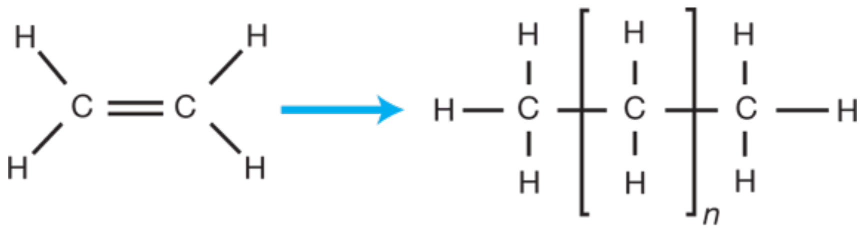
Reaction of the Day: Polyethylene



Ethylene Polyethylene

- Polyethylene is the most commonly used plastic in the world and can be made to have diverse properties.
- Over 90 million metric tons of polyethylene are produced globally each year.
- Polyethylene is used in power transmission, food packaging, consumer goods, electronics, and household goods.
- Polyethylene doesn’t biodegrade but does undergo photodegradation – light causes polyethylene chains to break, and so the pieces of plastic get smaller over time.
- Plastics like polyethylene have even been found 36,000 feet deep in the Mariana Trench.

aiche.org
Sciencedirect.com
Strom, E. T.; Rasmussen (2011)
Nationalgeographic.com

Today's Overview

- **Polymers**
  - Addition Polymerization vs. Condensation Polymerization
  - Cross-Linking
  - Elastomers, Thermoplastics, Thermosets
- **What do these have in common?**

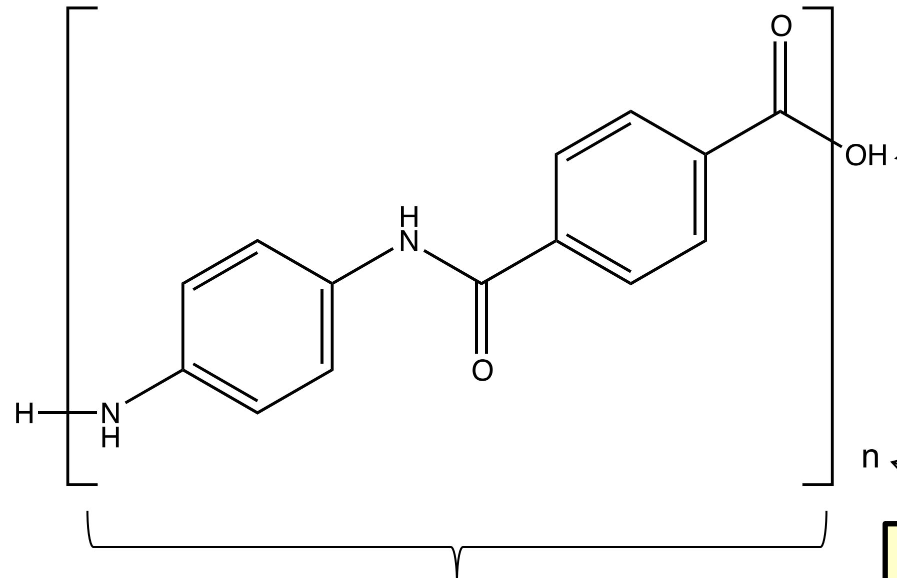
What are Polymers?

- **Polymer: Chain-like molecule composed of many (poly-) repeating structural units called monomers (-mers).**
  - Monomers can be any building block that connects together.

- **Natural Polymers:**
  - Rubber, leather, wool, DNA, proteins
- **Synthetic Polymers:**
  - Polyethylene, polypropylene, polyester, nylon, polyvinylchloride

Structure of a Polymer (Kevlar)

Terminal group:
This is where the next monomer can be added.



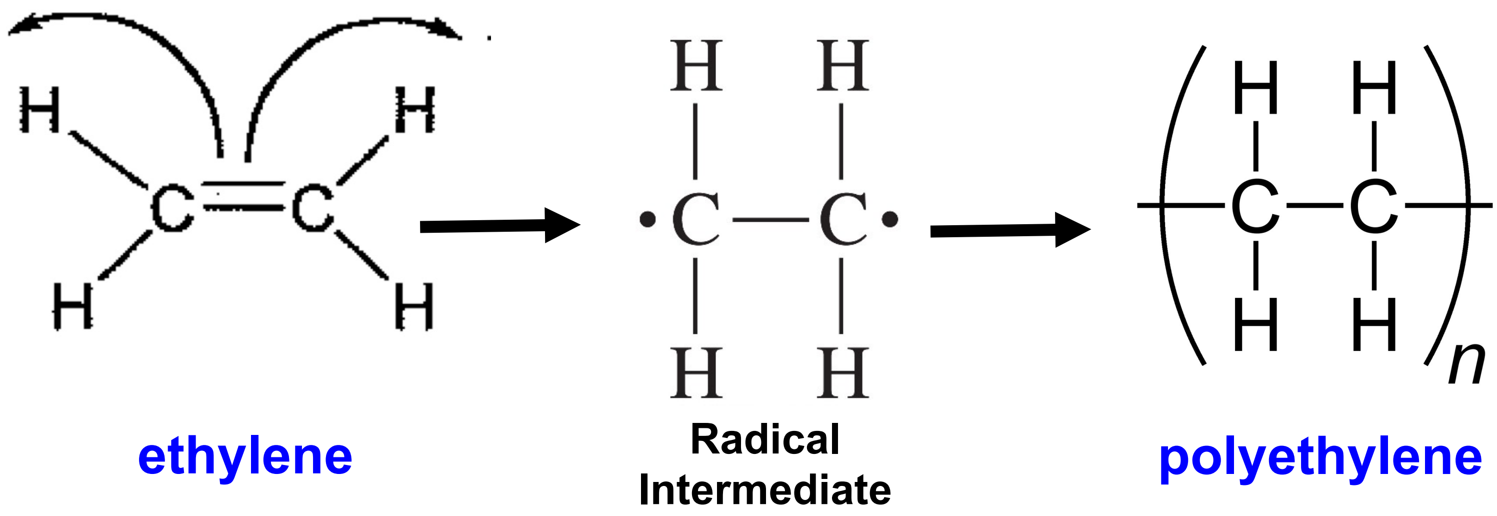
Terminal group.

Repeating Unit (Monomer)
Contained in Brackets

Number of monomers in a polymer chain.

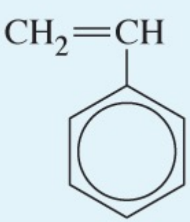
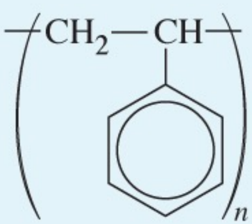
Addition Polymerization (Chain-Reaction Polymerization)

- **Double bonds open up to form "radical" unpaired electrons at the end of each chain.**
  - Formation of a bond is more stable than unpaired electrons, therefore these continue to build in a chain-reaction.



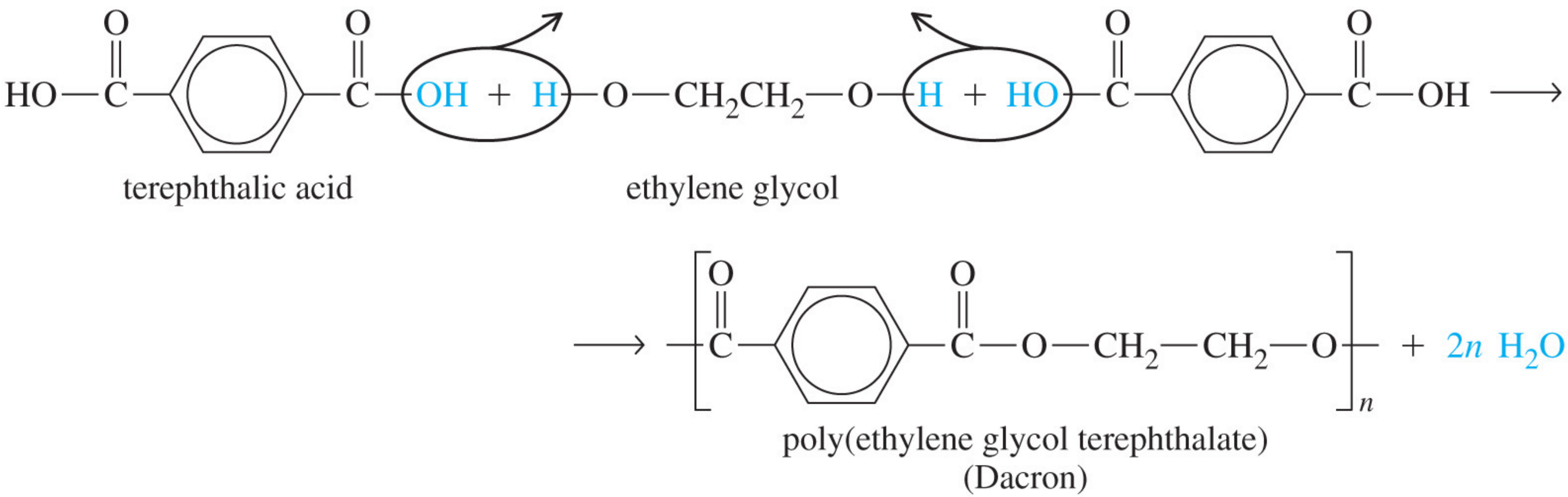
Common Addition Polymers

TABLE 27.5 Some Polymers Produced by Chain-Reaction Polymerization

Name	Monomer	Polymer	Uses
Polyethylene	$CH_2{=}CH_2$	$-\!\left(CH_2-CH_2\right)_n\!-$	Bags, bottles, tubing, packaging film
Polypropylene	$CH_2{=}CHCH_3$	$\left(CH_2-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}\right)_n$	Laboratory and household ware, artificial turf, surgical casts, toys
Poly(vinyl chloride) PVC	$CH_2{=}CHCl$	$\left(CH_2-\underset{\displaystyle Cl}{\underset{\mid}{CH}}\right)_n$	Bottles, floor tile, food wrap, piping, hoses
Poly(tetrafluoroethylene), Teflon	$CF_2{=}CF_2$	$-\!\left(CF_2-CF_2\right)_n\!-$	Bearings, insulation, nonstick surfaces, gaskets, industrial ware
Polystyrene			Packaging, refrigerator doors, cups, ice buckets, and coolers (as foam)

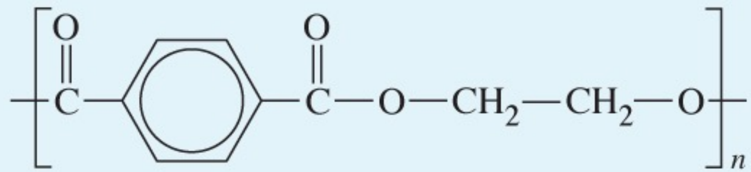
Condensation Polymerization (Step-Reaction Polymerization)

- **Two molecules join together and often eliminate a small molecule such as H_2O.**



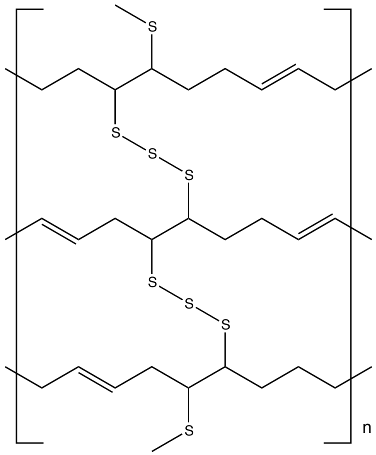
Common Condensation Polymers

TABLE 27.6 Some Polymers Produced by Step-Reaction Polymerization

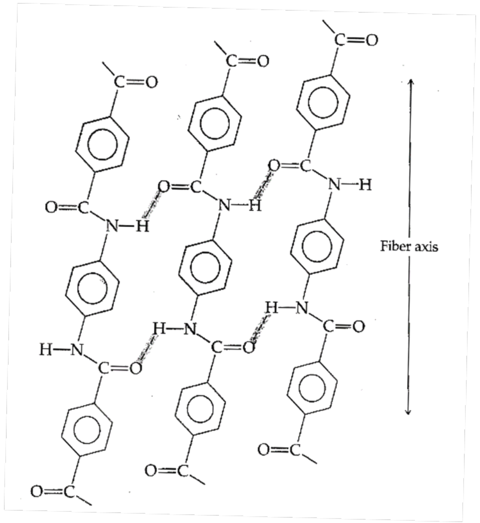
Name	Monomer	Polymer	Uses
Poly(ethylene glycol terephthalate) (Dacron)	$HOCH_2CH_2OH$ and 		Textile fabrics, twine and rope, fire hoses, plastic containers
Poly(hexamethyleneadipamide) nylon 66	$H_2N(CH_2)_6NH_2$ and $HOOC(CH_2)_4COOH$	$\left[\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-NH-(CH_2)_6-NH \right]_n$	Hosiery, rope, tire cord, parachutes, artificial blood vessels
Polyurethane	$HO(CH_2)_4OH$ and $OCN(CH_2)_6NCO$	$\left[O-(CH_2)_4O-\underset{O}{\underset{\Vert}{C}}-\overset{H}{\overset{\vert}{N}}-(CH_2)_6\overset{H}{\overset{\vert}{N}}-\underset{O}{\underset{\Vert}{C}} \right]_n$	Spandex fibers, bristles for brushes, cushions and mattresses (as foam)

Cross-Linking Connects Polymer Chains via Covalent Bond Formation or IMFs

- **Covalent bond formation lends properties to polymer chains that are not seen in the chains alone.**
  - Example: Isoprene into rubber via vulcanization.
- **Intermolecular forces (hydrogen bonding, dipole interactions, and dispersion forces)**
  - Example: Nylon 6,6; Kevlar
- **Polymer types, based on these properties:**
  - Thermoplastic
  - Thermoset
  - Elastomer



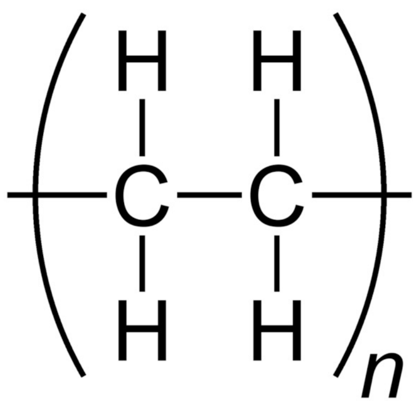
Vulcanized Rubber



Kevlar

Thermoplastic Polymers Exhibit Temperature-Dependent Properties

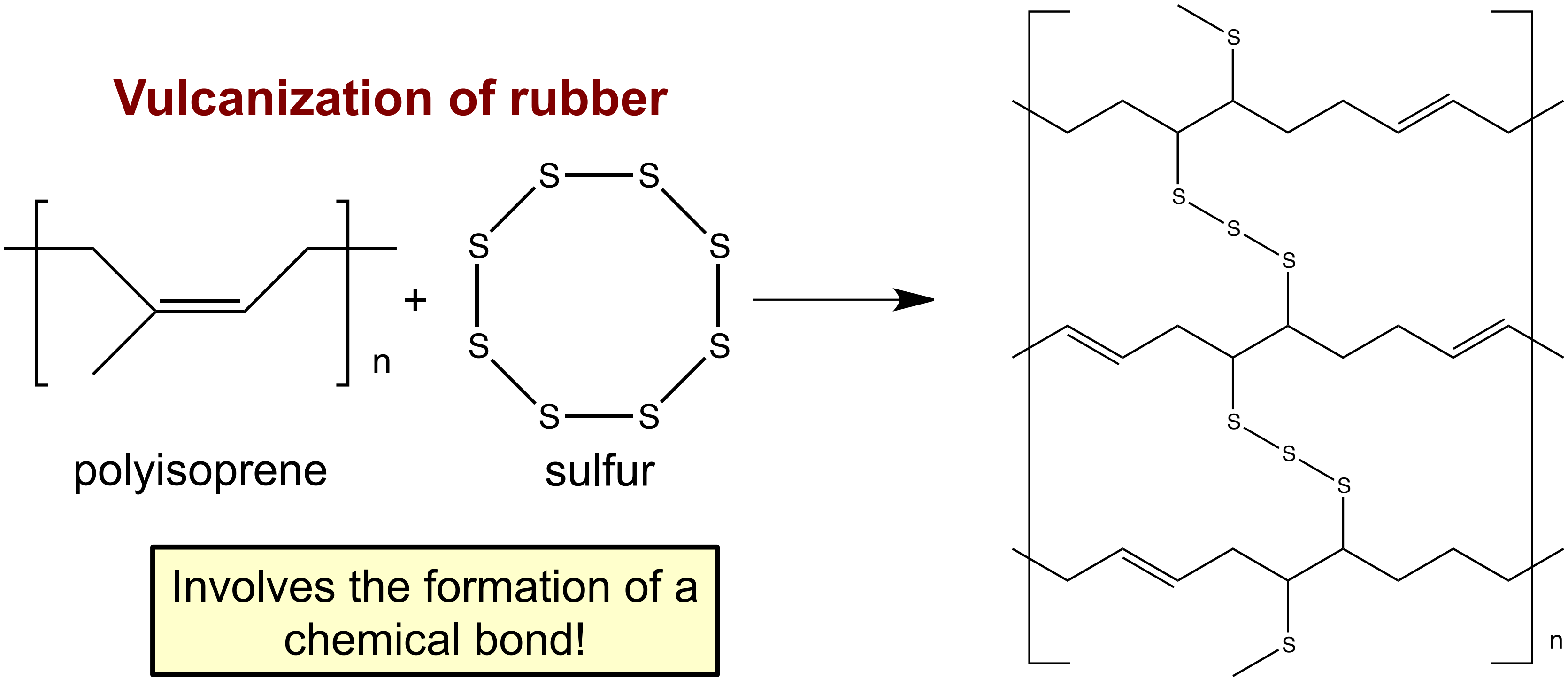
- **Above critical temperature, become fluid, or “glassy”.**
- **When cooled below critical temperature will retain shape of previous container.**
  - Reusable; Can be molded into new forms.
  - Example: Polyethylene bags



Thermoset Polymers Exhibit Irreversible Cross-Linking with Heat

- Above critical temperature, polymer undergoes irreversible cross-linking reaction.
- Upon cooling, polymer retains final form.

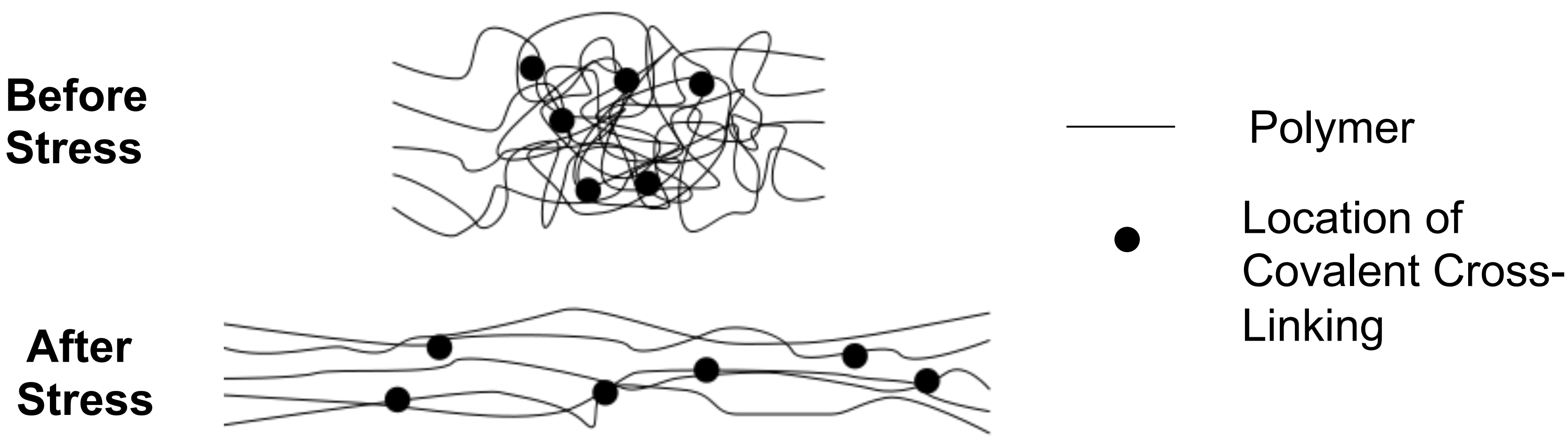
Vulcanization of rubber



Involves the formation of a chemical bond!

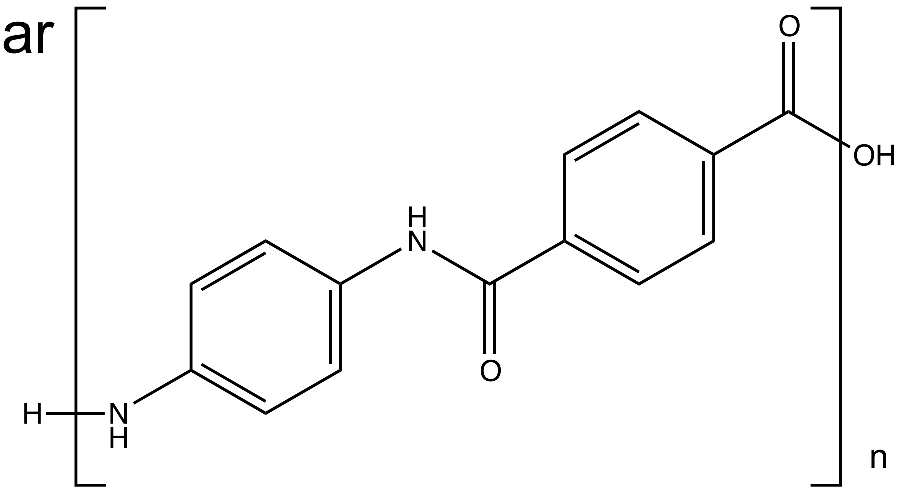
Cross-Linking in Elastomers Allows Reversible Stretching

- **Polymer reorganizes upon application of stress to redistribute force.**
  - Weak IMFs broken and re-formed to keep polymer chains associated with each other.
  - Will return to previous shape if previously "cured" or covalently cross-linked (*e.g.,* rubber).
  - Can be thermosets or thermoplastics.

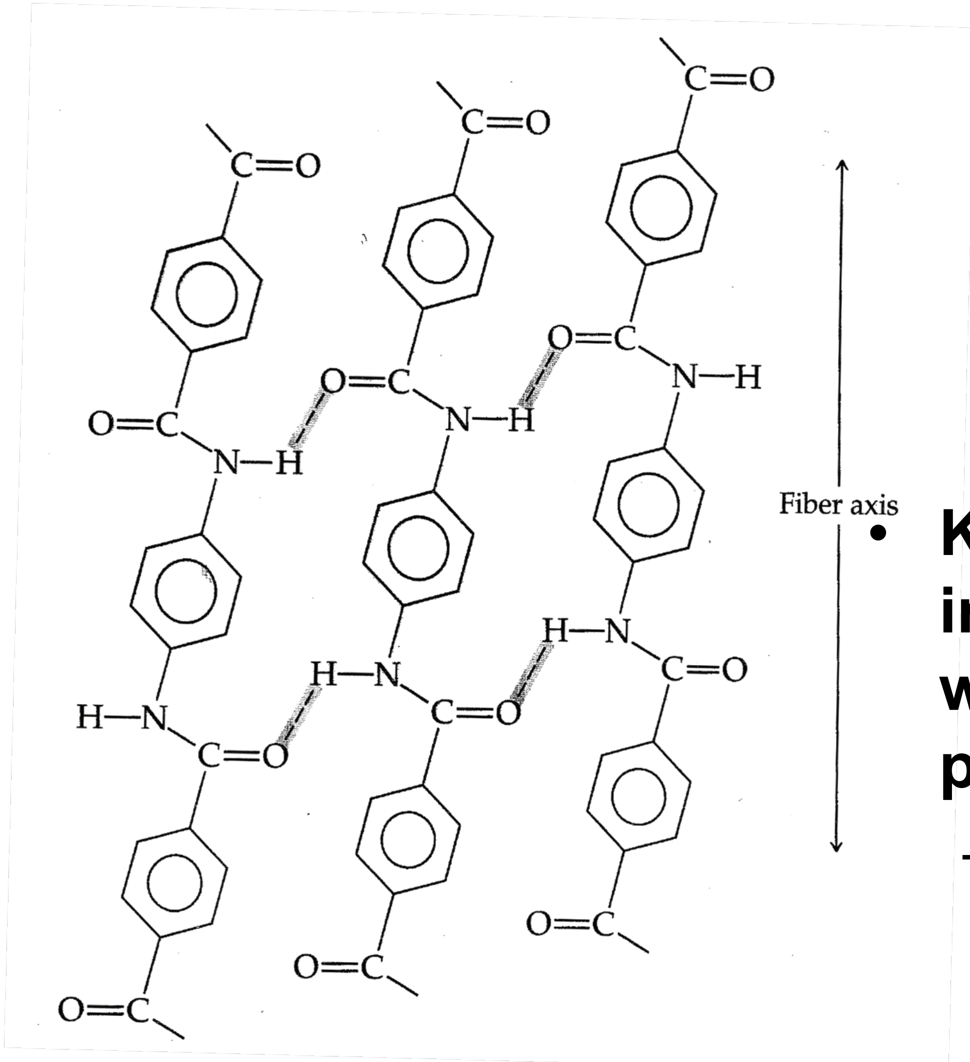


Cross-Linking via Intermolecular Forces (IMFs)

- **Depending on the monomer identity, chains may exhibit hydrogen-bonding or dipole-dipole interactions.**
  - As the polymer size increases, dispersion forces will also become important.
- **IMFs can be used to cross-link chains; however, these can be broken more easily than cross-linking via covalent bond formation.**
  - Example: Kevlar



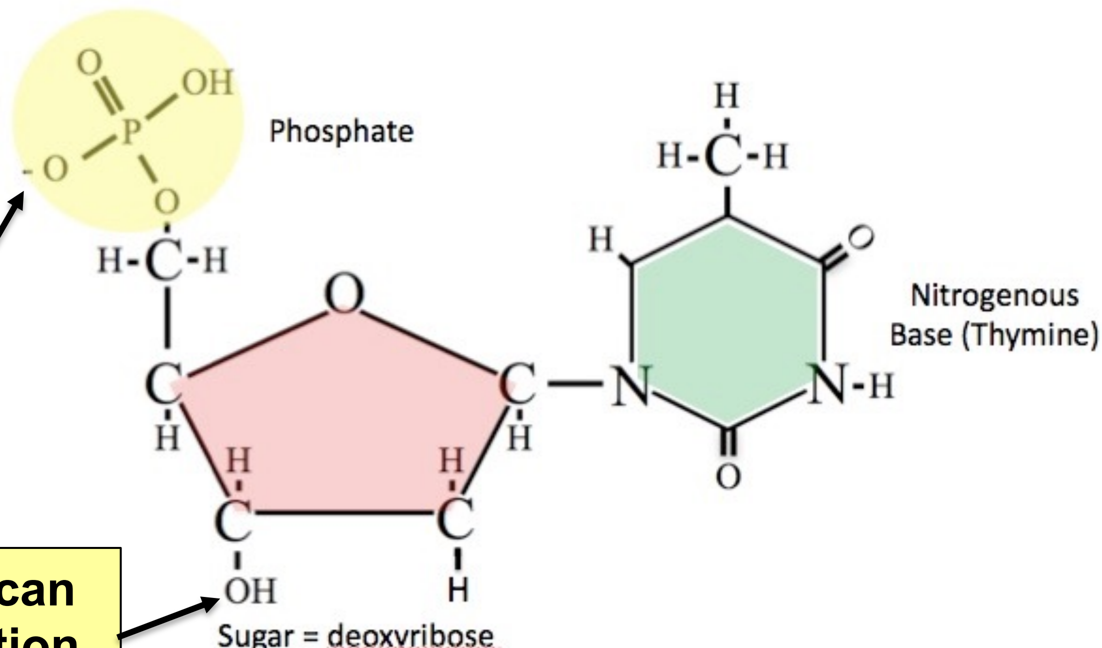
Cross-Linking of Kevlar™ Molecules via Intermolecular Forces



- **Kevlar fibers, connected via intermolecular forces, are woven into fabrics for bullet proof vests.**
  - These connections break, slowing the bullet, as it passes through.

DNA: A Polynucleotide

- **Repeating unit in DNA is a nucleotide.**
  - **Charged** phosphate group attached to deoxyribose sugar.
  - **Nitrogenous base** can be one of four components: Adenine, Cytosine, Guanine, or Thymine.

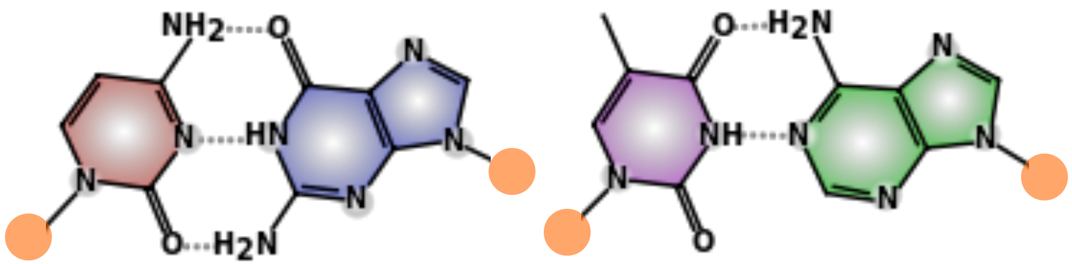


Additional Nucleotides can be added via Condensation Polymerization Here

Building Single-Stranded DNA: A High Information Content Polymer

- **Nucleotides are our building blocks.**
- **Two components can be controlled:**
  1. Length: The number of nucleotides.
  2. Base: The identity of the nucleotides.

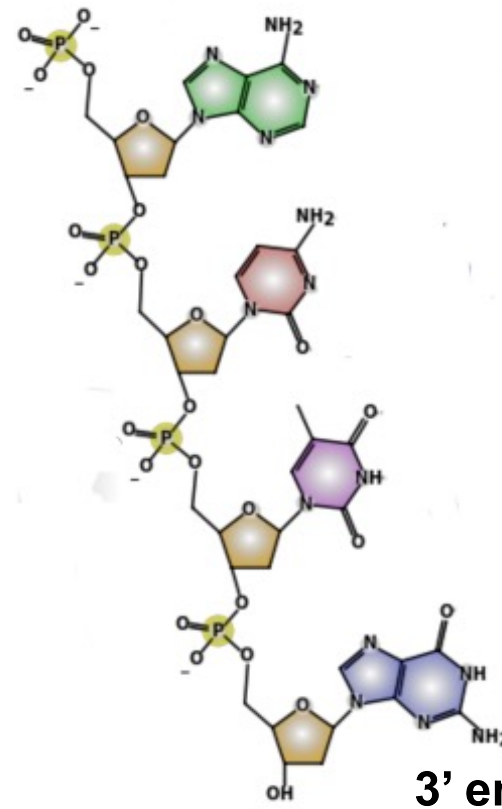
5': Ends with Phosphate
3': Ends with Sugar



Guanine   Cytosine   Thymine   Adenine

Note: These structures possess delocalized π orbitals and the ability to hydrogen bond.

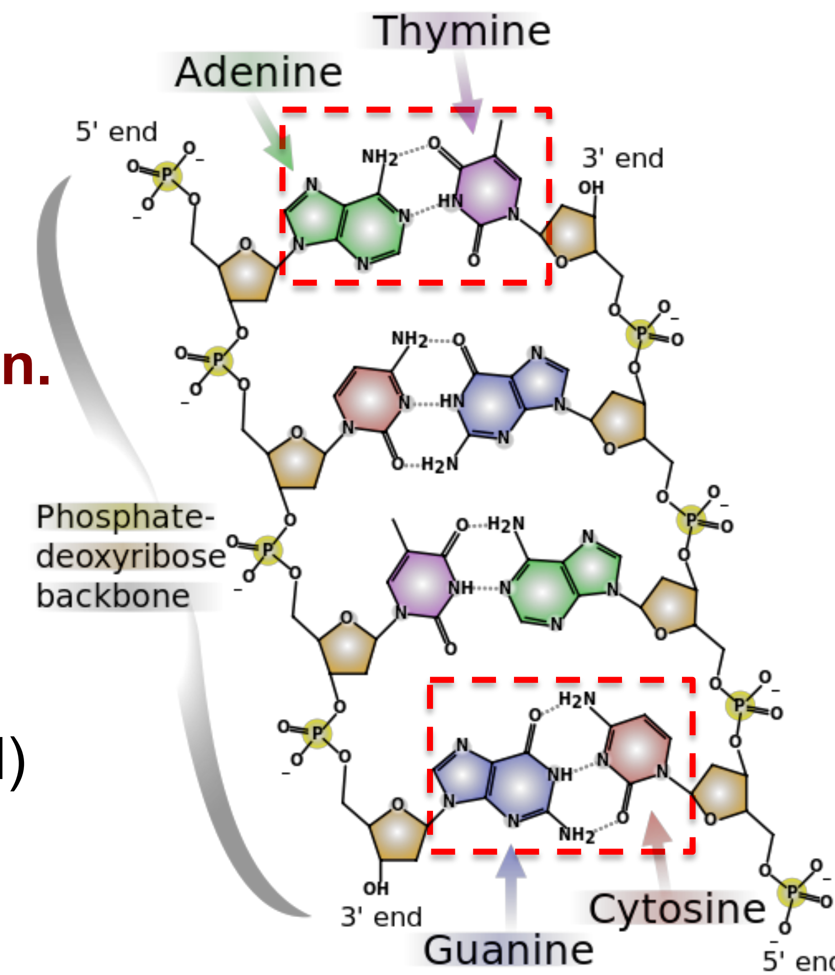
5' end



3' end

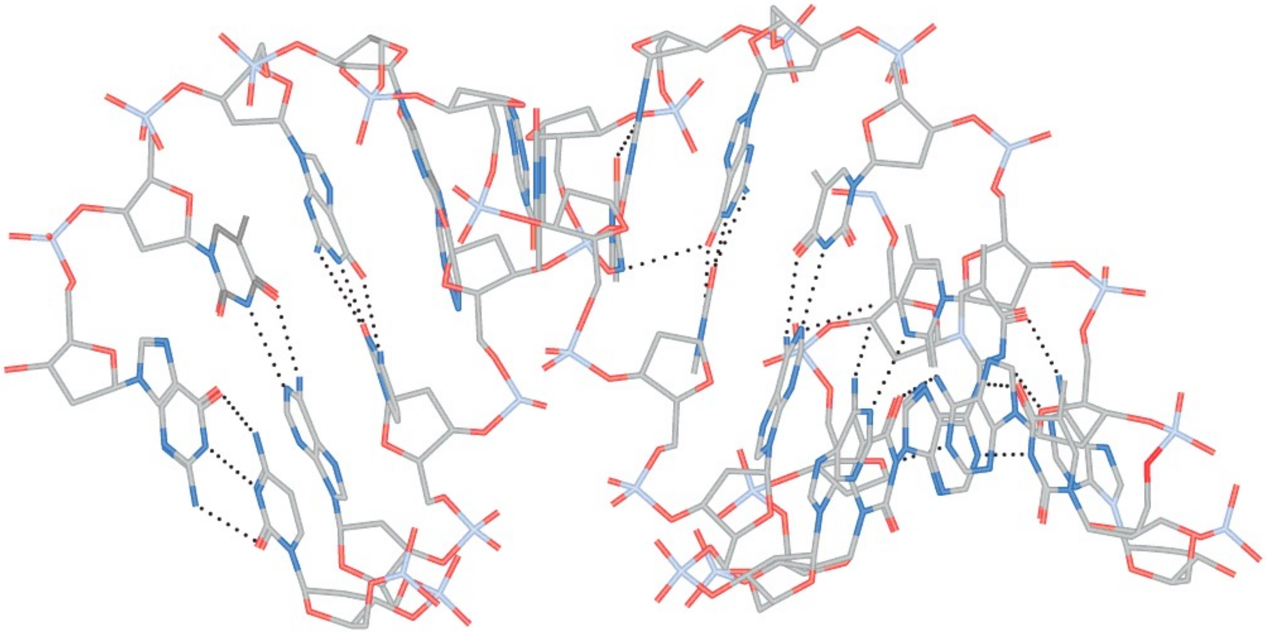
Combining Single Strands

- **Specific combinations of nucleotides will “recognize” each other and connect via hydrogen bonding.**
  - We call this process **hybridization.**
  - Adenine will connect to thymine via 2 H-bonds.
  - Guanine will connect to cytosine via 3 H-bonds.
  - Non-covalent connection (H-bond) means these can be broken and formed dynamically like in water.



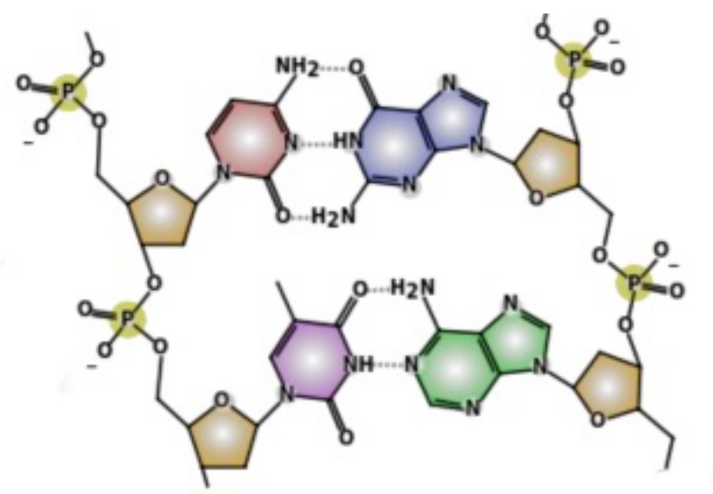
DNA Structure

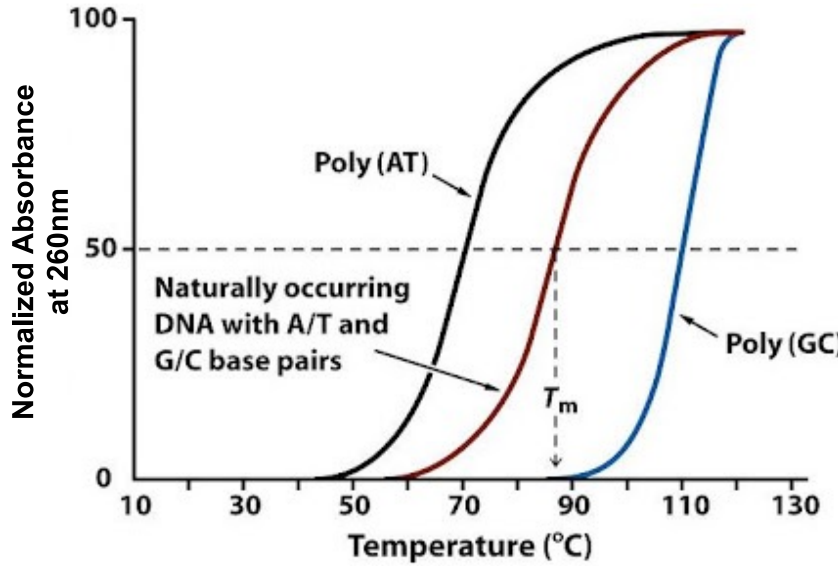
- **DNA duplexes form a double-helix structure**
  - Nitrogenous bases are along the center and the charged phosphates are along the outside.
  - Bases are stabilized in the center by **π-π stacking:** delocalized π orbitals overlap by stacking (similar to graphite).



Dehybridization Requires IMFs to be Broken Between DNA Strands

- **The more bases that are complementary between single strands (and the more G-C content), the more intermolecular forces.**
- **To separate these strands requires energy to break IMFs.**
  - Energy can come from the surroundings as temperature.



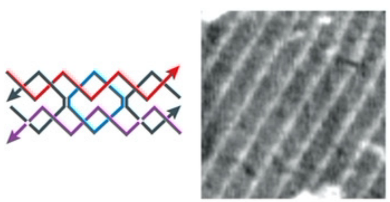


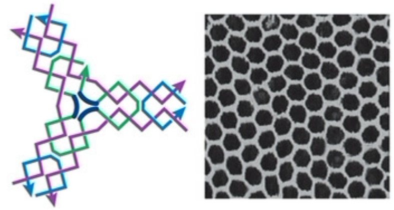
Q: Which of these DNA strands will have the greatest binding strength?

1. 3' AAGG 5' and 5' TTCC 3'
2. 3' AAGG 5' and 5' AAGG 3'
3. 3' GGCCGG 5' and 5' CCGGCC 3'
4. 3' TTACTA 5' and 5' AATGTT 3'

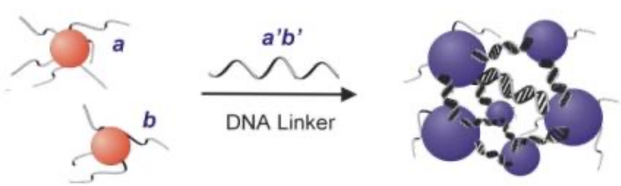
Uses of Synthetic DNA
(To Be Discussed Next Lecture)

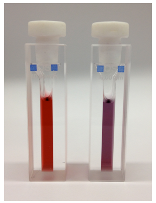
- **Making designer materials – DNA Nanotechnology. Repurposing the blueprint of life for materials chemistry**





- **Probes in biodetection -- measuring the presence or absence of a natural RNA or DNA sequence associated with a viral, bacterial, or genetic disease.**





- **Genetic medicines – specific sequences can intercept cellular machinery like RNA to stop the production of disease-causing proteins.**

Science, **1997**, *277*, 1078; *J. Am. Chem. Soc.* **2003**, *125*, 6, 1643; *Nature Rev. Mater.* **2018,** *3,* 17068.