chains or networks.
- They are characterized by unique physical and chemical properties that depend on the **type of monomer**, **chain length**, and **structure**.

Polymerization assembly:



Polymer examples:

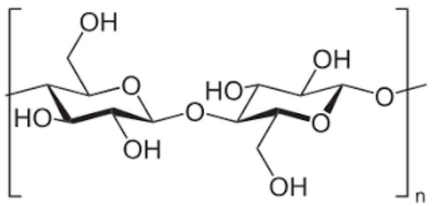


- Polymers are also actively researched for the purposes of: imaging, catalysis, nanomedicine, semiconductors, nanosensors, batteries etc…

Polymer types

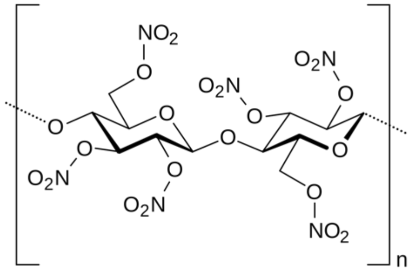
- They can be categorized based on their origins:

Natural



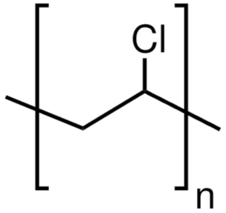
Example: Proteins, nucleic acids, cellulose

Semisynthetic



Example: Cellulose derivatives

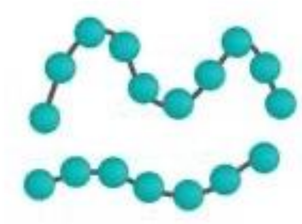
Synthetic



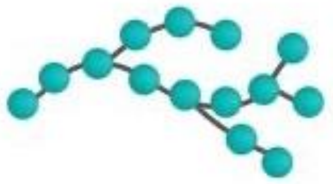
Examples: Polyvynil chloride, polyester

- They can also be categorized based on their assembly:

Linear



Branched



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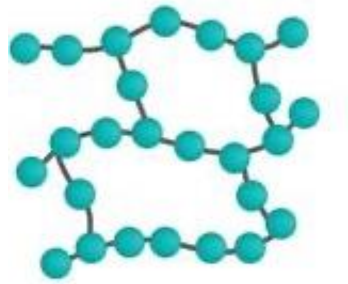


- They can also be categorized based on the type and origin of their chemical groups

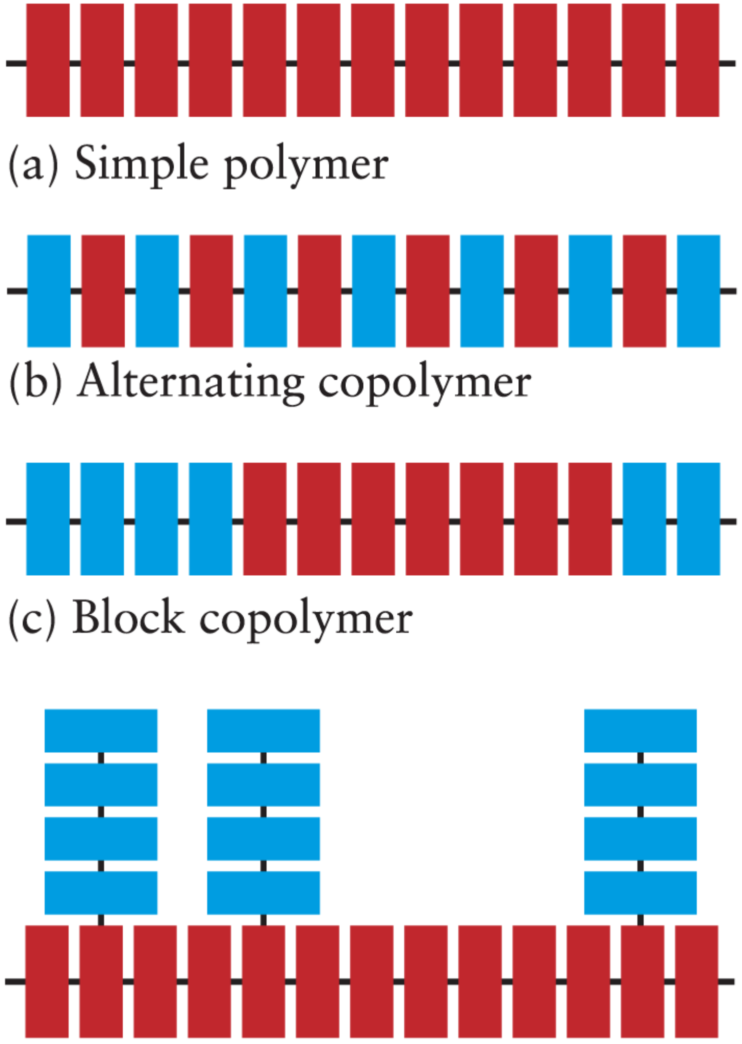
Copolymers and Composites

- **Single** polymer has only one repeating unit (e.g., polyethylene, PVC)
- Copolymers contain more than one type of repeating unit arranged in different ways:
  - Alternating (e.g., nylon)
  - Block (e.g., styrene/butadiene in chewing gum)
  - Graft (e.g., silicone/hydrogel in soft contact lenses)

- A composite consists of two or more substances combined into a heterogeneous material.

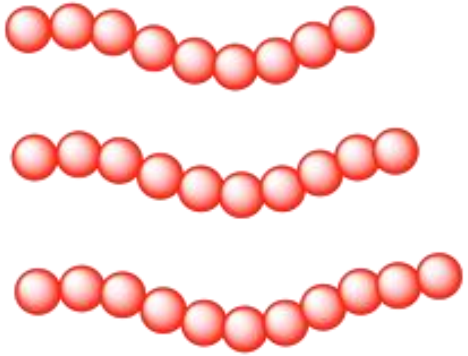
Seashells: Chitin + $CaCO_3$

Tennis rackets: Carbon fiber + Epoxyphenols

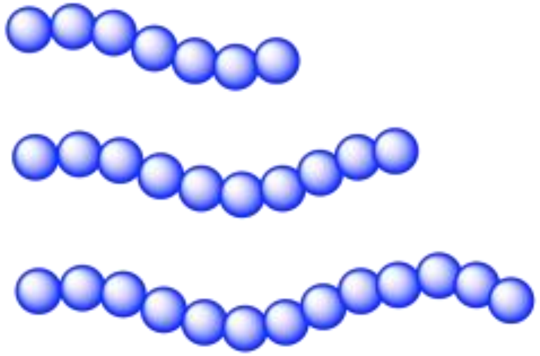


Polymer polydispersity

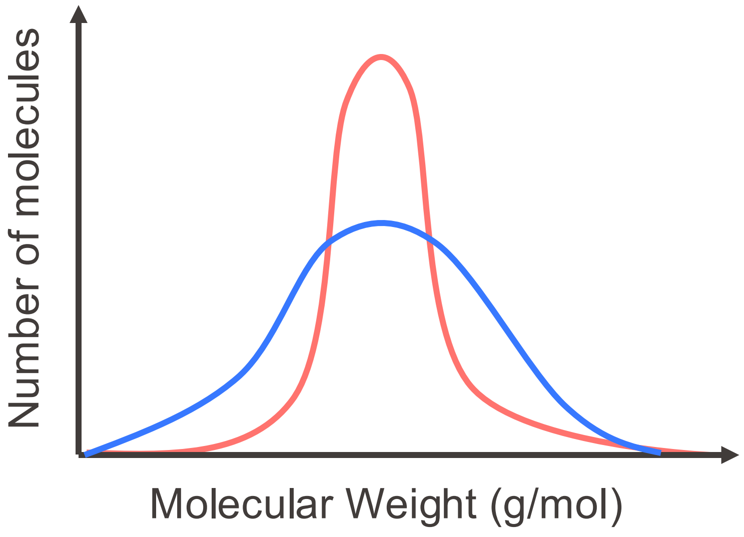
- All synthetic polymers are **polydisperse** in terms of their size, because chain termination causes random stopping points.
- Final product size is usually described as a distribution of lengths (in terms of monomer count) or molecular weights.



Narrower polydispersity



Wider polydispersity

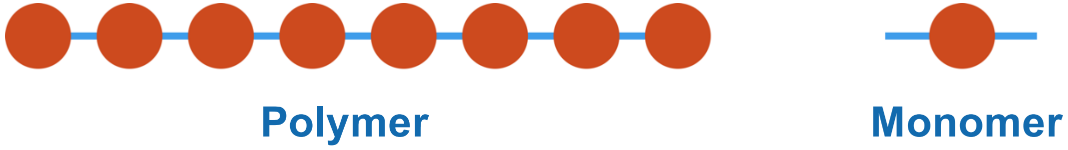


- Natural polymers such as proteins or nucleic acids can have a fixed length because they are created based on genetic templates (e.g., transcription and translation)

Polymerization reactions

- A **polymerization** reaction is a chemical process in which monomers join together through **repeated bonding** into a polymer.
- There are 2 main types of reactions that result in polymer formation:

  - **Addition** reactions (chain-growth polymerization)

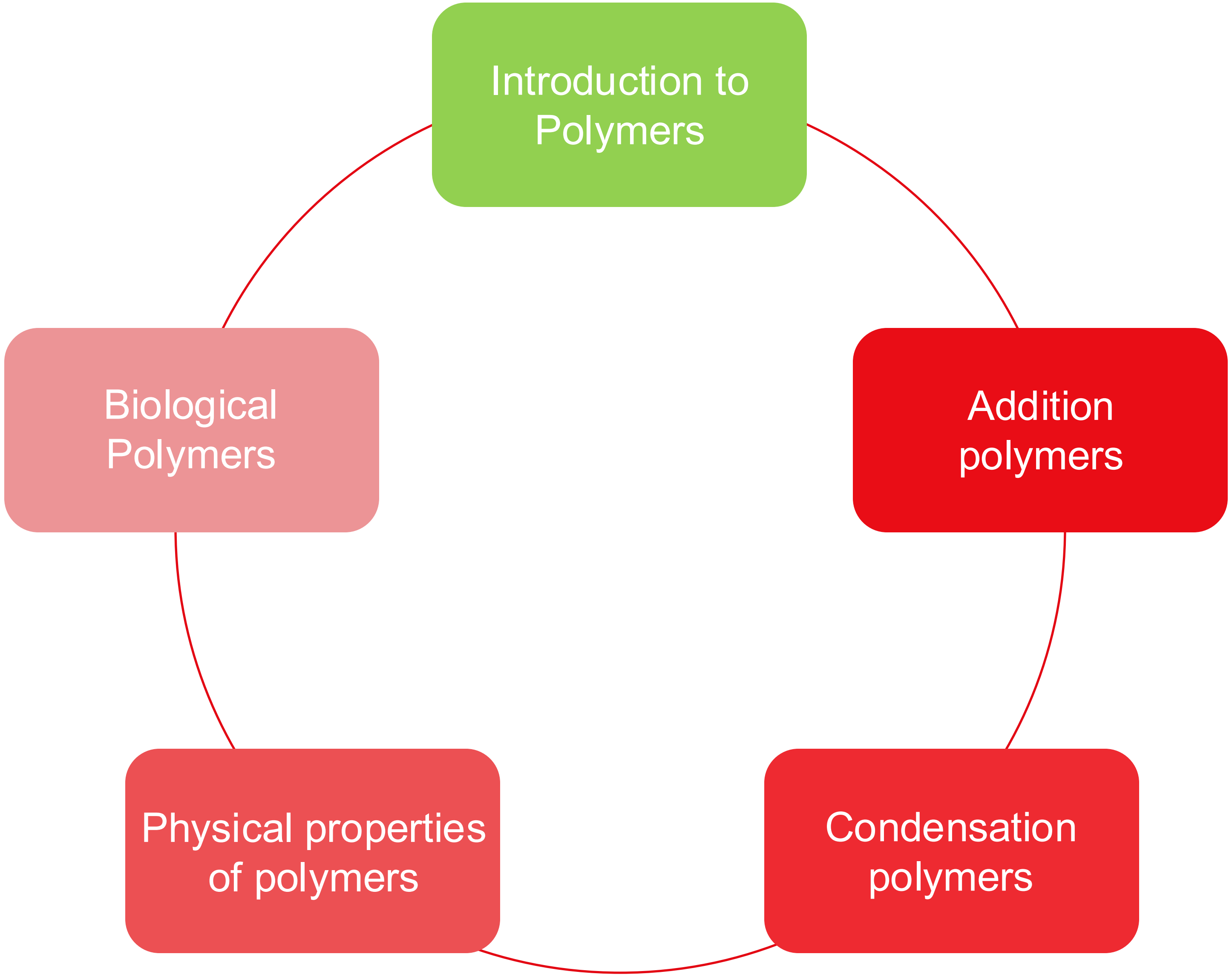


Simple addition of groups without by-products

  - **Condensation** reactions (step-growth polymerization)

Release of a smaller group in the reaction

Plan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Addition polymers

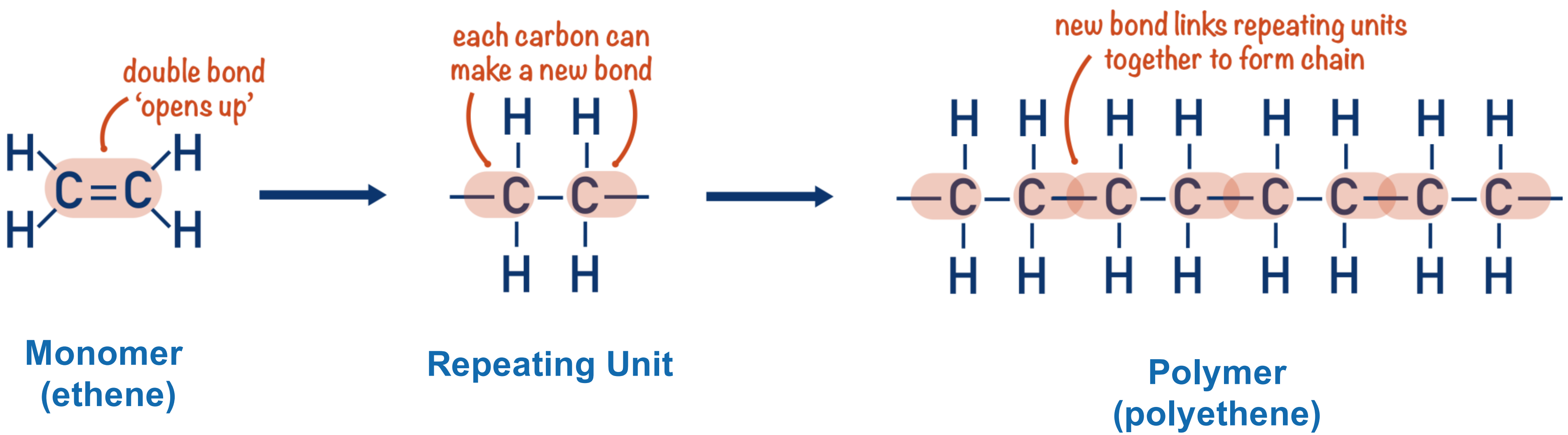
- Addition polymerization is a reaction in which unsaturated monomers join together through bond rearrangement and without the formation of by-products.

Example reaction: Ethene → Polyethene

$$n\ CH_2{=}CH_2(g) \rightarrow (-CH_2-CH_2-)_n\ (s)$$

$n \sim 10^3 - 10^5$

Plastics, films, containers…



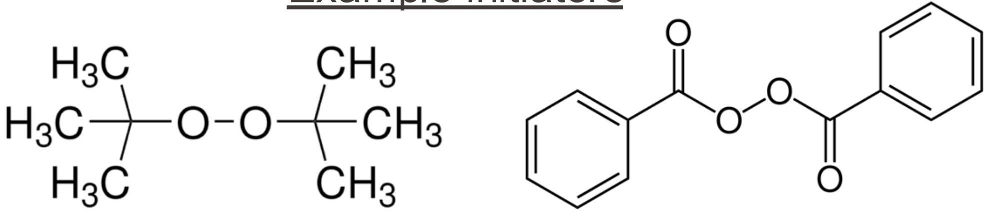
Addition reaction steps

- The polymer forms through a chain reaction involving **initiation**, **propagation**, and **termination**.

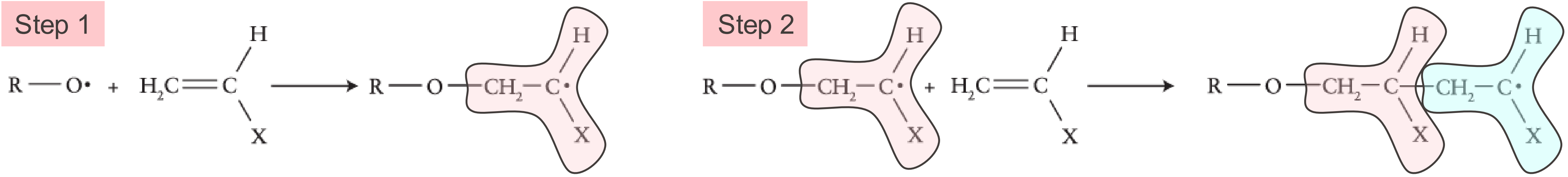
- **Initiation**: Reactive species is first formed (typically via free radical groups)

$$R\text{-}O\text{-}O\text{-}R \rightarrow R\text{-}O\cdot + \cdot O\text{-}R$$

Example initiators



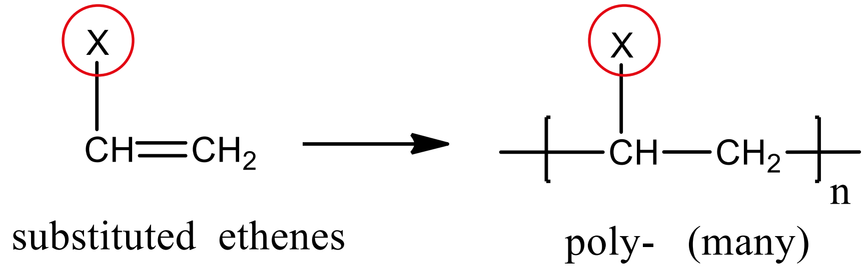
- **Propagation**: Chain growth by repeated monomer addition.



- **Termination**: Pairs of chains link together into single nonradical species

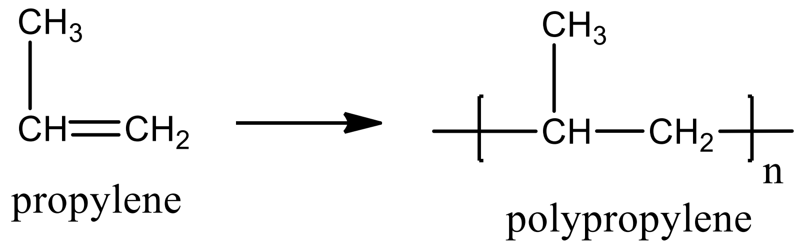
Alkene-based polymers

- Form from alkene monomers that become the repeating units in the polymers.

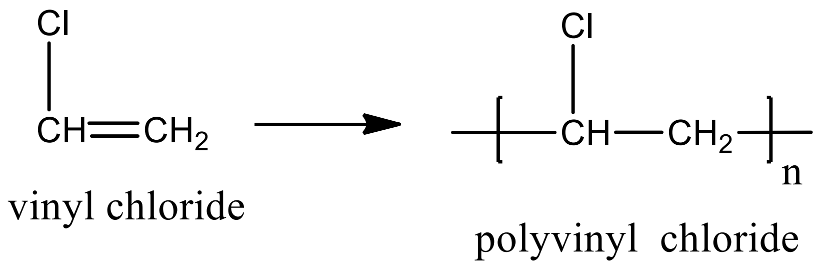


- General formula for these monomers is CH**X**═CH_2

  - If **X** is a methyl group, polymer is polypropylene (PP)

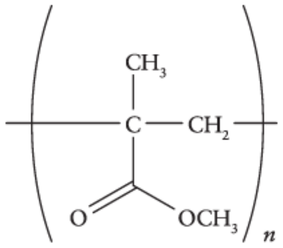


  - If **X** is a single atom, Cl, polymer formed is polyvinyl chloride (PVC)



Alkene-based polymers

- Depending on the substituent group the resulting polymers will differ in appearance, rigidity, transparency, and resistance to weathering.

Monomer name	Polymer formula	Common name
ethene*	$–(CH_2\text{-}CH_2)_n–$	polyethylene
vinyl chloride	$–(CHCl\text{-}CH_2)_n–$	polyvinyl chloride
styrene	$–(CH(C_6H_5)\text{-}CH_2)_n–$	polystyrene
acrylonitrile	$–(CH(CN)\text{-}CH_2)_n–$	Orlon, Acrilan
propene*	$–(CH(CH_3)\text{-}CH_2)_n–$	polypropylene
methyl methacrylate		Plexiglass, Lucite
tetrafluoroethene*	$–(CF_2\text{-}CF_2)_n–$	Teflon, PTFE†

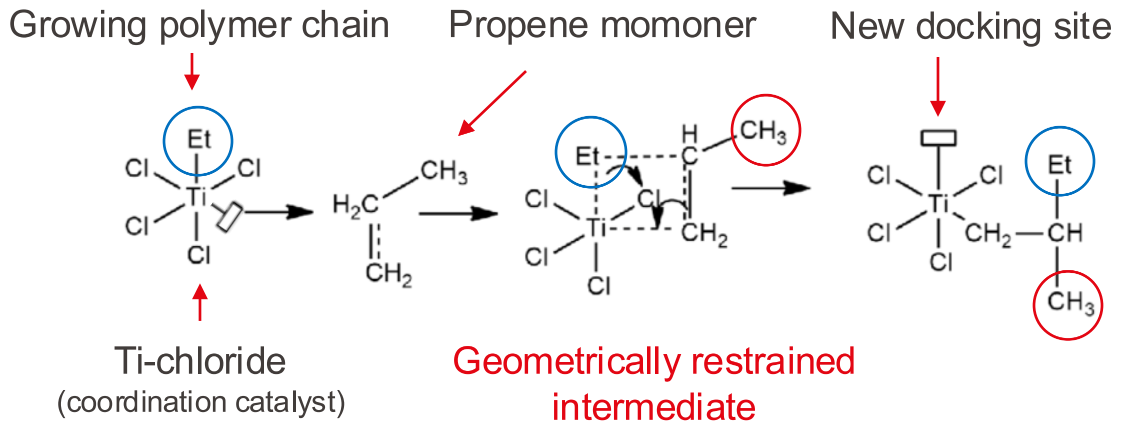
Polyethylene

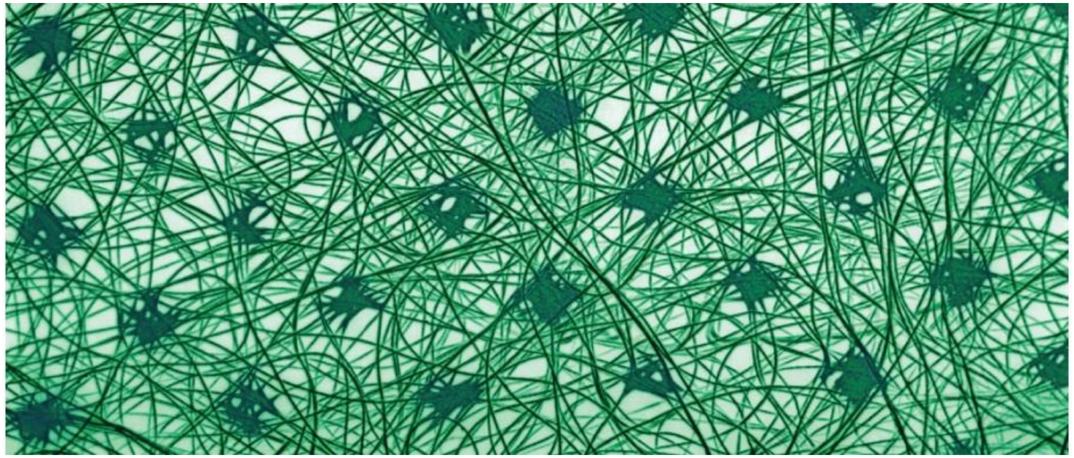
Plexiglass

Teflon

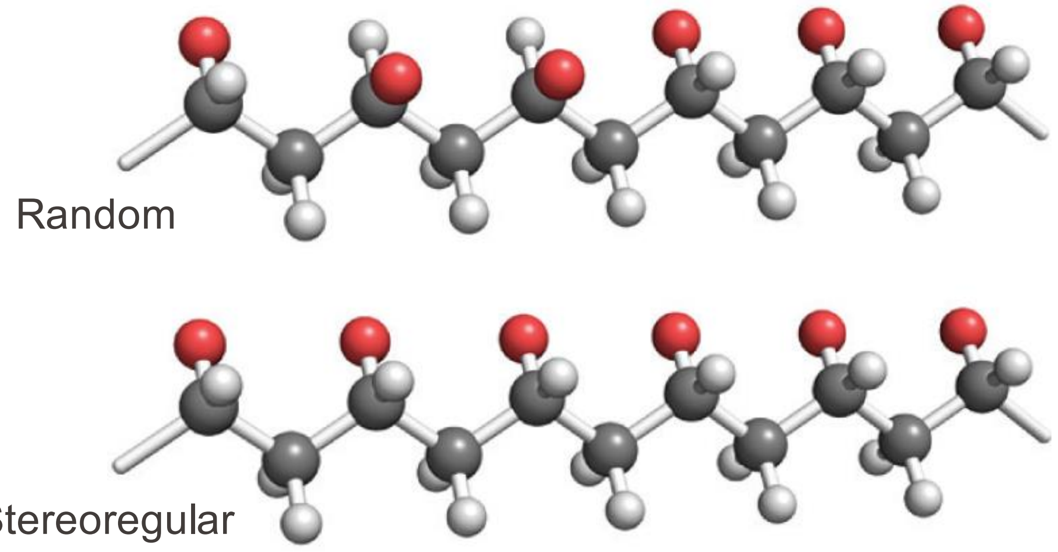
Stereoregular addition polymers

- Controlling the orientation of monomers:
  - ➢ Random product = amorphous, sticky, not easily applied in materials
  - ➢ Use of Ziegler-Natta catalyst (coordination catalysis) gives a more uniform product.
  - ➢ Uniform product is **stereoregular** and packs to form crystalline, dense material



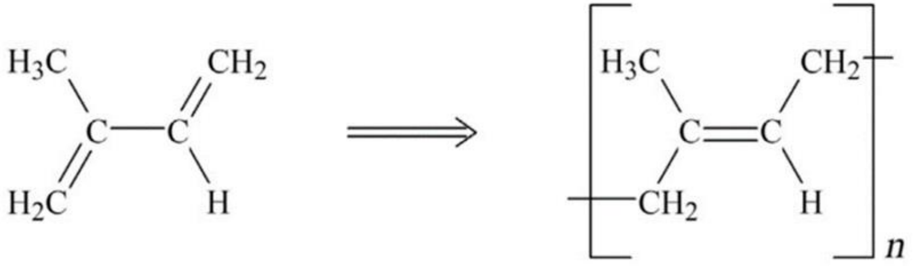


Fibers created by stacking of stereoregular polypropylene



Isoprene polymers

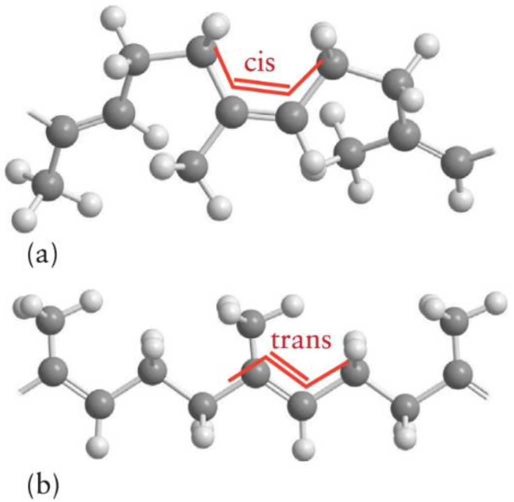
- Rubber - polymer of isoprene.
  - Obtained from the **rubber tree** as **latex**, an aqueous suspension of rubber polymers and other plant molecules.
  - Soft white solid; becomes softer when warm.



Isoprene Polyisoprene

Chris Hellier/Alamy.

- Natural rubber can come in different forms:
  - Natural rubber is all cis (enzyme catalyzed); soft, tacky, can be deformed.
  - Trans polyisoprene also exists (gutta-percha) but is harder; Used to fill root canals in teeth.



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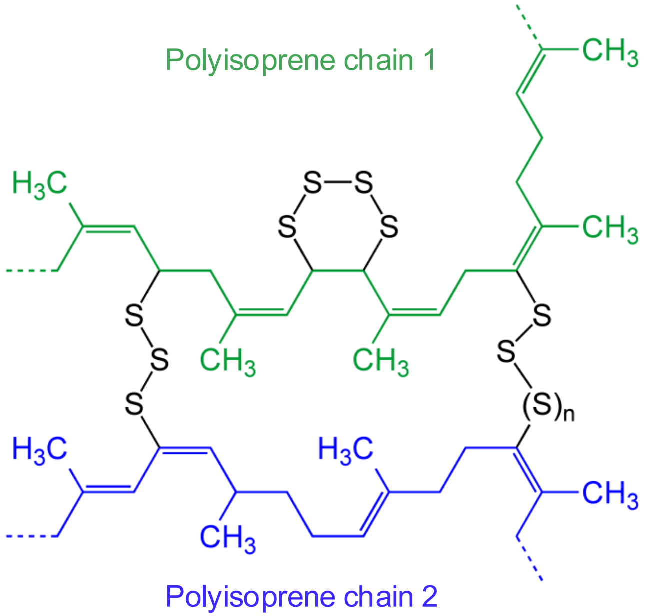
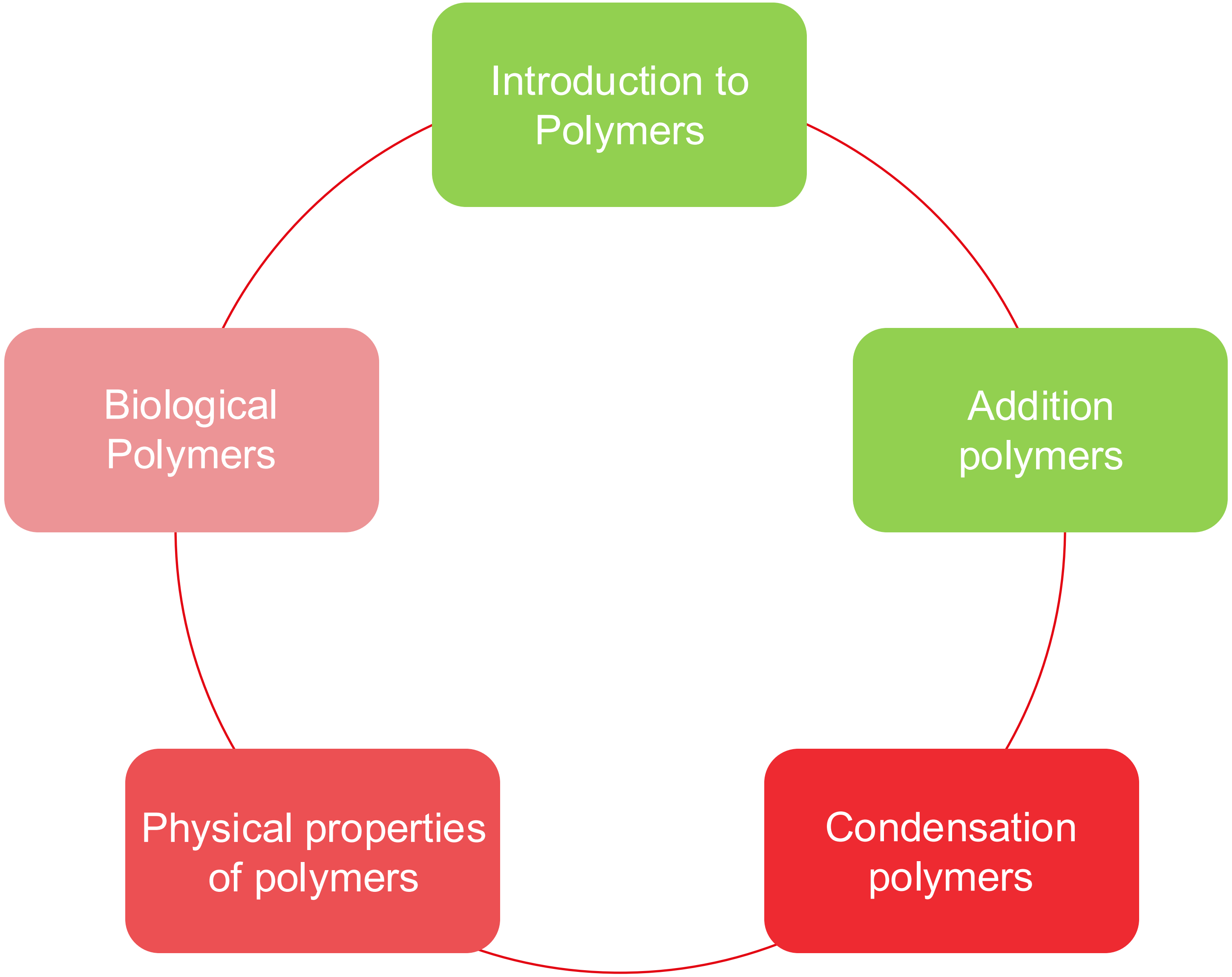
Isoprene polymers

- Natural rubber based on cis-polyisoprene is soft, easy to break, and does not exhibit much elasticity (can be permanently deformed).
- The elastic properties in rubber are achieved through the **vulcanization** process



- Heating natural rubber with elemental **sulfur** (or sulfur-based compounds) at about 150–170 °C creates **crosslinks** between the polyisoprene chains.
- These sulfur crosslinks give the material its **mechanical strength and elasticity**.

Plan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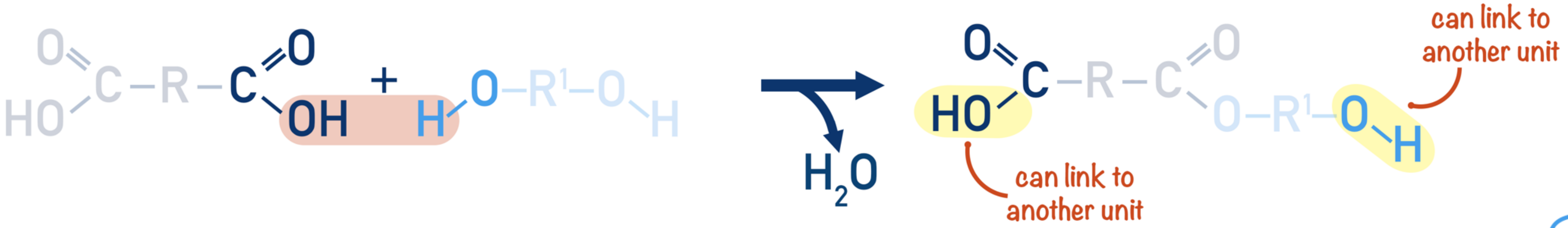
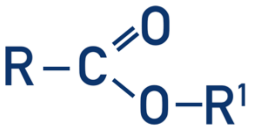
Condensation polymers

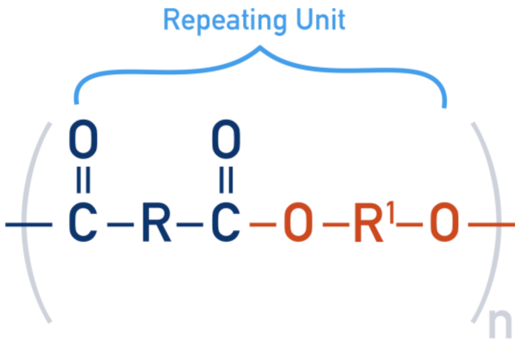
- Condensation is a reaction in which monomers join together while simultaneously eliminating small molecules, such as **water** or **methanol**, to form a polymer.
- Some common properties of condensation chemistry:
  - Monomers have **functional groups on each end of the molecule**.
  - Produces new functional groups between monomers, often **esters** and **amides**.
  - The reaction is asymmetric in that it requires **2 different functional groups** to create a link
  - The two groups can both be present on the same molecule or come from 2 molecules





Ester

Ester group alone is insufficient to make polymeric chains.

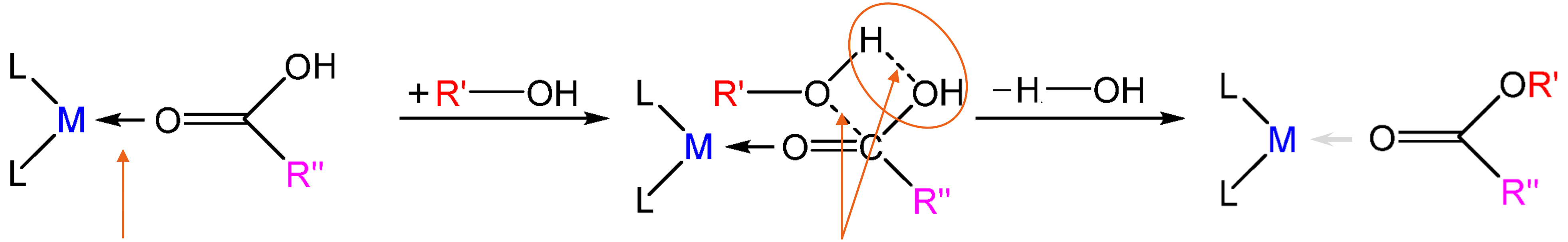


Polyester

Condensation reaction mechanism

- Polyester formation is catalyzed by **metal salts** or **metal alkoxides** (-OR), which accelerate esterification through Lewis-acid and/or general acid–base mechanisms.

Example: Lewis acid coordination mechanism (ML_2 is a metal-ligand complex; M = Ti, Sb or Sn)



Metal (M) acts as Lewis acid accepting one electron pair of O into LUMO orbital

This polarizes the C = O bond making the C suitable for nucleophilic attack

Ester formation reduces the electron-deficiency of C and the catalyst is released

- Each step requires two functional groups (–COOH and –OH) to react, which reduces undesirable side reactions compared to radical addition polymerizations

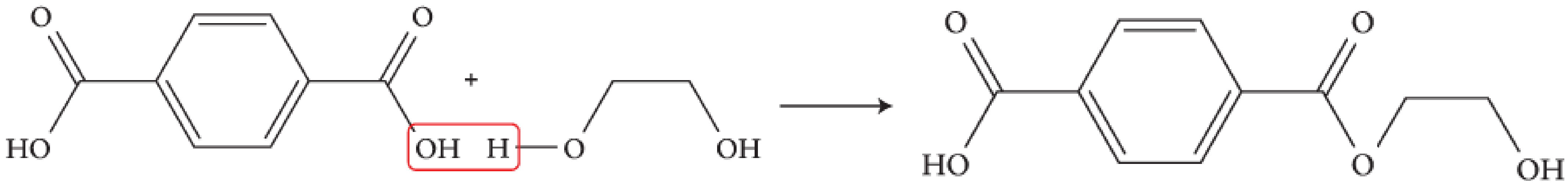
Condensation polymers - Polyesters

- Carboxylic acid and alcohol monomers combine to make polyesters, in a reaction that involves release of a water molecule

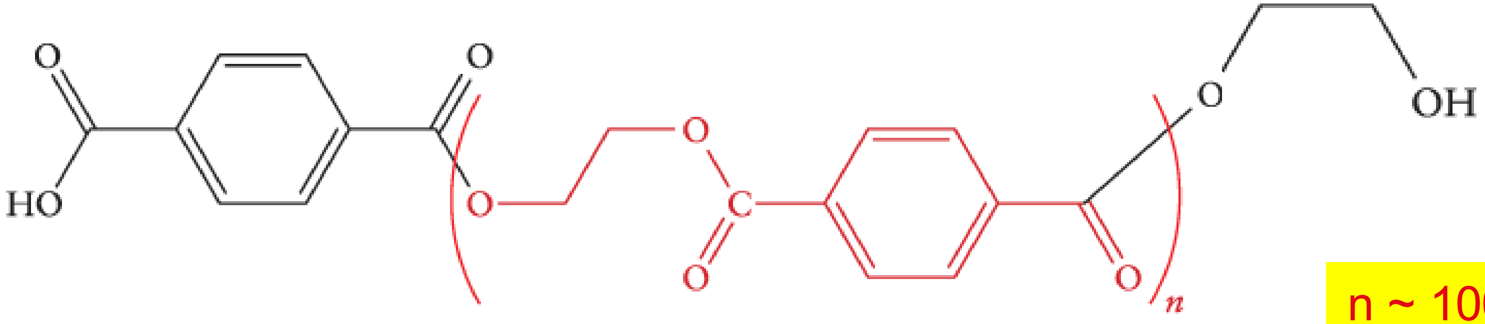
Benzene-1,4-dioic acid
(terephthalic acid)

Ethane-1,2-diol
(Ethylene glycol)

Mono(2-hydroxyethyl) terephthalate (MHET)



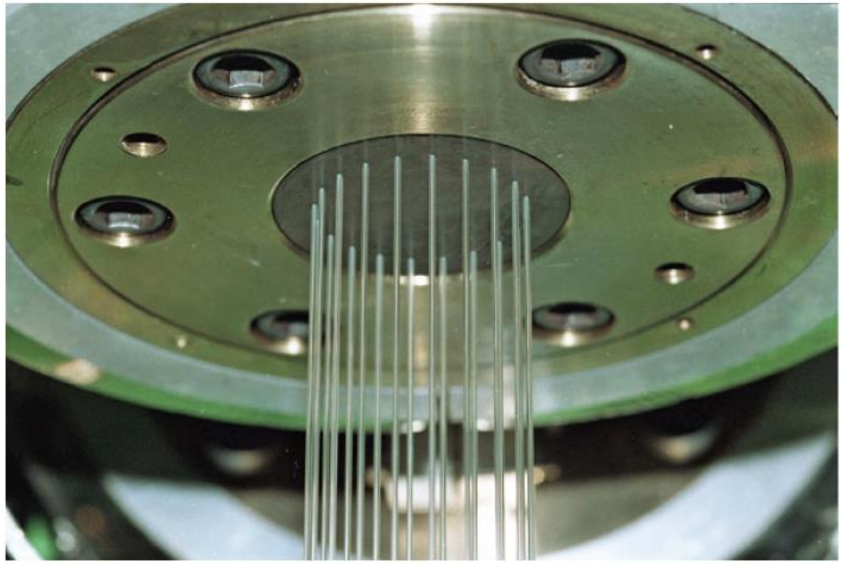
- The continuation of the chain leads to polyethylene terephthalate (PET)



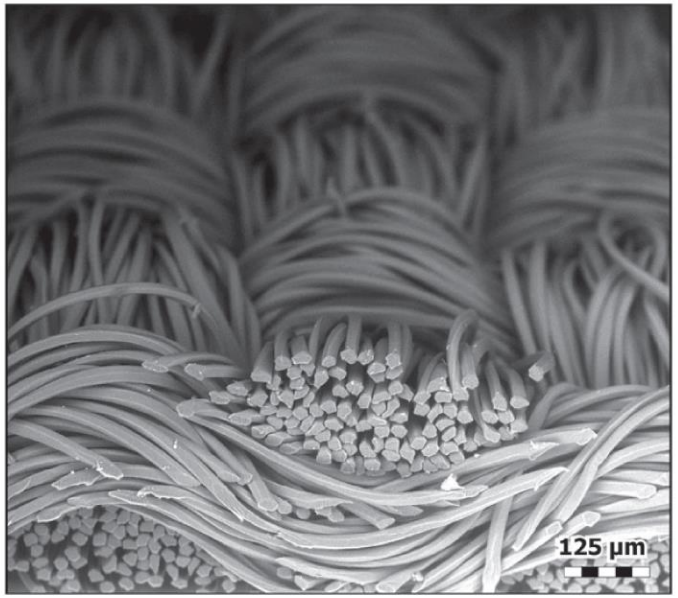
n ~ 100-300

Condensation polymers - Polyesters

- The liquid PET polymer can be molded into different shapes (e.g., plastic bottles, hoses, containers)
- In an industrial setting it is pushed through small holes on a spinneret to make fibers used for clothing.


Courtesy Sunline Co., Ltd.

Industrial spinneret

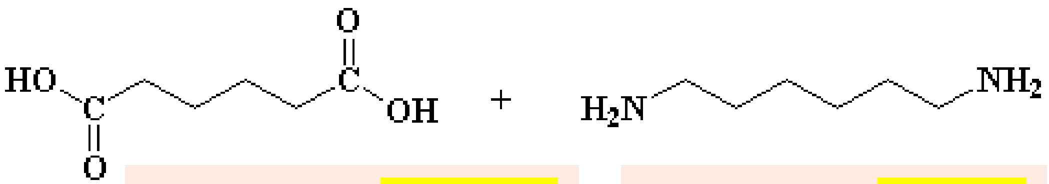


E.P. Vicenzi/Smithsonian's Museum Conservation Institute and NIST

Polyester fibers in a woven surgical mask.

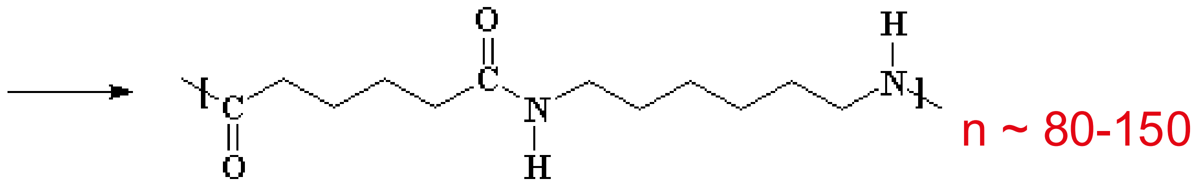
Condensation polymers - Polyamides

- A polyamide is a polymer formed by the repeated joining of monomers through amide (peptide) linkages
- Typically produced by condensation between a **carboxylic acid** (or acid derivative) and an **amine**
- This class of polymers includes **nylons**, **aramids** (e.g., Kevlar), as well as **proteins**
- **Nylon-6,6**, made with 1,6-diaminohexane and adipic acid.



Hexane-1,6-dioic acid
(Adipic acid)

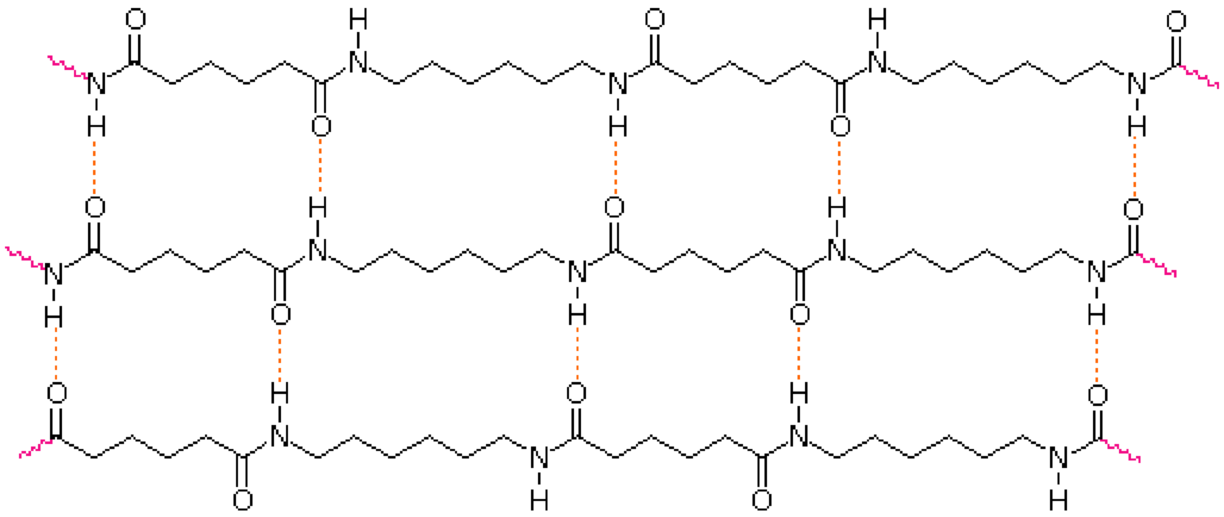
Hexane-1,6-diamine
(1,6-diaminohexane)

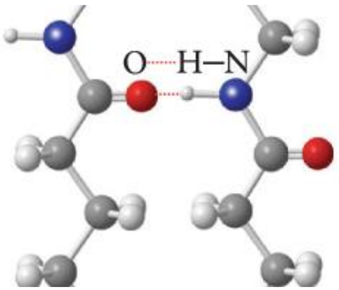


Nylon 6,6

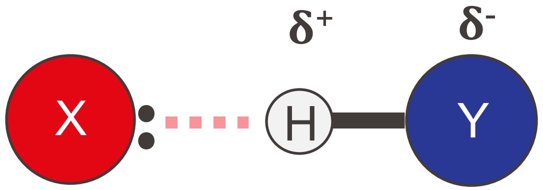
Condensation polymers - Polyamides

- The long polyamide (nylon) chains can be spun into fibers or molded.
- **Hydrogen bonding** between **neighboring chains** increases the strength of nylon fibers (~1.5-fold stronger, with ~1.8-fold greater elasticity compared to PET).
- Non-covalent interactions in the form of London dispersion forces and hydrogen bonds hold the polymer chains together.





A **hydrogen bond** is a **strong dipole-dipole attraction** in which a hydrogen atom covalently bonded to a highly electronegative atom (**N, O, or F**) interacts with a lone pair on another electronegative atom.

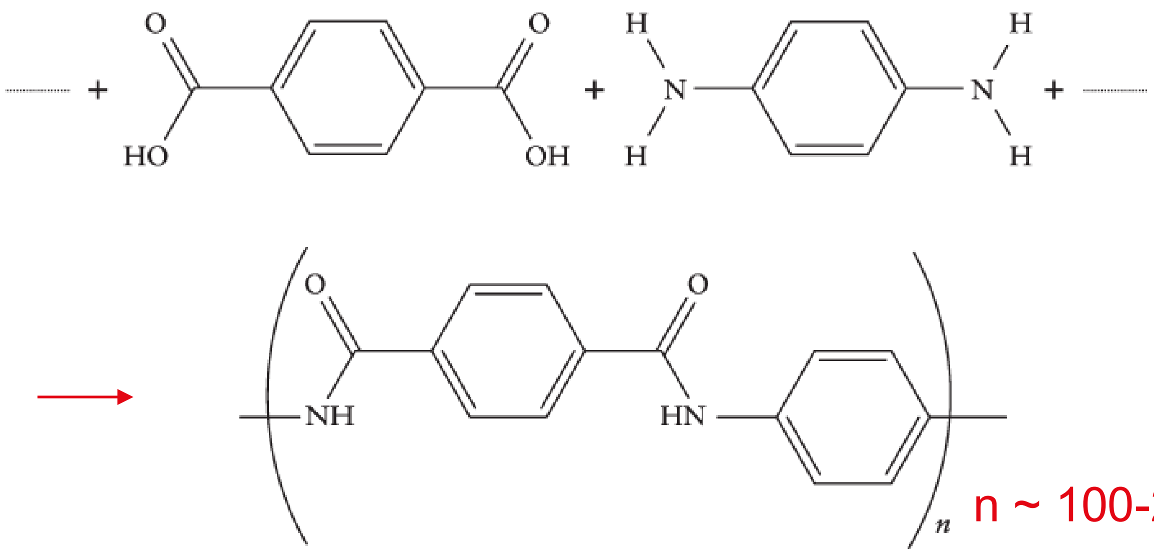


Condensation polymers - Polyamides

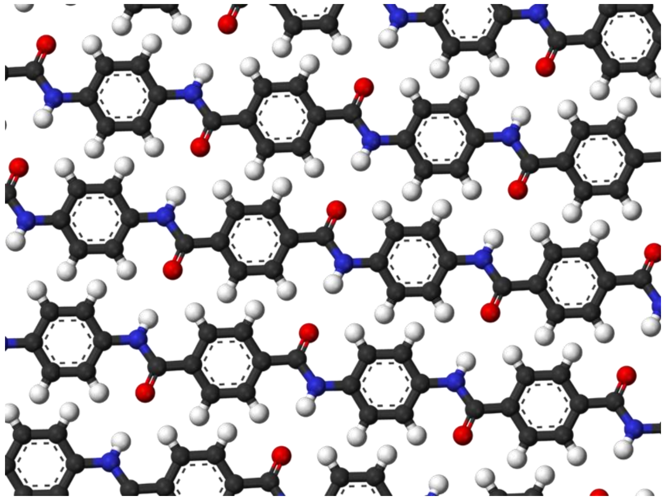
- Kevlar is a polyamide made from **terephthalic acid** and ***para*-phenylenediamine**

Benzene-1,4-dioic acid
(terephthalic acid)

Benzene-1,4-diamine
(*p*-phenylenediamine)



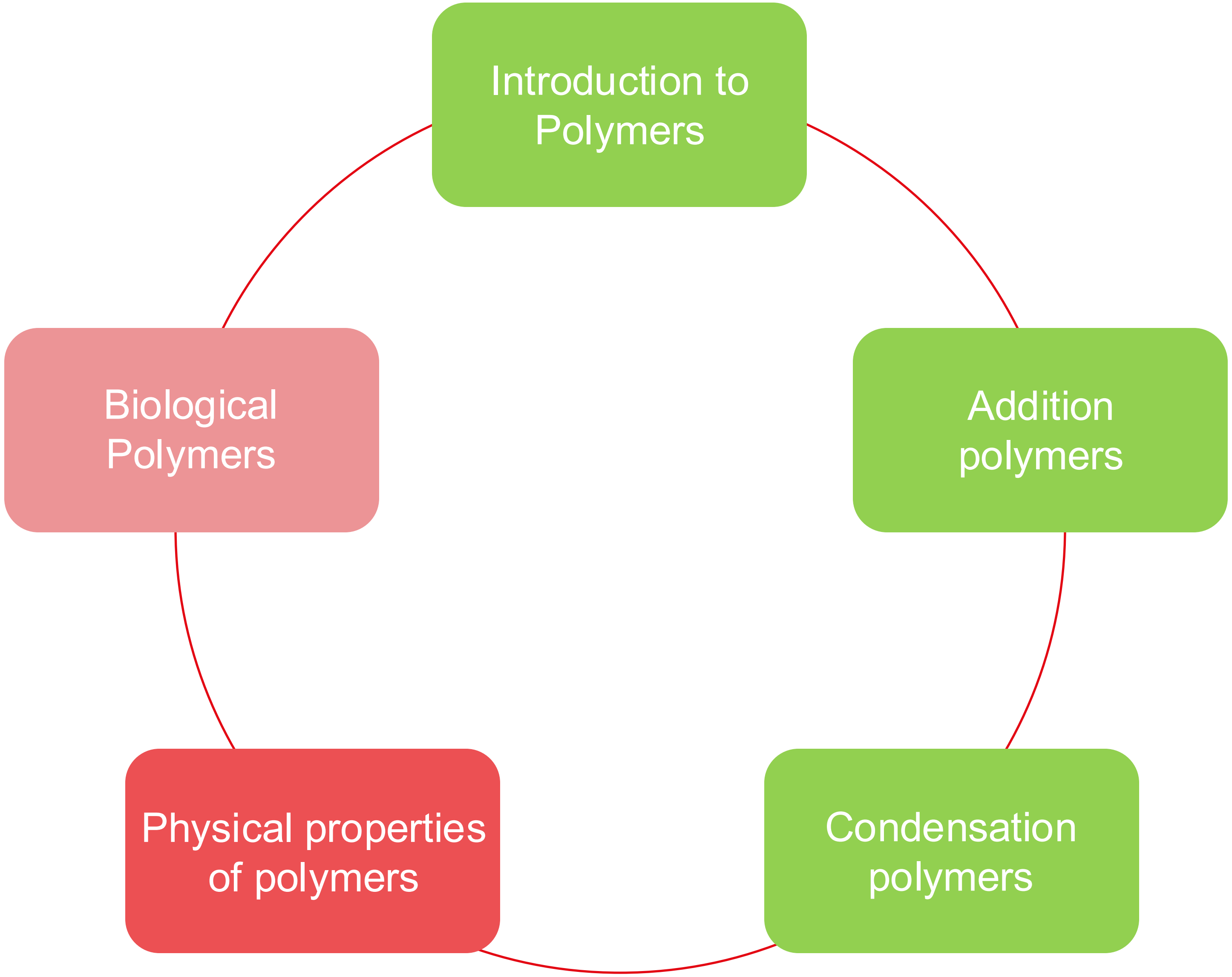
n ~ 100-250



One (**crystalline**) layer of kevlar

- It has exceptional mechanical and thermal stability due to **rigid bond structure**, **interchain hydrogen bonding** and **stacking of benzene rings** (like in DNA).
- Originally intended as a lightweight replacement for steel, especially in tires. Later used in body armor, helmets, aerospace, ropes, and composites

Plan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Thermal properties of polymers

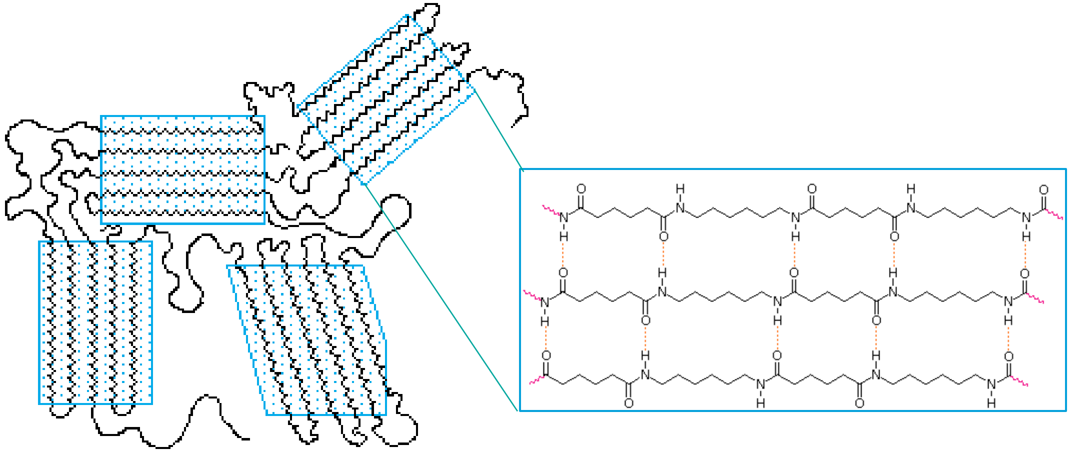
- Polymers melt over a temperature range, not at a single Tm. Melting curves are used to assess quality and homogeneity of material.
- Longer chains generally have higher Tm due to better packing and stronger intermolecular forces.
- Longer polymer chains have much higher melt viscosity because of increased entanglement.
- Hydrogen bonding and other strong interactions raise Tm by stabilizing ordered structures.
- Branched chains pack less well → Lower Tm

Polyethylene chain length	Typical Melting Point (°C)
70 units	60–80 ˚C
700 units	100–120 ˚C
~1000-10’000 units	125–135 ˚C
~10’000-100’000 units	135–140 ˚C

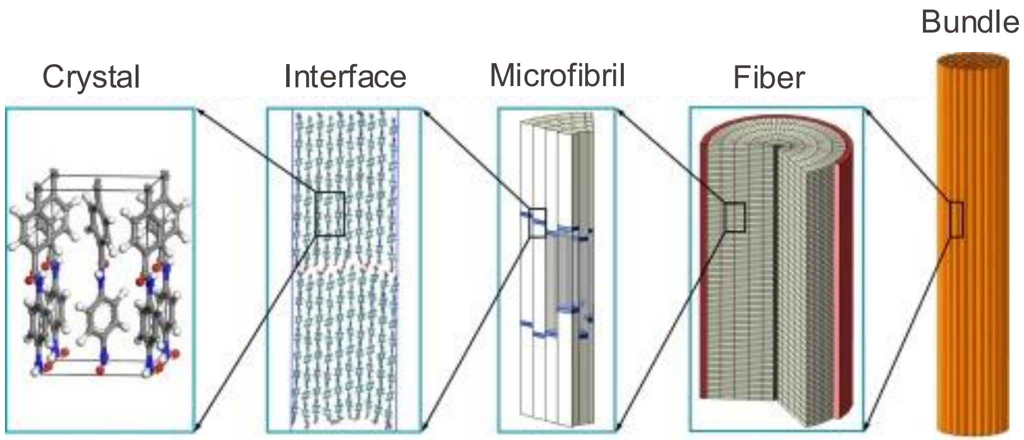
Polymer	Typical Melting Point (°C)
Polypropylene (PP)	160–170 ˚C
Polystyrene (PS)	90–110 ˚C
Polyvinyl chloride (PVC)	75–105 ˚C (softening)
Polycarbonate (PC)	145-155 ˚C (softening)
Polyethylene terephthalate (PET)	250–260 ˚C
Nylon-6,6	255–265 ˚C
Kevlar	No melt; decomposes >500 ˚C
Polytetrafluoroethylene (Teflon)	327 ˚C

Mechanical strength of polymers

- Both the thermal stability and mechanical strength of polymers are strongly influenced by the capacity to pack chains into ordered, **crystalline** sub-structures.
- The functional groups of the monomer contribute to the interaction capacity (e.g., London dispersion forces, hydrogen bonding, π–π stacking etc.)



Crystalline packing of polymers

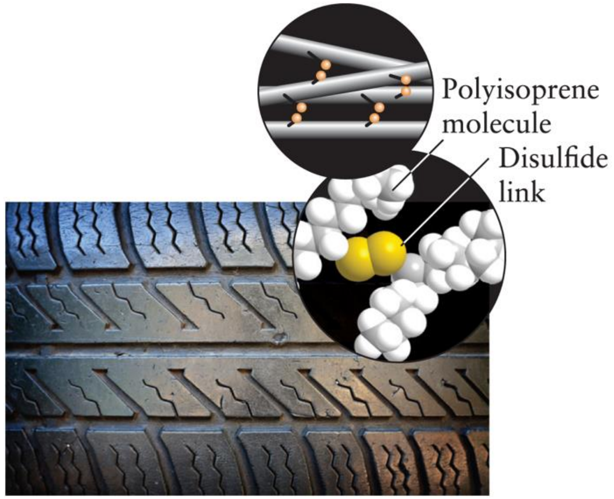


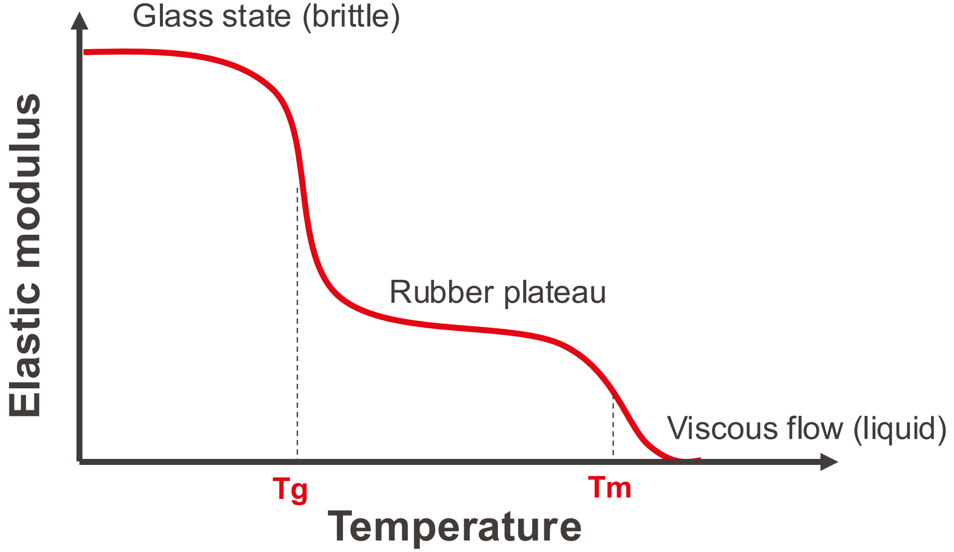
The origin of kevlar's mechanical and thermal stability

- These materials (e.g., Kevlar or PE) can be stronger than steel but weigh only a fraction

Elasticity of polymers

- **Elasticity** is the ability of a polymer to deform under stress and then return to its original shape when the stress is removed.
- Elasticity comes from chain **mobility** and **entropy**: Coiled chains straighten under stress and recoil when released
- Polymers must be above **glass transition temperature** (T_g) to be elastic





- Most plastics applied in everyday solid products are used **below their T_g** temperature and are in glassy or semi-glassy (partially crystalline) state.

Degradation and Recycling

- Addition polymers (PE, PP, PS) are exceptionally resistant to chemical degradation due to the lack of reactive groups in their backbones.
- Condensation polymers (PET, nylon) contain polar functional groups in their backbones, which are more susceptible to hydrolysis, enzymatic, and photo-degradation.

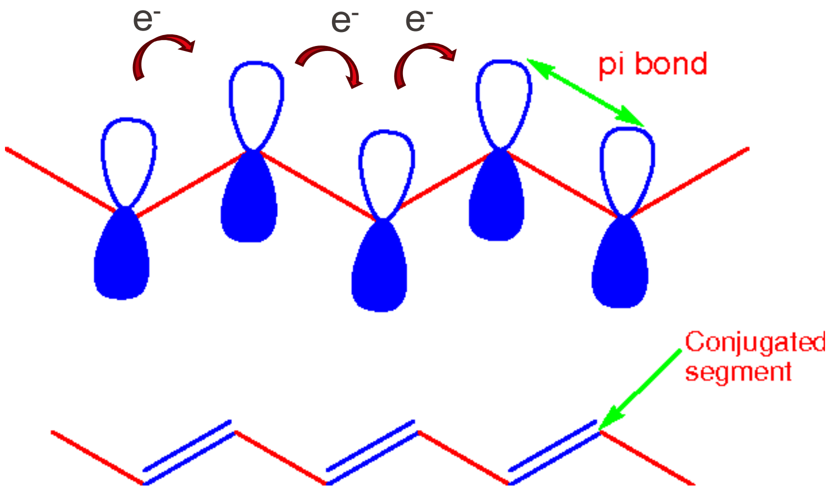
Table 10E.2 Recycling Codes

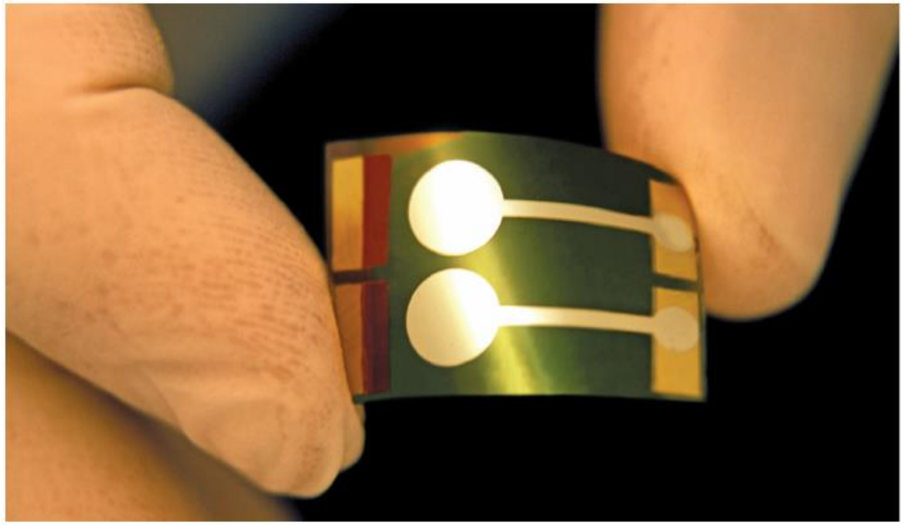
Recycling code		Polymer	Recycling code		Polymer
1	1 PETE	polyethylene terephthalate	5	5 PP	polypropylene
2	2 HDPE	high-density polyethylene	6	6 PS	polystyrene
3	3 PVC	polyvinyl chloride	7	7 OTHER	other
4	4 LDPE	low-density polyethylene			

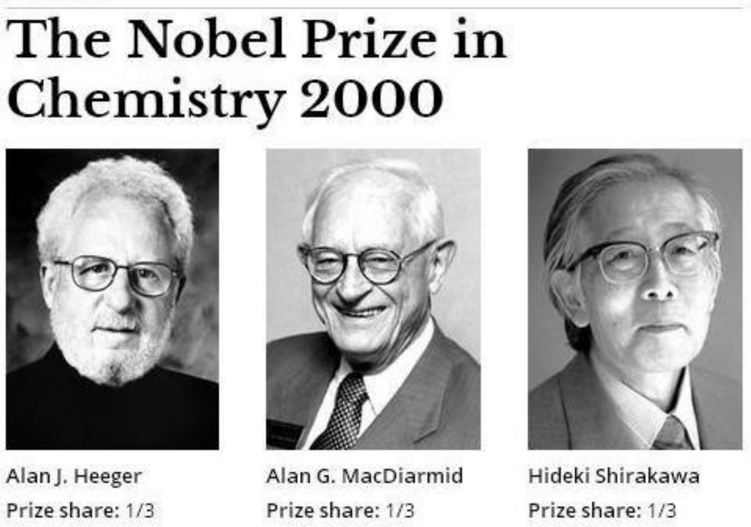
- Recycling extends the life of polymers by turning them into new materials.

Polymers can be conductive

- A serendipitous experiment in the 1970s led to the discovery of conductive polymers.
- Metals conduct electricity because their valence electrons move freely through the material.
- Electrons in delocalized π-bonds can move along a polymer by occupying nearby unfilled molecular orbitals (LUMOs).



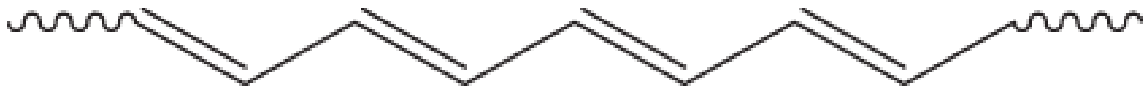

Patrick Landmann/Science Source.



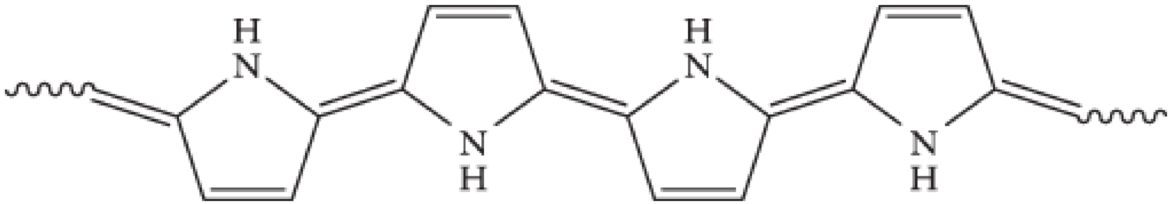
Conductive polymers - An exciting research field

- This chain arrangement allows electrons to be **delocalized** along a one-dimensional nanowire, driven by the external electric field or chemical doping.

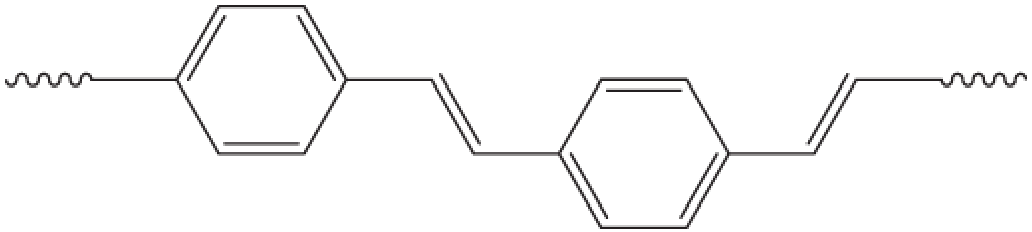
polyacetylene (the first conductive polymer)



polypyrrole

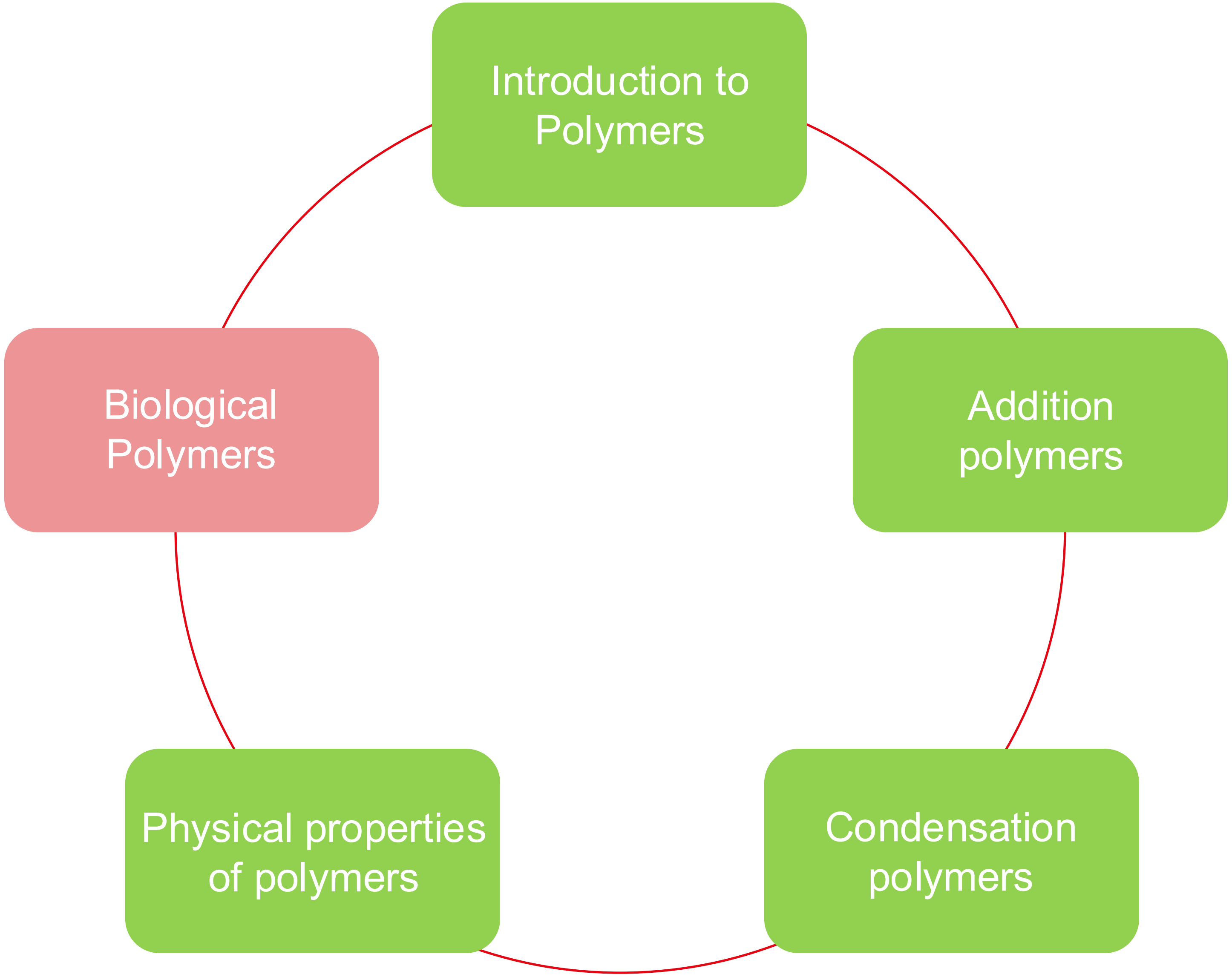


poly-p-phenylenevinylene, PPV



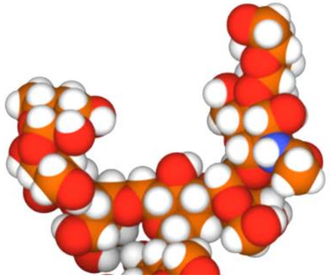
- Bond conjugation allows polymers to absorb light and convert it into energy (as in solar cells), as well as to emit light under an electric field (similar to LEDs).

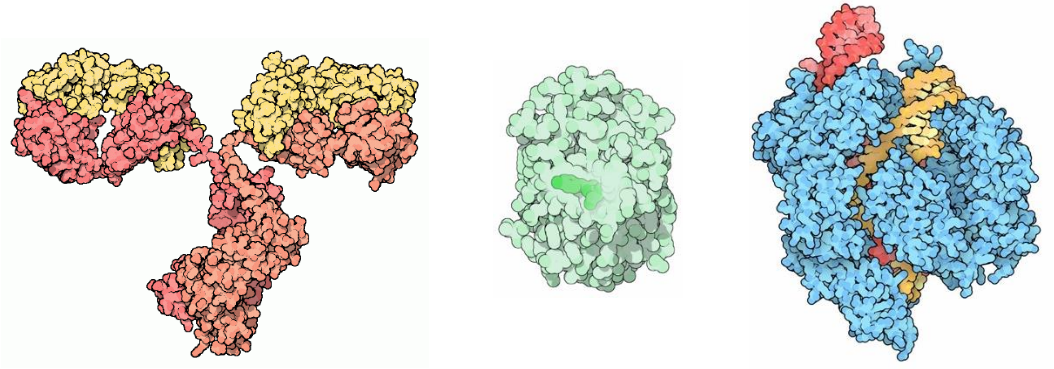
Plan


Introduction to Polymers
Addition polymers
Condensation polymers
Physical properties of polymers
Biological Polymers

The main types of biomolecules

- Examples of different biomolecules and their functions





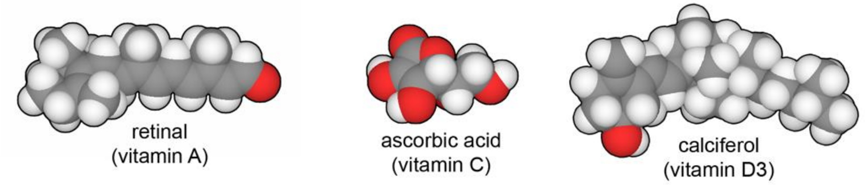
"the workhorses of the cell"

Lipids
- Building membranes
- Energy storage
- Cell signaling

Carbohydrates
- Energy storage
- Nucleic acid component
- Cell signaling

Proteins
- Enzymes
- Membrane transport
- Metabolite cariers
- Immune defense
- Structural support
- Cell motility
- Gene regulation
- Cell signaling

Nucleic acids
- Carrier of genetic information
- Enzyme components

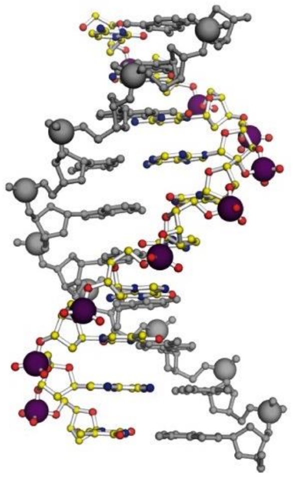


Other biomolecules
- Vitamins, metabolytes, enzyme co-factors, inorganic biomolecules, biological pigments...

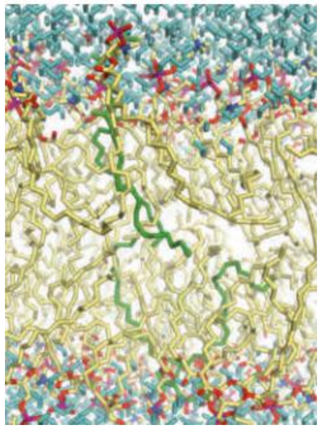
Biological macromolecules are polymers

Macromolecular Structure

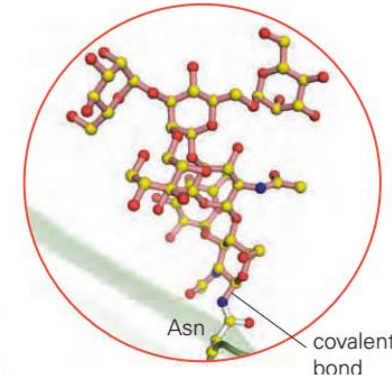
Nucleic Acids



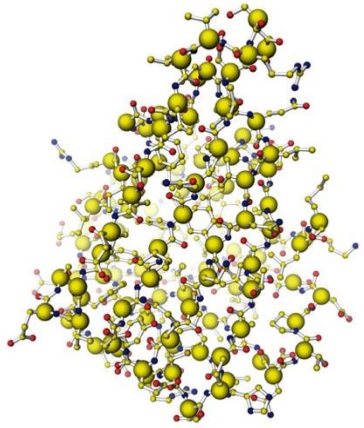
Lipids



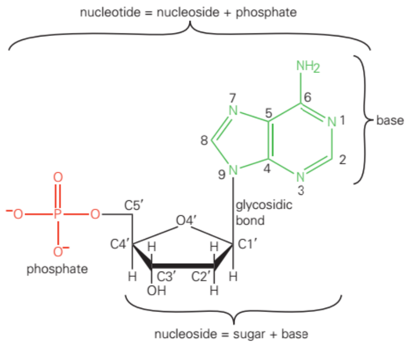
Carbohydrates



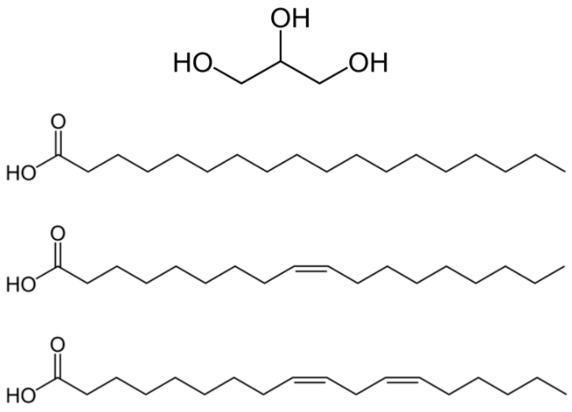
Proteins



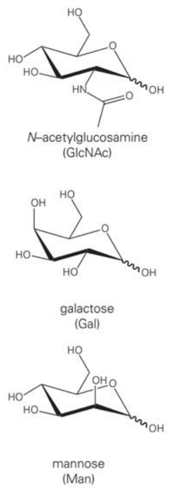
Building Block



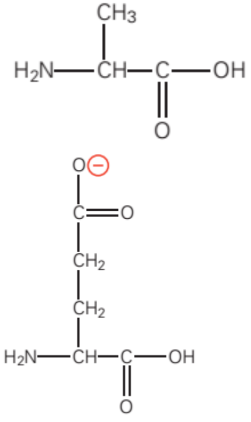
Nucleotides



Fatty acids, glycerol



Monosaccharides

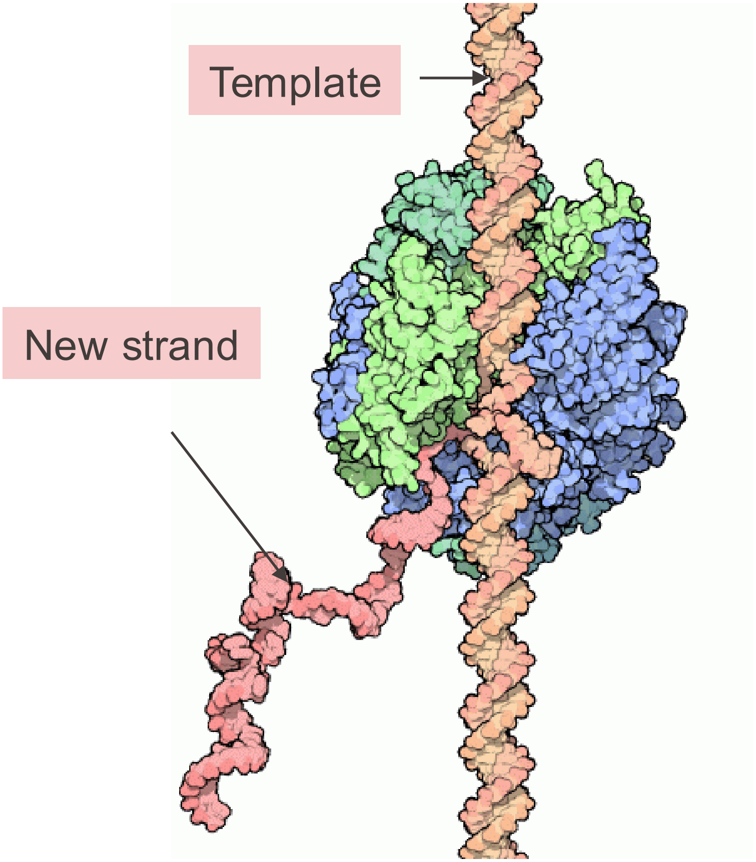


Amino acids

Unique assembly biological polymers

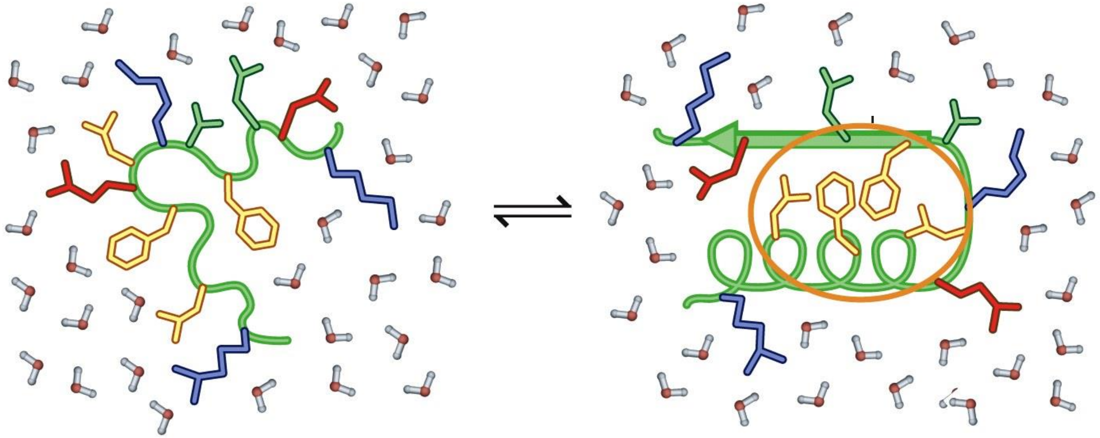
- Biological polymer assembly is unique:
  - Proteins and nucleic acids are built from defined genetic templates
  - Assembly is driven by highly specific enzymatic catalysis
  - Precise folding yields functional structures (structure → function)
  - Occurs in aqueous environments under mild conditions
  - Inherent stereochemistry shapes folding and activity
  - Each macromolecule uses a diverse set of building blocks

Template based production of RNA



Model of RNA polymerase in action (adapted from rcsb.org).

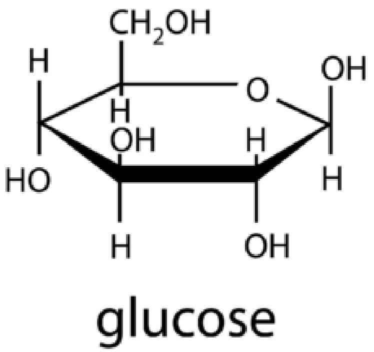
Protein folding into a functional conformation

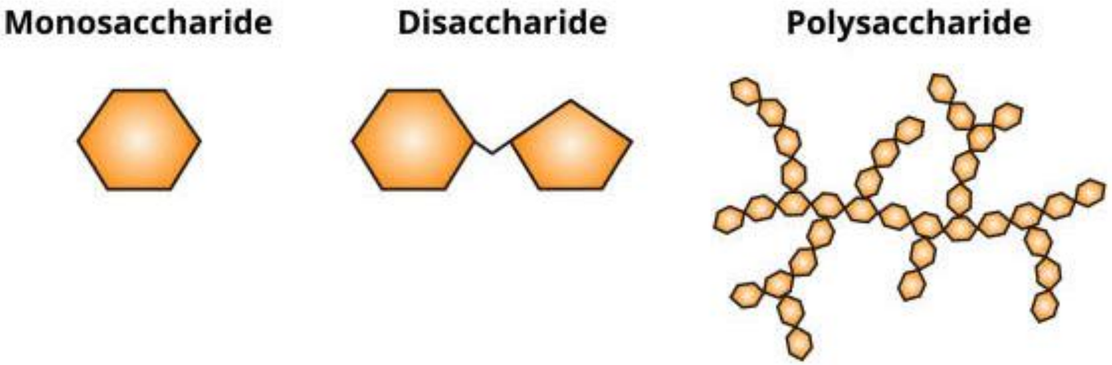


Carbohydrates

Greek: **γλυκύς** (glykys) = sweet
Sanskrit: **śarkarā** = sugar

- **Carbohydrates** all have the general formula $C_n(H_2O)_n$, which suggests they are a hydrate of carbon.
- Includes **starches**, **cellulose**, and simple sugars (e.g., **glucose**)
- Carbohydrates have many -OH groups, and so they may also be regarded as alcohols.

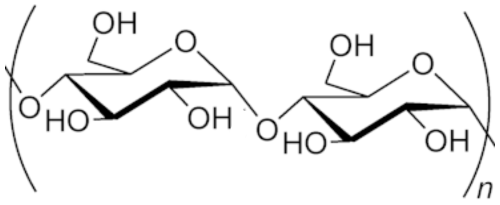




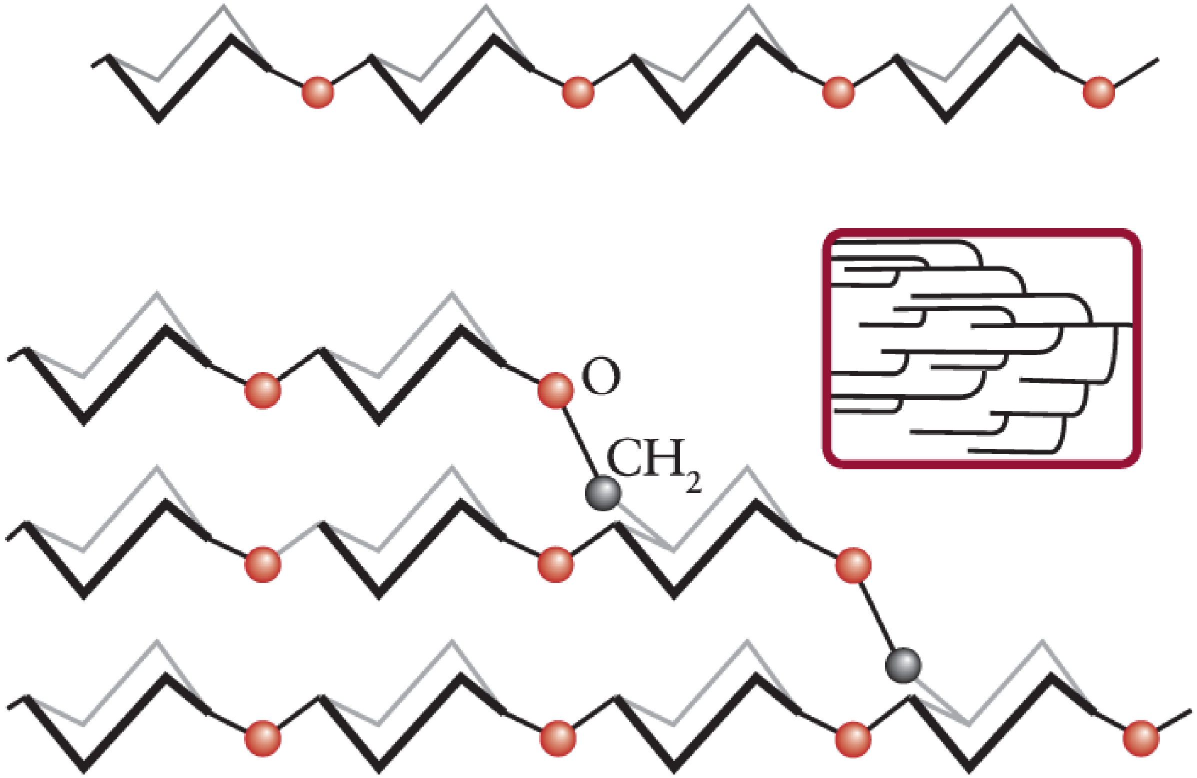
- Monosaccharides like glucose assemble into longer chains called **polysaccharides**
- Linkage is via **ether** (glycosidic) bonds established through a **condensation** reaction

Carbohydrate polymers - Starch

- Many polysaccharides are polymers made of glucose, including starch.



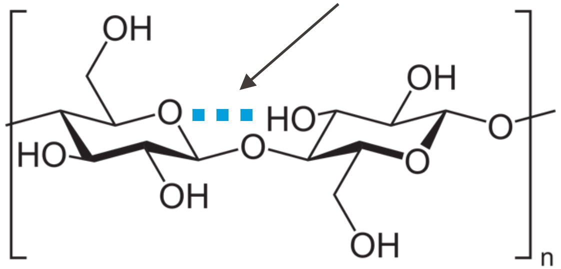
- Starch is made up of two components:
  - Unbranched chains of glucose – **amylose** (top)
  - Branched chains of glucose – **amylopectin** (bottom).



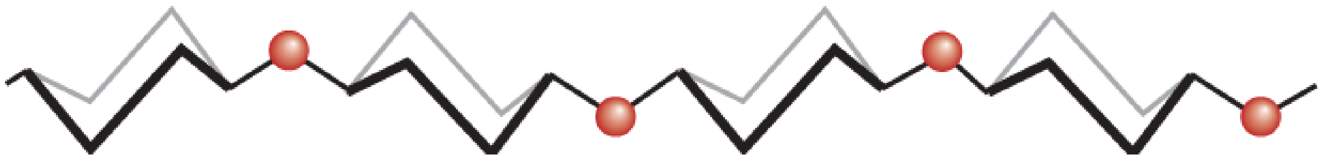
- Linkages are via specific atoms for linear chain ($C_1 \rightarrow C_4$) and branches ($C_1 \rightarrow C_6$)

Carbohydrate polymers - Cellulose

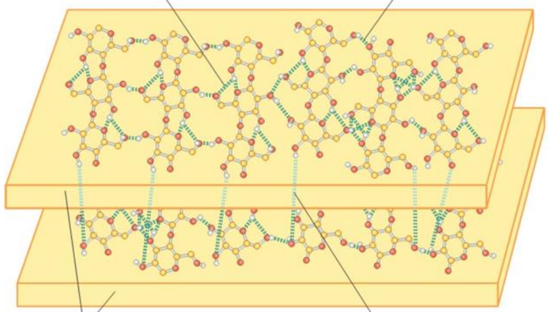
- Most abundant organic molecule and polymer in the world!



- Cellulose has the same glucose molecules, linked differently, forming flat, ribbon-like strands.



- Hydrogen bonds between cellulose chains lock them into a stable, layered structure that is more mechanically robust than starch (hence the use in paper and textile)

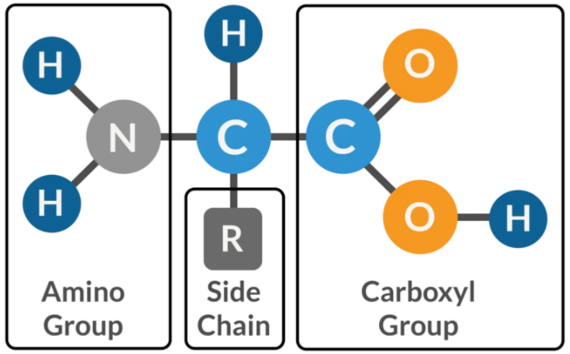


Greek: *“proteios” (πρωτεῖος)* = primary

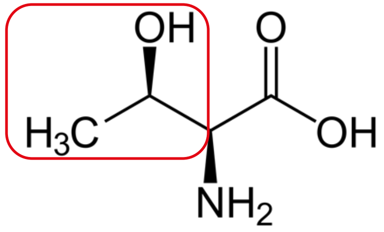
Proteins: Building blocks

- Protein molecules are condensation copolymers of up to **20 different naturally occurring amino acids**

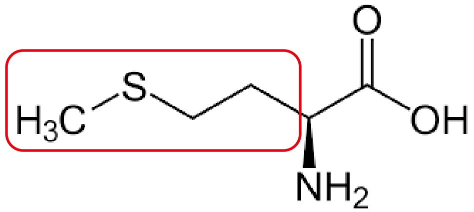
- Each amino acid has the same general structure:
  - A **central carbon atom (α-carbon)**
  - Attached to a **hydrogen atom (H)**
  - An **amino group (–NH_2)**
  - A **carboxyl group (–COOH)**
  - A **side chain (R group)** that determines its chemical properties.



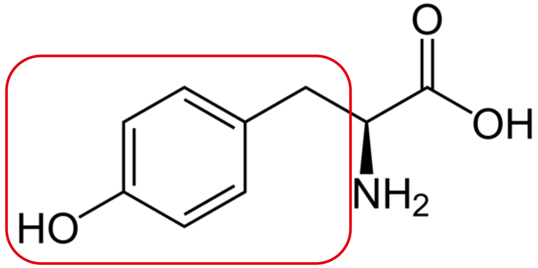
Threonine



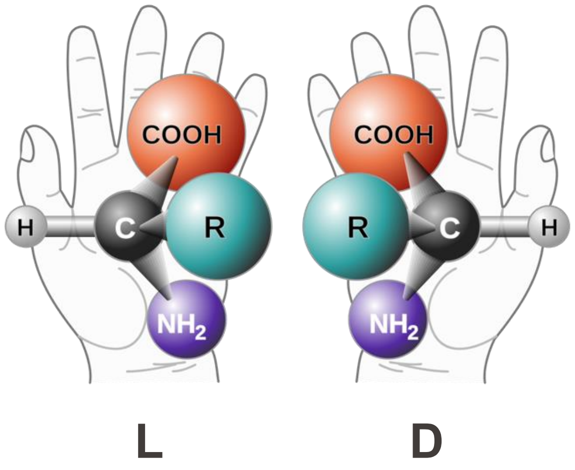
Methionine



Tyrosine

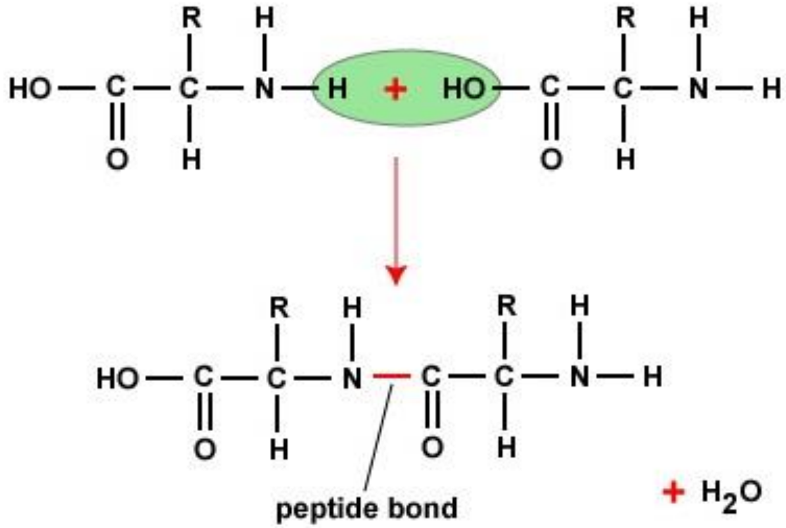


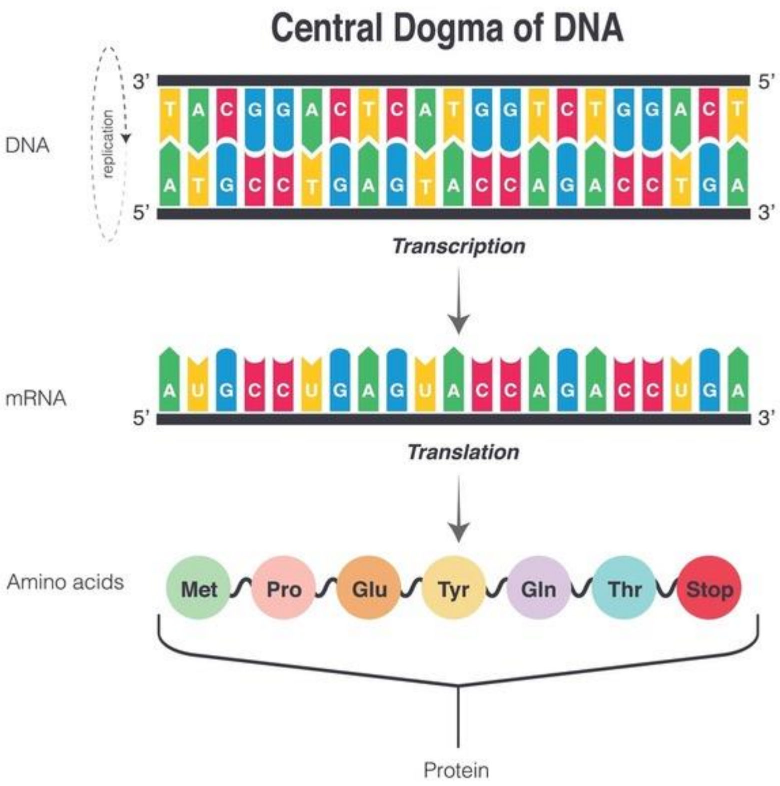
All amino acids that make proteins are in the L stereoisomeric form



Proteins: Peptide bond

- The proteins are formed through a condensation reaction that leads to the formation of amide (peptide) bond
- Typically, proteins are **linear** polymers of ~10^2-10^4 amino-acids whose exact order is defined by the corresponding gene sequence (DNA)





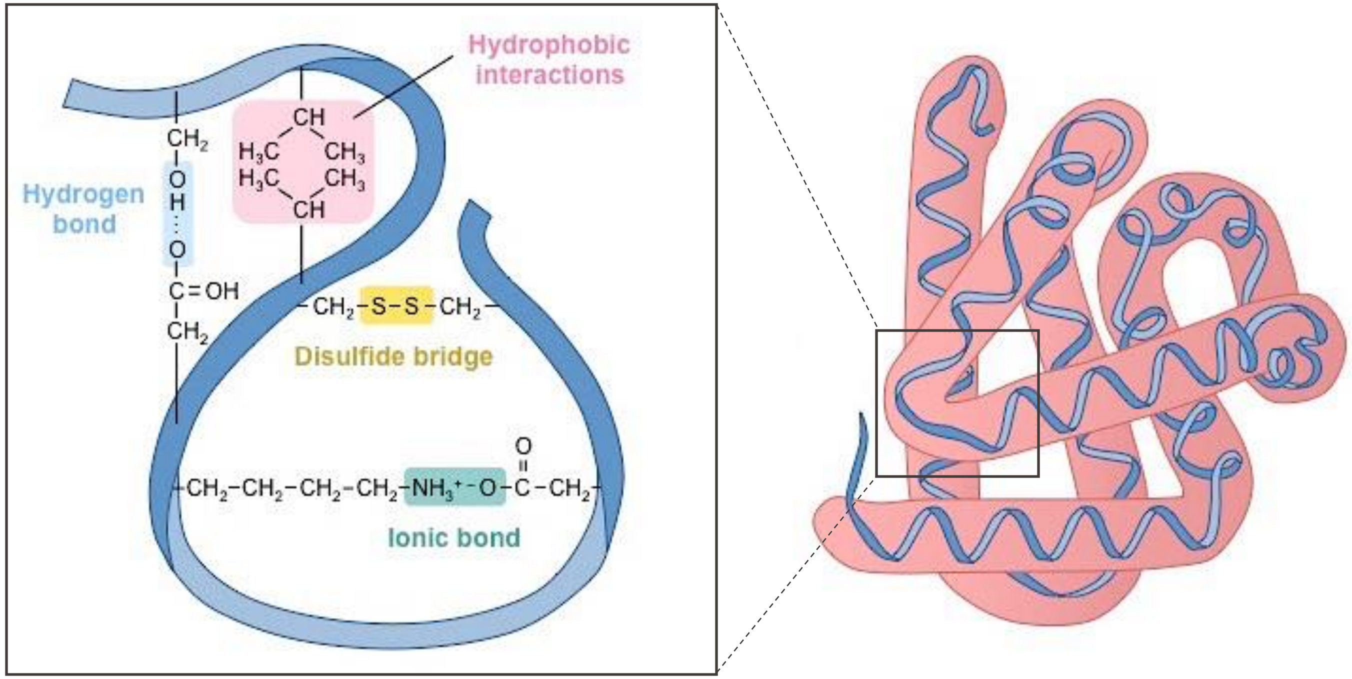
- While their backbone resembles that of simple amide polymers, the diversity of amino-acids and their precise sequential order profoundly shape protein structure and function.

Protein folding

- A protein's sequence determines how its atoms will organize in 3D space (= structure) and which molecules it can interact with.

The main types of non-covalent interactions:

- Hydrogen bonding
- London dispersion forces
- Dipole-dipole interactions
- Hydrophobic interactions
- Ionic (electrostatic) interactions

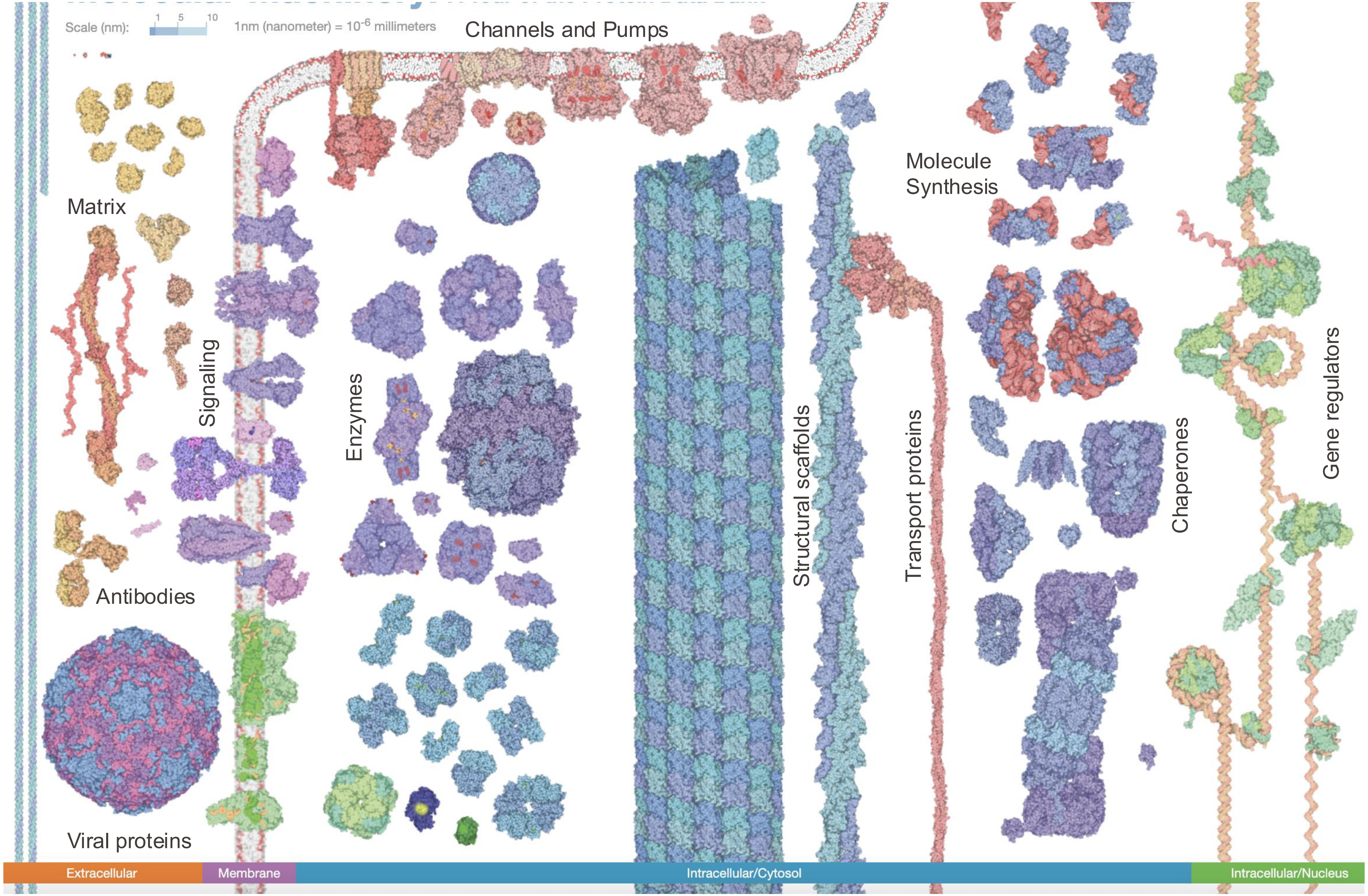


Local non-covalent interactions

Overall 3D structure

- The structure emerges from a combination of **covalent** and **non-covalent** interactions between amino acids, either adjacent in the chain or brought together during folding.

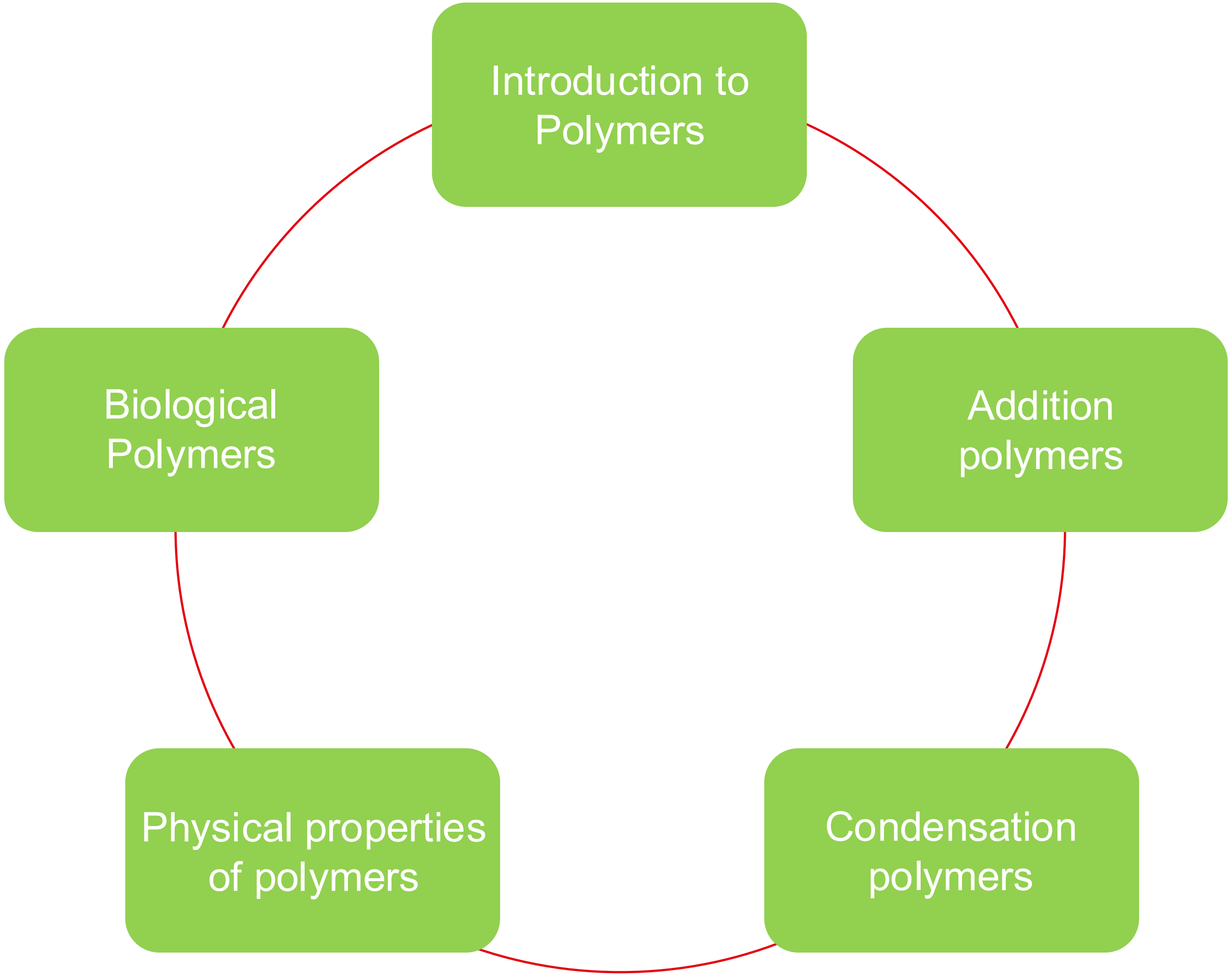
Protein diversity



Bacterial cells ~ 4’000 proteins

Human cells ~ 80’000-200’000 proteins

Plan



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