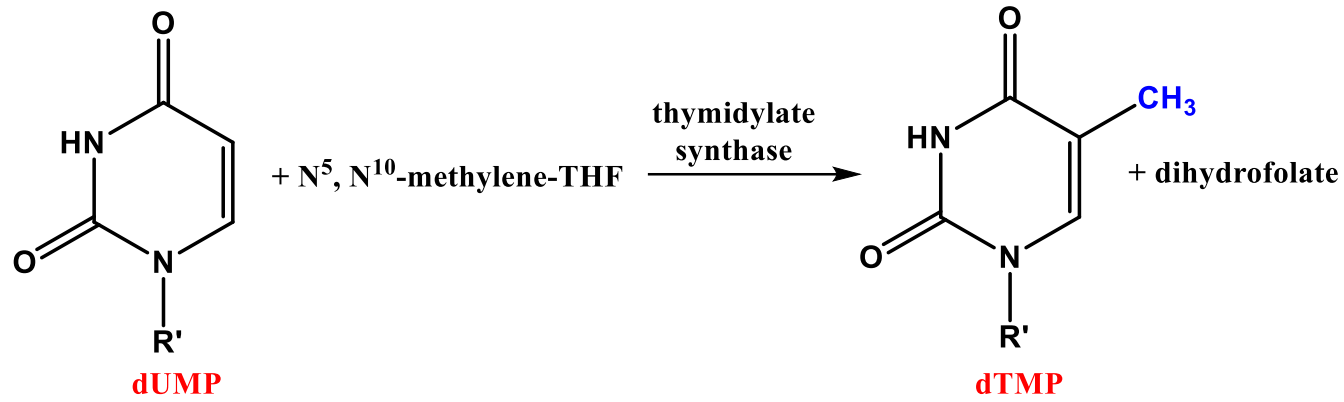


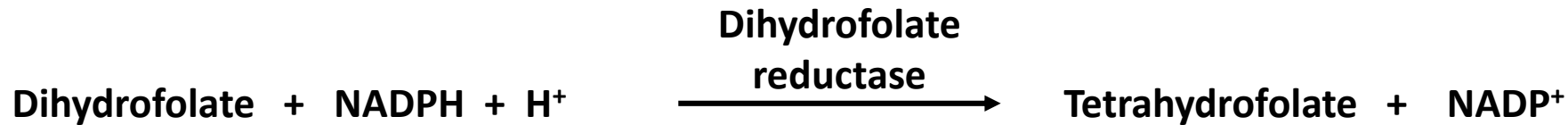
COURSE : SC202 (CHEMISTRY)
DR. SANGITA TALUKDAR
LECTURE-13
DATE: 8.2.2021

Important Conversions of dUMP and cytosine

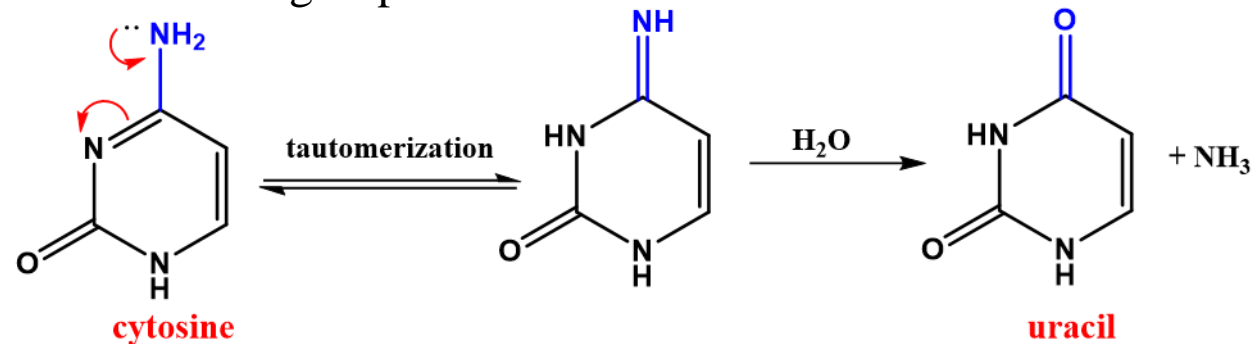
1. dTMP is formed when dUMP is methylated, with coenzyme N⁵, N¹⁰-methylenetetrahydrofolate supplying the methyl group.



R' = 2'-deoxyribose-5-P



2. Cytosine can tautomerize to form an imine, which can be hydrolyzed to uracil. The overall reaction is called a **deamination** since it removes an amino group



Thus, the presence of thymine instead of uracil in DNA prevents potentially lethal mutations..

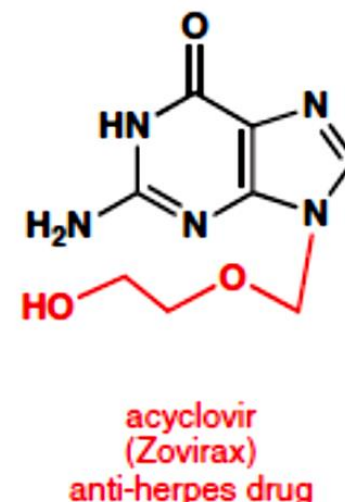
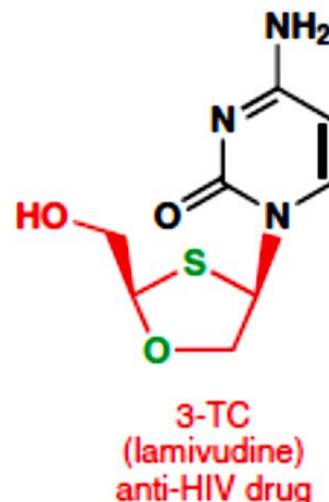
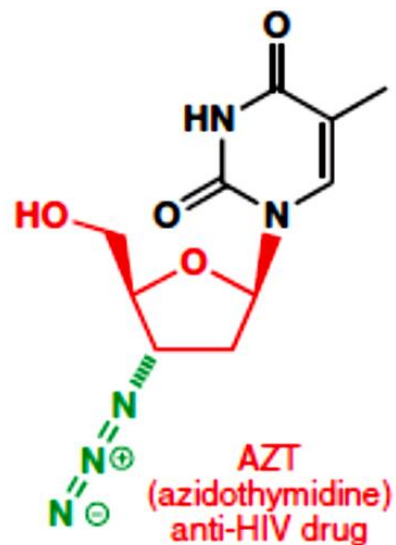
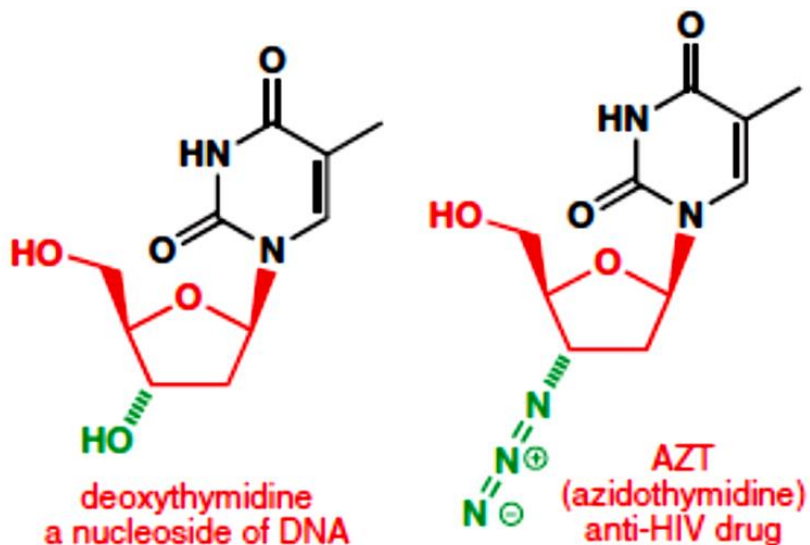
There are three kinds of RNA—

messenger RNA (mRNA) whose sequence of bases determines the sequence of amino acids in a protein, **ribosomal RNA (rRNA)**, a structural component of ribosomes, and **transfer RNA (tRNA)**, the carriers of amino acids for protein synthesis.

HIV and AIDS are treated with modified nucleosides

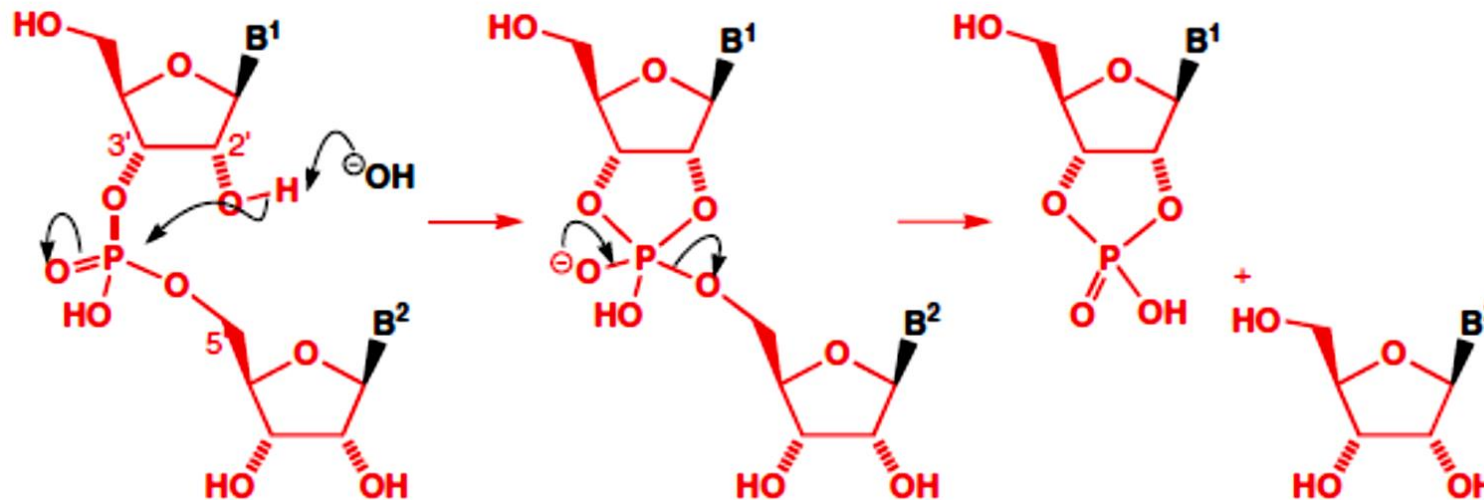
Modified nucleosides are among the best antiviral compounds.

1. The anti-HIV drug AZT (zidovudine) is a slightly modified DNA nucleoside (3'-azidothymidine). It has an azide at C3' instead of the hydroxyl group in the natural nucleoside.
2. Another modified nucleoside 3-TC (lamivudine) is active against AZT-resistant viruses. This drug is based on cytosine with the sugar replaced by a different heterocycle.
3. Acyclovir (Zovirax), the cold sore (herpes) treatment, is a modified guanosine in which there is no ring at all and no stereochemistry.

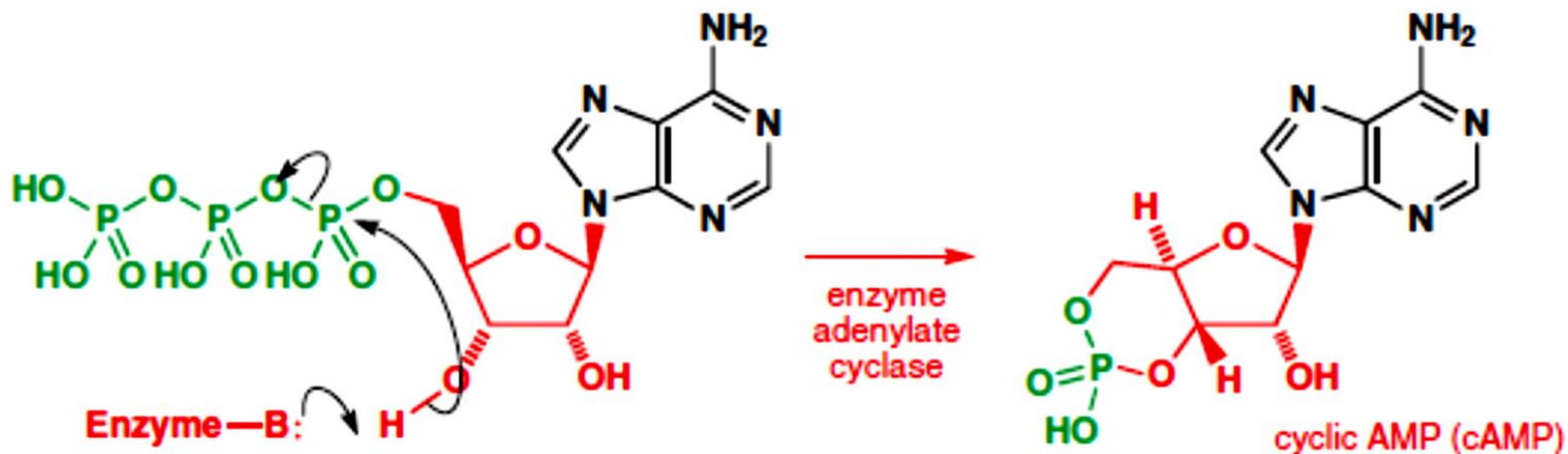


Cyclic nucleosides and stereochemistry

DNA is more stable than RNA because its sugars lack the 2' hydroxyl groups. In ribonucleic acids, the fact that the 2'- and 3'-OH groups are on the same side of the ring makes alkaline hydrolysis exceptionally rapid by intramolecular nucleophilic catalysis.



Another cyclic phosphate is important as a biological messenger that helps to control such processes as blood clotting and acid secretion in the stomach. It is cyclic AMP (cAMP), formed enzymatically from ATP by nucleophilic displacement of pyrophosphate by the 3'-OH group.



Lipids

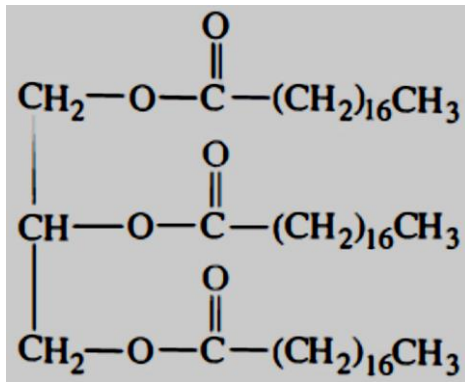
Lipids (fats) are the important components of cell membranes. Steroids, prostaglandins, fats, oil, waxes, terpenes, and even the colorful carotenes in the falling leaves are all lipids.

There are two major classes of lipids: complex lipids and simple lipids.

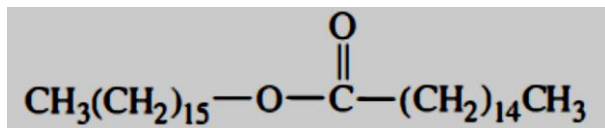
Complex lipids are those that are easily hydrolyzed to simpler constituents. Most complex lipids are esters of long-chain carboxylic acids called fatty acids. The two major groups of fatty acid esters are waxes and glycerides. Waxes are esters of long-chain alcohols, and glycerides are esters of glycerol.

Simple lipids are those that are not easily hydrolyzed by aqueous acid or base.

Examples of complex lipids

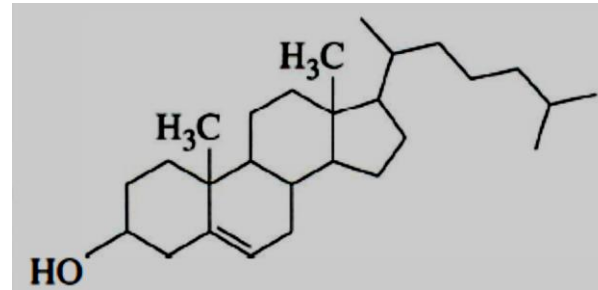


tristearin, a fat

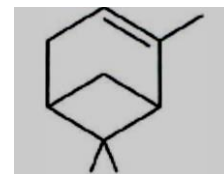


spermaceti (cetyl palmitate), a wax

Examples of simple lipids



cholesterol, a steroid

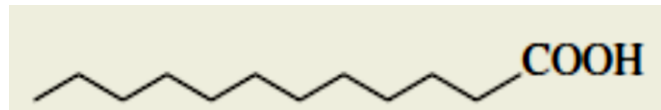


α -pinene, a terpene

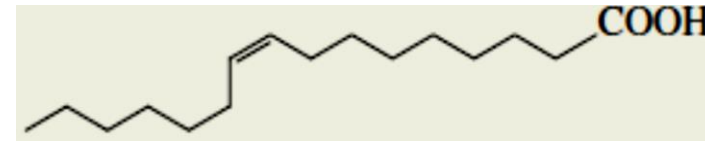
Examples of lipids. Complex lipids contain ester functional groups that can be hydrolyzed to acids and alcohols. Simple lipids are not easily hydrolyzed.

Fatty acids are carboxylic acids with long hydrocarbon chains. Fatty acids can be saturated with hydrogen (and therefore have no carbon–carbon double bonds) or unsaturated (have carbon–carbon double bonds). Fatty acids with more than one double bond are called **polyunsaturated fatty acids**.

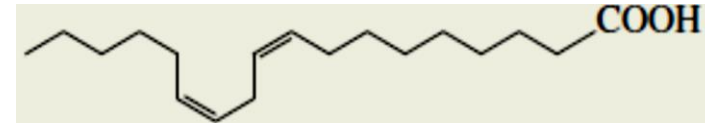
The physical properties of a fatty acid depend on the length of the hydrocarbon chain and the degree of unsaturation. The melting points of saturated fatty acids increase with increasing molecular weight because of increased van der Waals interactions between the molecules.



lauric acid (44° C)



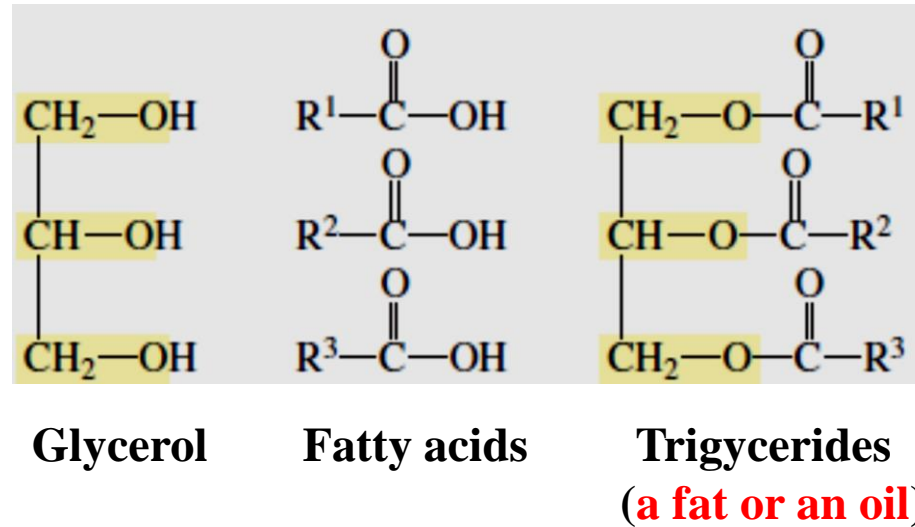
palmitoleic acid (0° C)



linoleic acid (-5° C)

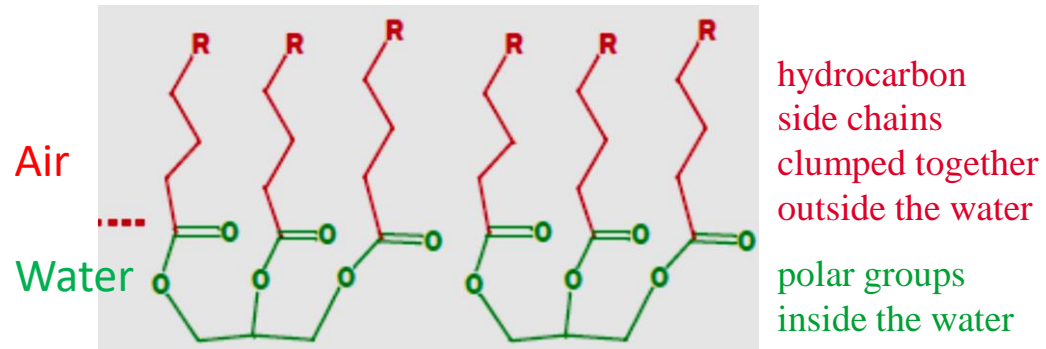
The double bonds in unsaturated fatty acids generally have the **cis** configuration. This configuration produces a bend in the molecules, which prevents them from packing together as tightly as fully saturated fatty acids. As a result, unsaturated fatty acids have fewer intermolecular interactions and, therefore, lower melting points than saturated fatty acids with comparable molecular weights. The melting points of the unsaturated fatty acids decrease as the number of double bonds increases.

Glycerides are simply fatty acid esters of the triol glycerol. The most common glycerides are triglycerides (triacylglycerols), in which all three of the glycerol – OH groups have been esterified by fatty acids.

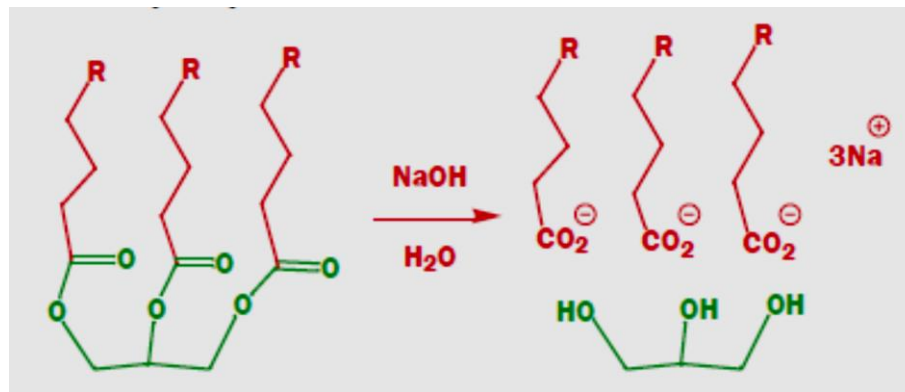


Triacylglycerols that are solids or semisolids at room temperature are called **fats**. Fats are usually obtained from animals and are composed largely of triacylglycerols with either saturated fatty acids or fatty acids with only one double bond. The saturated fatty acid tails pack closely together, giving the triacylglycerols relatively high melting points, causing them to be solids at room temperature.

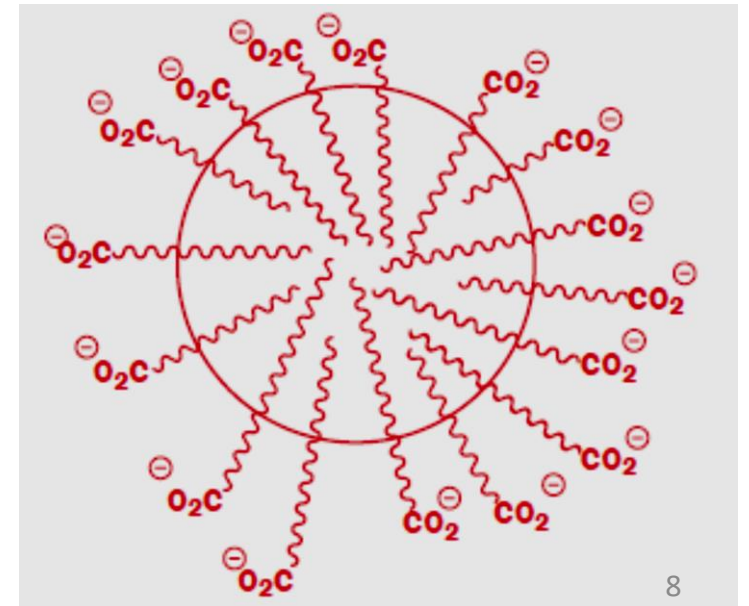
Liquid triacylglycerols are called **oils**. Oils typically come from plant products such as corn, soybeans, olives, and peanuts. They are composed primarily of triacylglycerols with unsaturated fatty acids that cannot pack tightly together. Consequently, they have relatively low melting points, causing them to be liquids at room temperature.



When triglycerides are boiled up with alkali, the esters are hydrolysed and a mixture of carboxylate salts and glycerol is formed. This was how soap was made—hard soap was the sodium salt and soft soap the potassium salt.

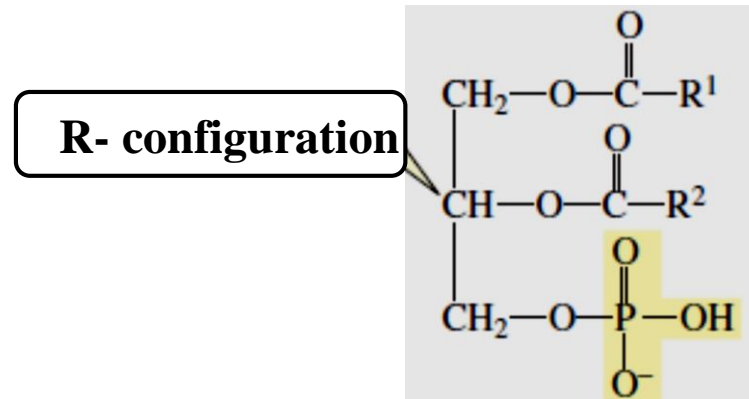


When a soap is suspended in water, the carboxylate groups have a strong affinity for the water and so oily globules or **micelles** are formed with the hydrocarbon side chain inside. It is these globules that remove greasy dirt from you or your clothes.



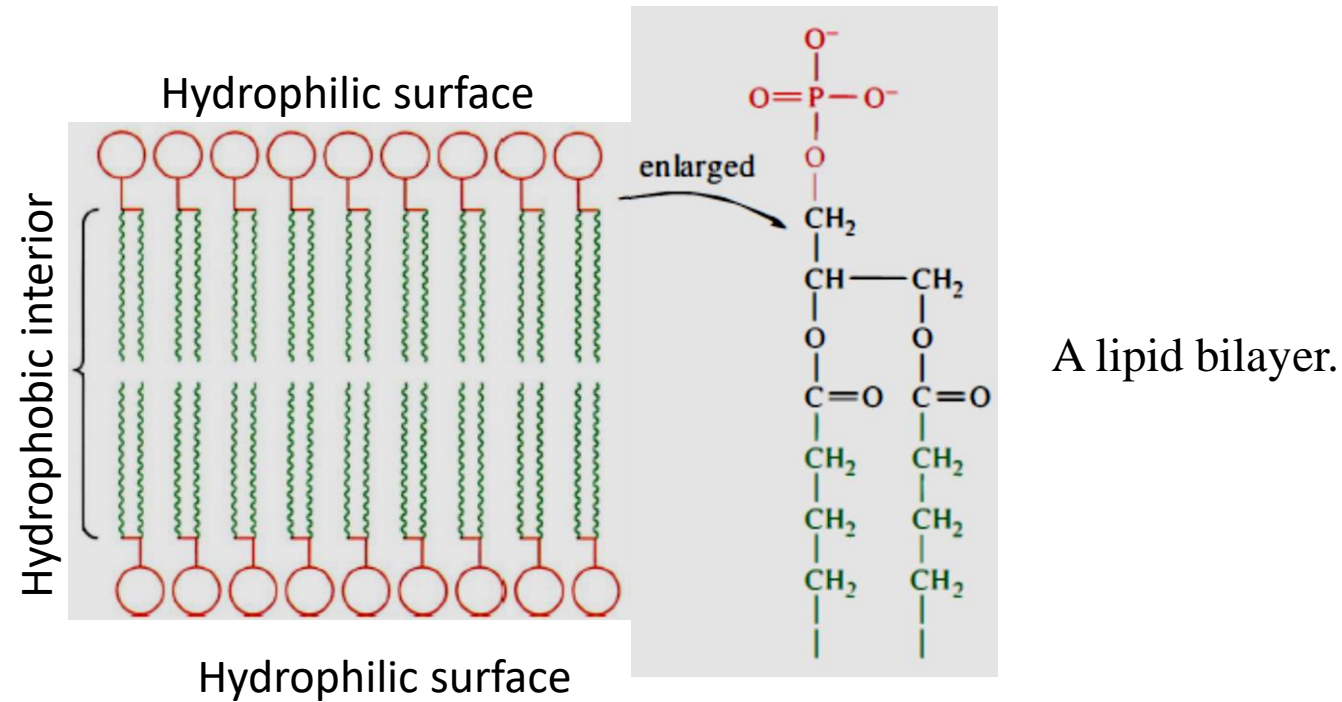
Phospholipids

Phosphoacylglycerols (also called **phosphoglycerides**) are the major components of cell membranes. They are similar to triacylglycerols except that a terminal OH group of glycerol is esterified with phosphoric acid rather than with a fatty acid, forming a **phosphatidic acid**. Because phosphoacylglycerols are lipids that contain a phosphate group, they are classified as **phospholipids**. The C-2 carbon of glycerol in phosphoacylglycerols has the *R* configuration.

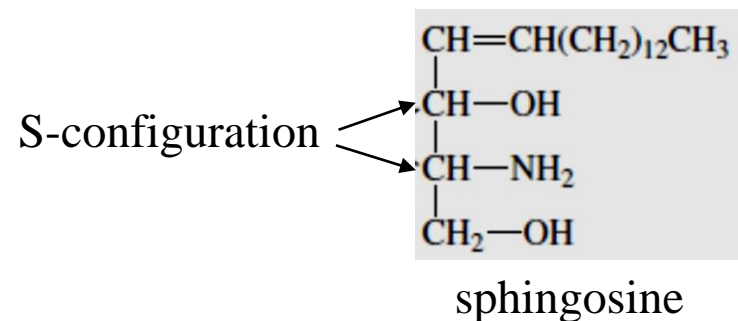


a phosphatidic acid

Phosphoacylglycerols form membranes by arranging themselves in a **lipid bilayer**. The polar heads of the phosphoacylglycerols are on the outside of the bilayer, and the fatty acid chains form the interior of the bilayer. Cholesterol—a membrane lipid—is also found in the interior of the bilayer. A typical bilayer is about 50 Å thick.



Sphingolipids are also found in membranes. They are the major lipid components in the myelin sheaths of nerve fibers. Sphingolipids contain sphingosine instead of glycerol. In sphingolipids, the amino group of sphingosine is bonded to the acyl group of a fatty acid. Both asymmetric carbons in sphingosine have the *S* configuration.



Macromolecules

A **polymer** is a large molecule made by linking together repeating units of small molecules called **monomers**. The process of linking them together is called **polymerization**.

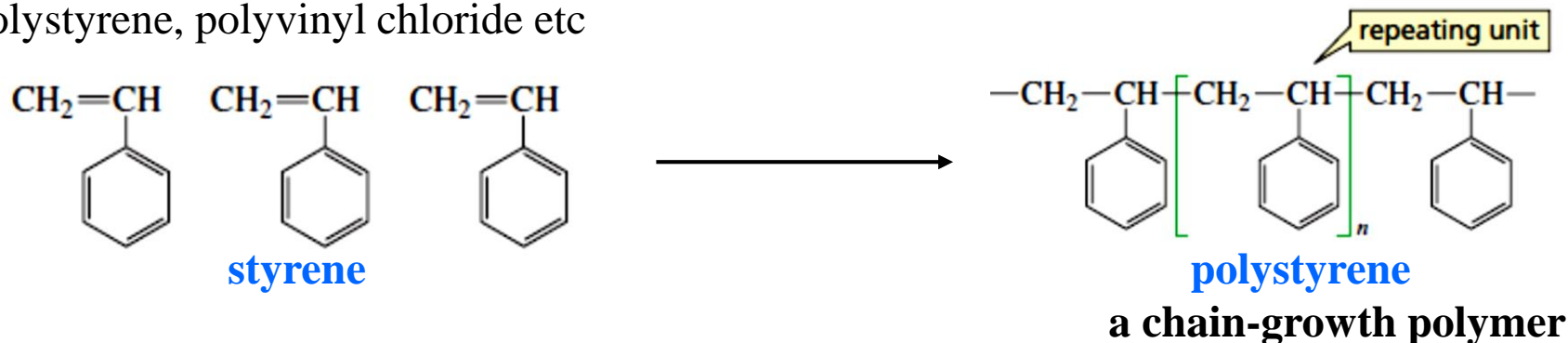


Polymers can be divided into two broad groups: **synthetic polymers** and **biopolymers** (natural polymers). Synthetic polymers are synthesized by scientists, whereas biopolymers are synthesized by organisms. Examples of biopolymers are DNA, RNA etc.

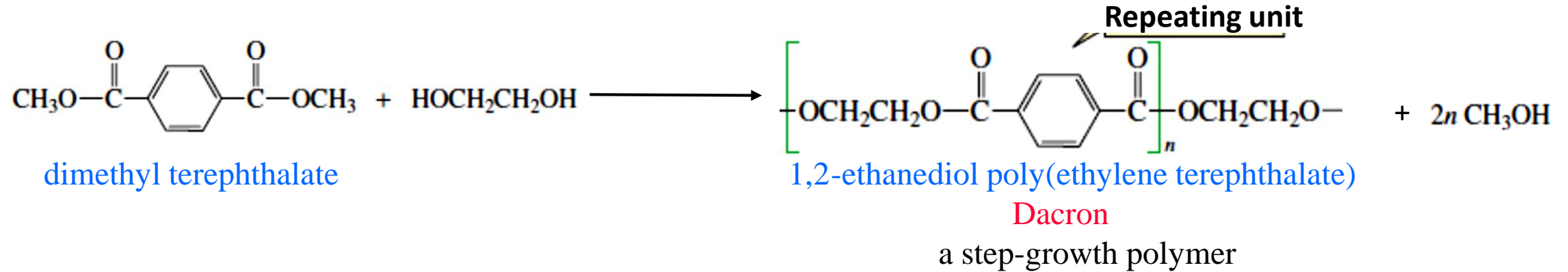
Classes of Synthetic Polymers

1. **Addition polymers** result from the rapid addition of one molecule at a time to a growing polymer chain, usually with a reactive intermediate (cation, radical, or anion) at the growing end of the chain. Addition polymers are sometimes called **chain-growth polymers**, because growth usually occurs at the end of a chain.

Eg. Polystyrene, polyvinyl chloride etc



Condensation polymers, also called **step-growth polymers**, are made by combining two molecules while removing a small molecule, generally water or an alcohol. The reacting molecules have reactive functional groups at each end.. Dacron® is an example of a step-growth polymer.



Dacron® is the most common of the group of polymers known as **polyesters**—polymers with many ester groups. Polyesters are used for clothing and are responsible for the wrinkle-resistant behavior of many fabrics. Polyester is also used to make the plastic film called Mylar®, needed in the manufacture of magnetic recording tape.

Addition Polymers/ Chain-growth polymers

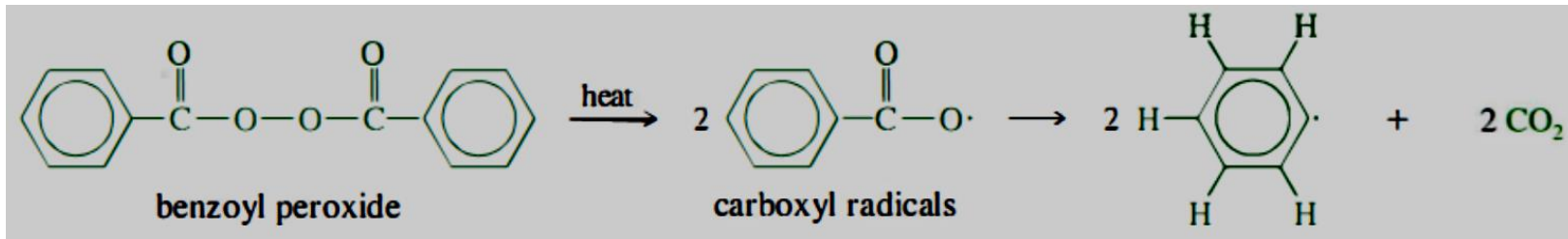
Chain-growth polymerization proceeds by one of three mechanisms: **radical polymerization**, **cationic polymerization**, or **anionic polymerization**. Each mechanism has three distinct phases: an *initiation step* that starts the polymerization, *propagation steps* that allow the chain to grow, and *termination steps* that stop the growth of the chain.

Some Important Chain-Growth Polymers and Their Uses

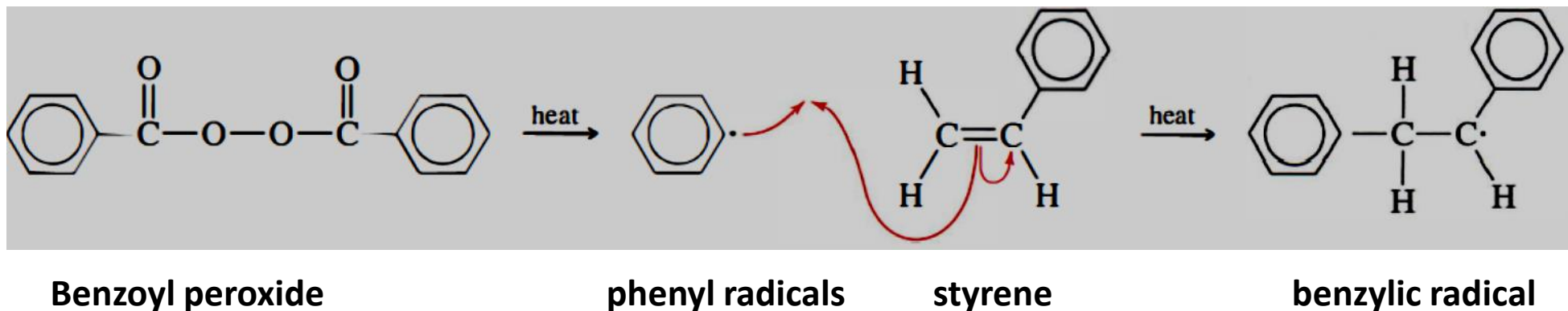
Monomer	Repeating unit	Polymer name	Uses
$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$	polyethylene	film, toys, bottles, plastic bags
$\text{CH}_2=\text{CH}-\text{Cl}$	$-\text{CH}_2-\text{CH}-\text{Cl}$	poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$\text{CH}_2=\text{CH}-\text{CH}_3$	$-\text{CH}_2-\text{CH}-\text{CH}_3$	polypropylene	molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	$-\text{CH}_2-\text{CH}-\text{C}_6\text{H}_5$	polystyrene	packaging, toys, clear cups, egg cartons, hot drink cups
$\text{CF}_2=\text{CF}_2$	$-\text{CF}_2-\text{CF}_2-$	poly(tetrafluoroethylene) Teflon [®]	nonsticking surfaces, liners, cable insulation
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	$-\text{CH}_2-\text{CH}-\text{C}\equiv\text{N}$	poly(acrylonitrile) Orlon [®] , Acrilan [®]	rugs, blankets, yarn, apparel, simulated fur
$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COCH}_3$	$-\text{CH}_2-\text{C}(\text{CH}_3)(\text{COCH}_3)-$	poly(methyl methacrylate) Plexiglas [®] , Lucite [®]	lighting fixtures, signs, solar panels, skylights
$\text{CH}_2=\text{CH}-\text{OCCH}_3$	$-\text{CH}_2-\text{CH}-\text{OCCH}_3$	poly(vinyl acetate)	latex paints, adhesives

Free-Radical Polymerization

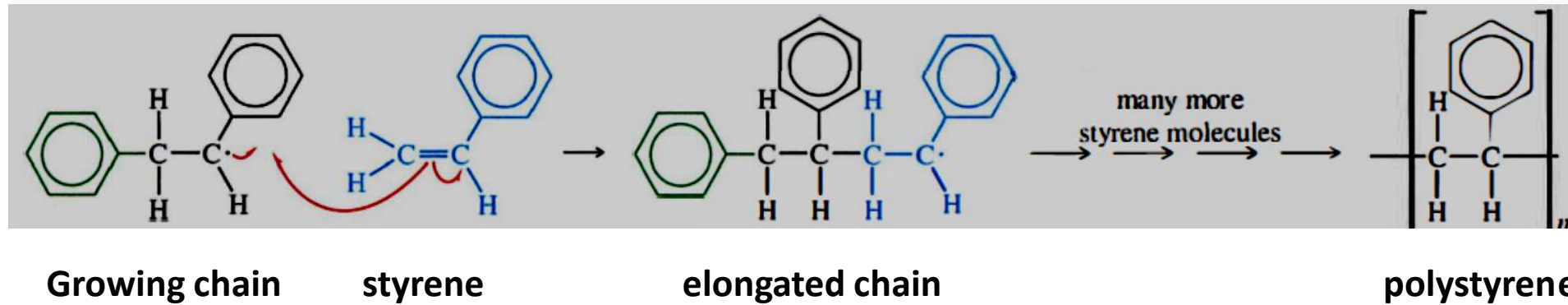
Free-radical polymerization results when a suitable alkene is heated with a radical initiator. For example, styrene polymerizes to polystyrene when it is heated to 100° C in the presence of benzoyl peroxide. This chain-growth polymerization is a free-radical chain reaction. Benzoyl peroxide cleaves when heated to give two carboxyl radicals, which quickly decarboxylate to give phenyl radicals.



Initiation step: The initiator forms a radical that reacts with the monomer to start the chain.



Propagation step: Another molecule of monomer adds to the chain.

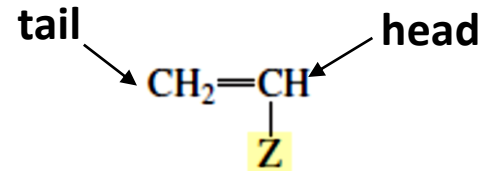


Eventually, the chain reaction stops because the propagating sites are destroyed. Propagating sites can be destroyed when two chains combine at their propagating sites; when two chains undergo *disproportionation*, with one chain being oxidized to an alkene and the other being reduced to an alkane; or when a chain reacts with an impurity that consumes the radical.

The molecular weight of the polymer can be controlled by a process known as **chain transfer**. In chain transfer, the growing chain reacts with a molecule XY in a manner that allows $X\cdot$ to terminate the chain, leaving behind $Y\cdot$ to initiate a new chain. XY can be a solvent, a radical initiator, or any molecule with a bond that can be cleaved homolytically.

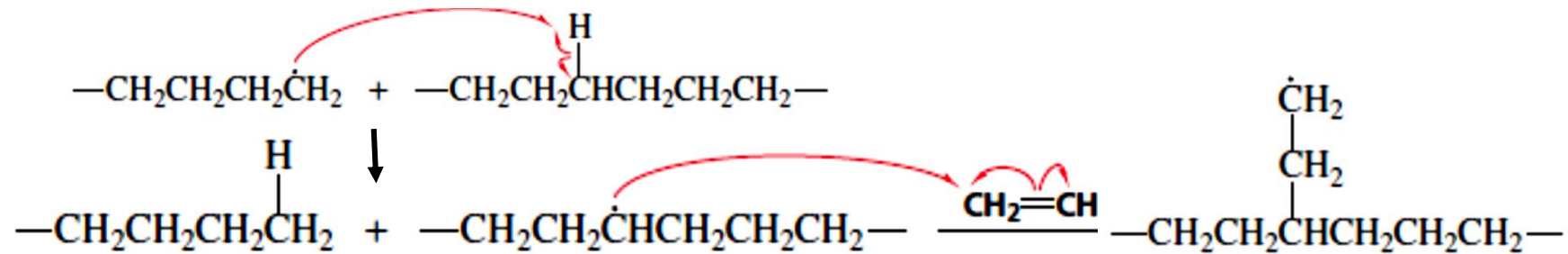


Chain-growth polymerization of monosubstituted ethylenes exhibits a marked preference for **head-to-tail addition**, where the head of one monomer is attached to the tail of another.

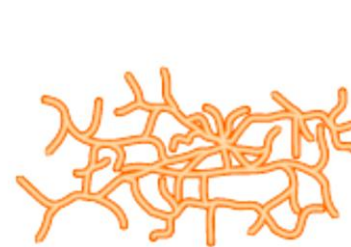


Branching of the Polymer Chain

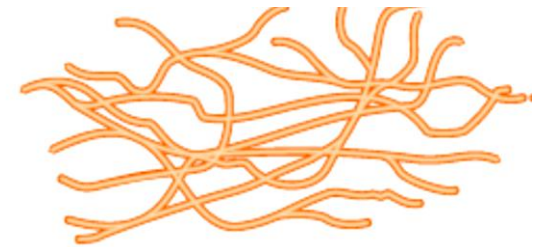
If the propagating site abstracts a hydrogen atom from a chain, a branch can grow off the chain at that point.



Abstraction of a hydrogen atom from a carbon near the end of a chain leads to short branches, whereas abstraction of a hydrogen atom from a carbon near the middle of a chain results in long branches. Branching greatly affects the physical properties of the polymer. As linear unbranched chains can pack together more closely than branched chains can, so linear polyethylene (known as high-density polyethylene) is a relatively hard plastic while branched polyethylene (low-density polyethylene) is a much more flexible polymer, used for trash bags and dry-cleaning bags.



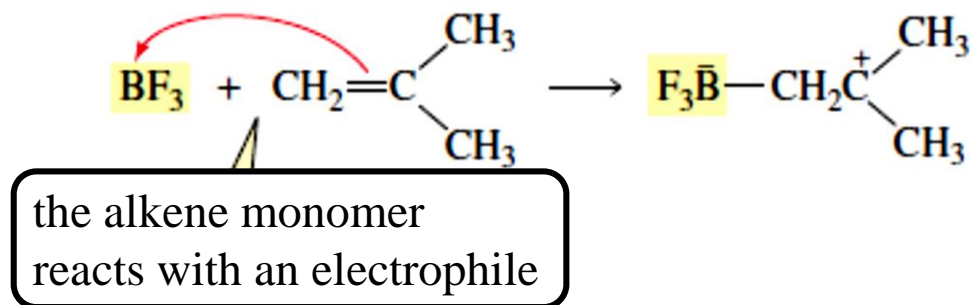
chain with short branches



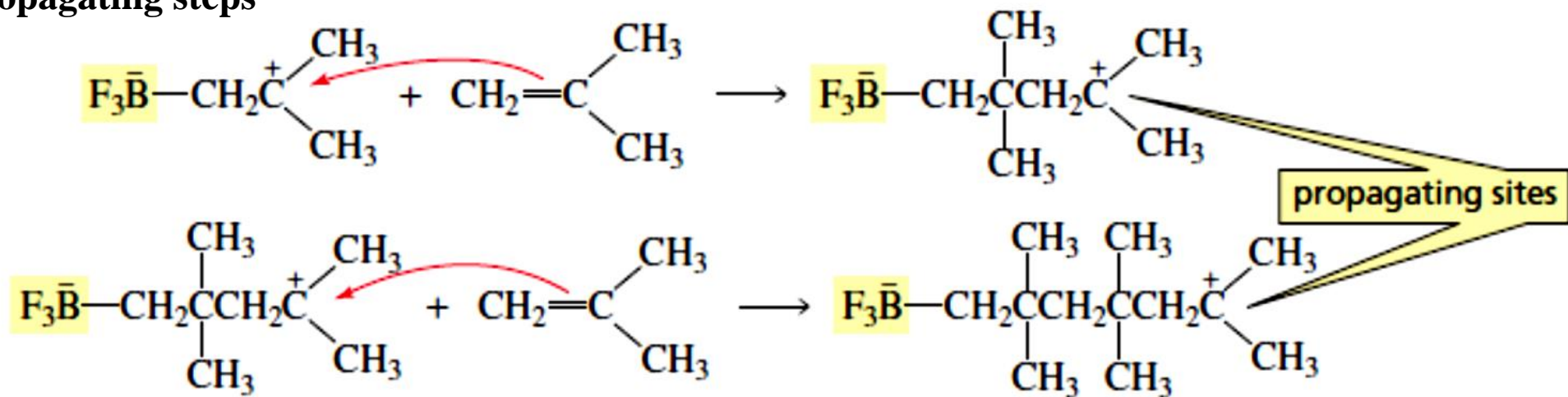
chain with long branches

Cationic polymerization occurs by a mechanism similar to the free-radical process, except that it involves carbocation intermediates. Strongly acidic catalysts are used to initiate cationic polymerization. BF_3 is a particularly effective catalyst, requiring a trace of water or methanol as a co-catalyst.

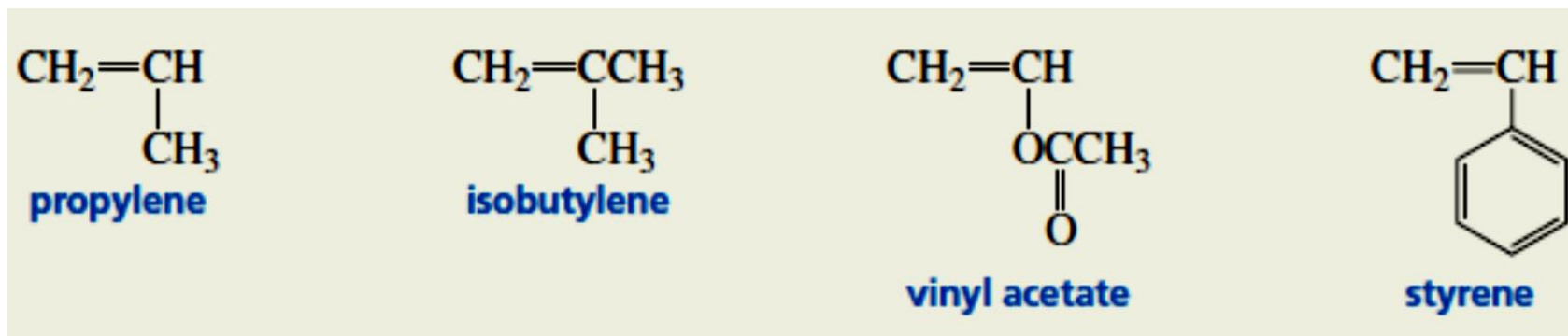
chain-initiating step



chain-propagating steps



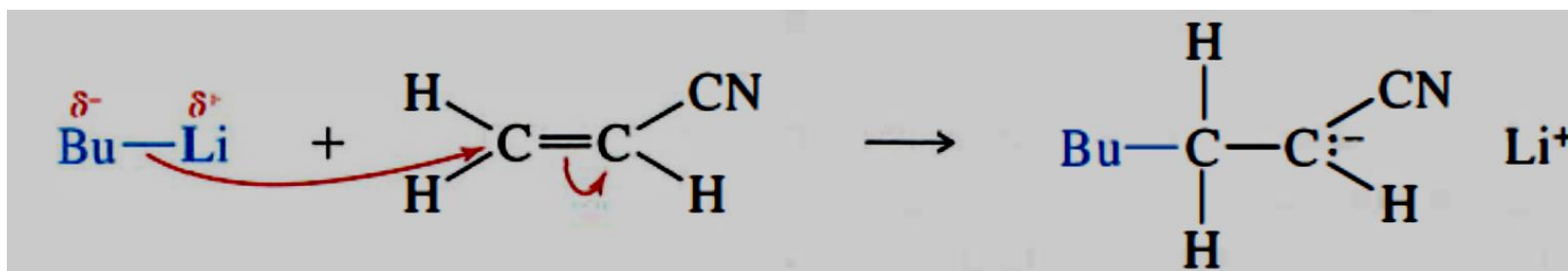
Monomers that are best able to undergo polymerization by a cationic mechanism are those with substituents that can stabilize the positive charge at the propagating site by donating electrons inductively or by resonance.



Anionic polymerization occurs through carbanion intermediates. Effective anionic polymerization requires a monomer that gives a stabilized carbanion when it reacts with the anionic end of the growing chain.

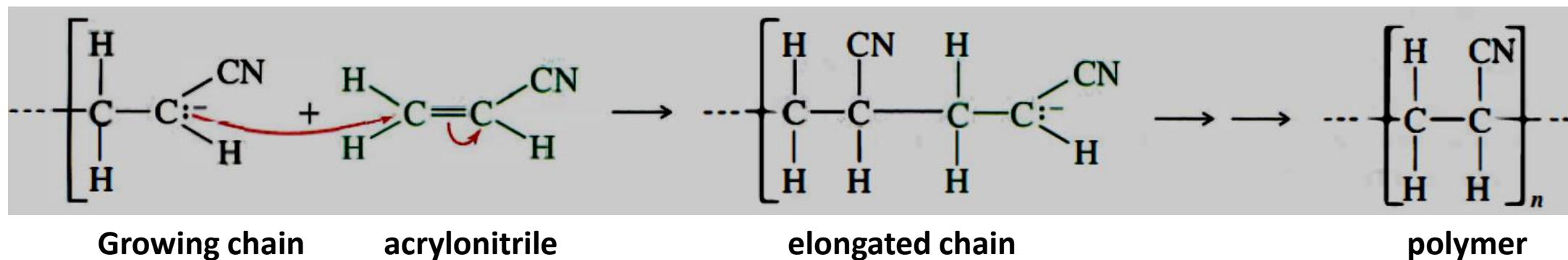
Anionic polymerization is usually initiated by a strong carbanion-like reagent such as an organolithium or Grignard reagent. Conjugate addition of the initiator to a monomer molecule starts the growth of the chain

Initiation step: The initiator adds to the monomer to form an anion.

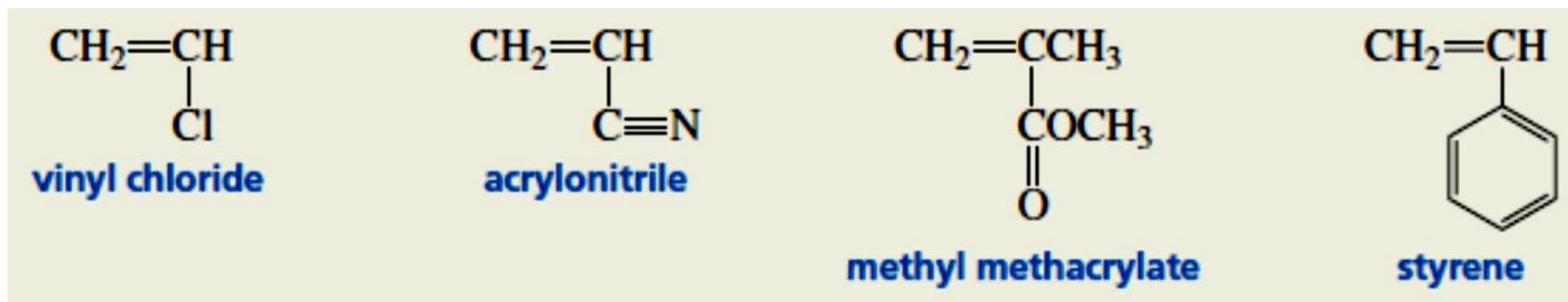


Stabilized anion

Propagation step: Another molecule of monomer adds to the chain.



Examples of Alkenes That Undergo Anionic Polymerization

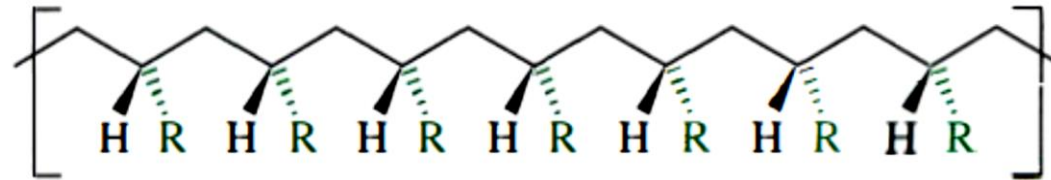


Stereochemistry of Polymers

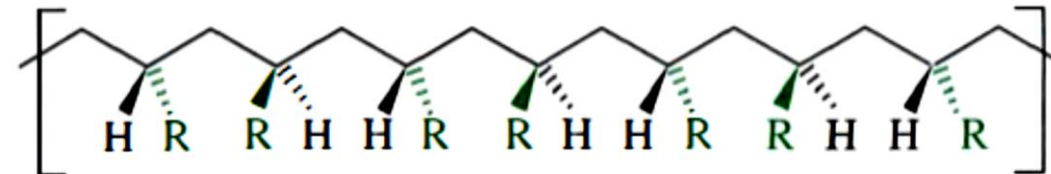
Polymers formed from monosubstituted ethylenes can exist in three configurations: isotactic, syndiotactic, and atactic.

- An **isotactic polymer** has all of its substituents on the same side of the fully extended carbon chain.
- In a **syndiotactic polymer**, the substituents regularly alternate on both sides of the carbon chain.
- The substituents in an **atactic polymer** are randomly oriented.

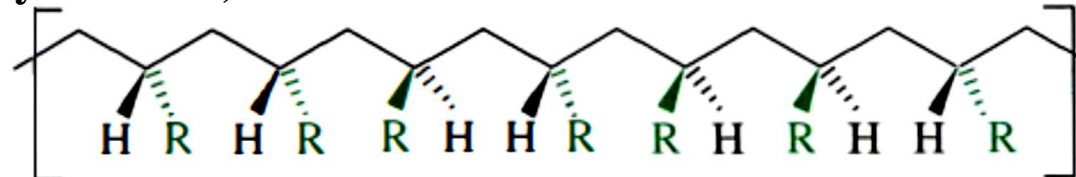
isotactic polymer (same side)



syndiotactic polymer (both sides)



atactic polymer (randomly oriented)

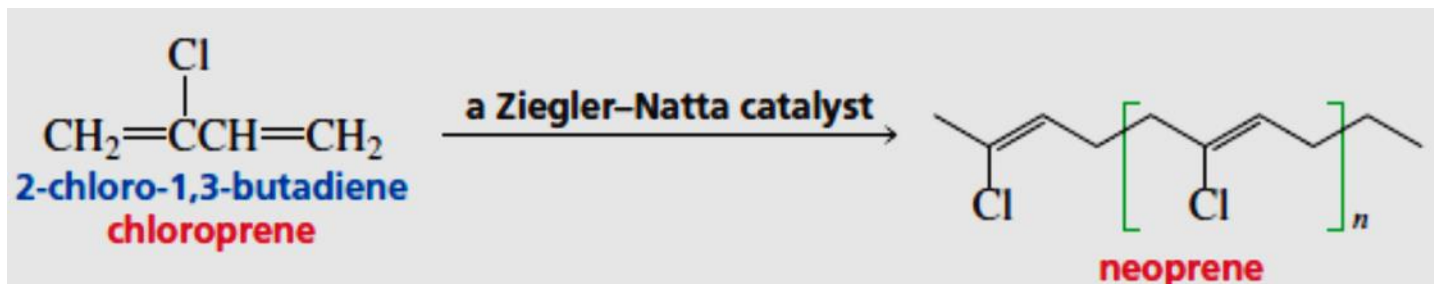
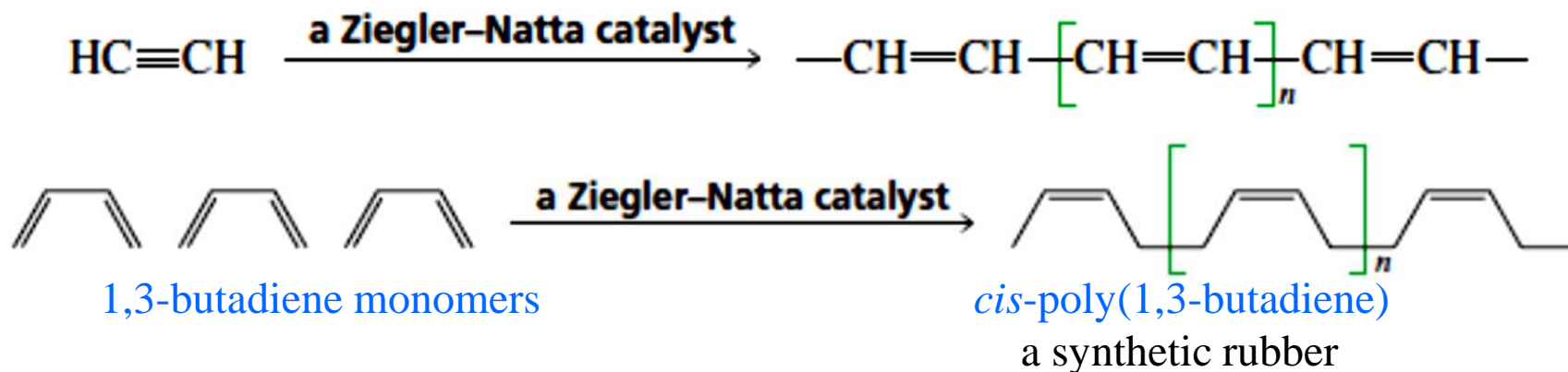


Polymers in the isotactic or syndiotactic configuration are more likely to be crystalline solids because positioning the substituents in a regular order allows for a more regular packing arrangement. Polymers in the atactic configuration are more disordered and cannot pack together as well, so these polymers are less rigid and, therefore, softer.

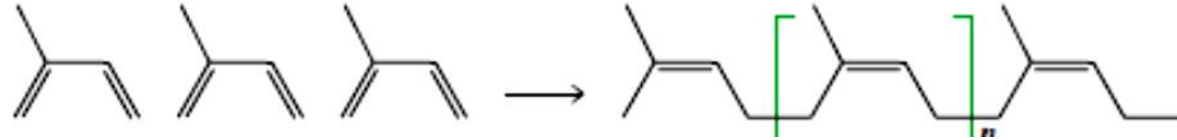
Ziegler-Natta catalyst

A **Ziegler-Natta** catalyst is an organometallic complex, often containing titanium and aluminum. A typical catalyst is formed by adding a solution of TiCl_4 (titanium tetrachloride) to a solution of $(\text{CH}_3\text{CH}_2)_3\text{Al}$ (triethyl aluminum). **Karl Ziegler and Giulio Natta** discovered that aluminum-titanium initiators catalyze the polymerization of alkenes, with two major advantages over other catalysts:

1. The polymerization is completely stereoselective. Either the isotactic form or the syndiotactic form may be made, by selecting the proper Ziegler-Natta catalyst.
2. Because the intermediates are stabilized by the catalyst, very little hydrogen abstraction occurs. The resulting polymers are linear with almost no branching.



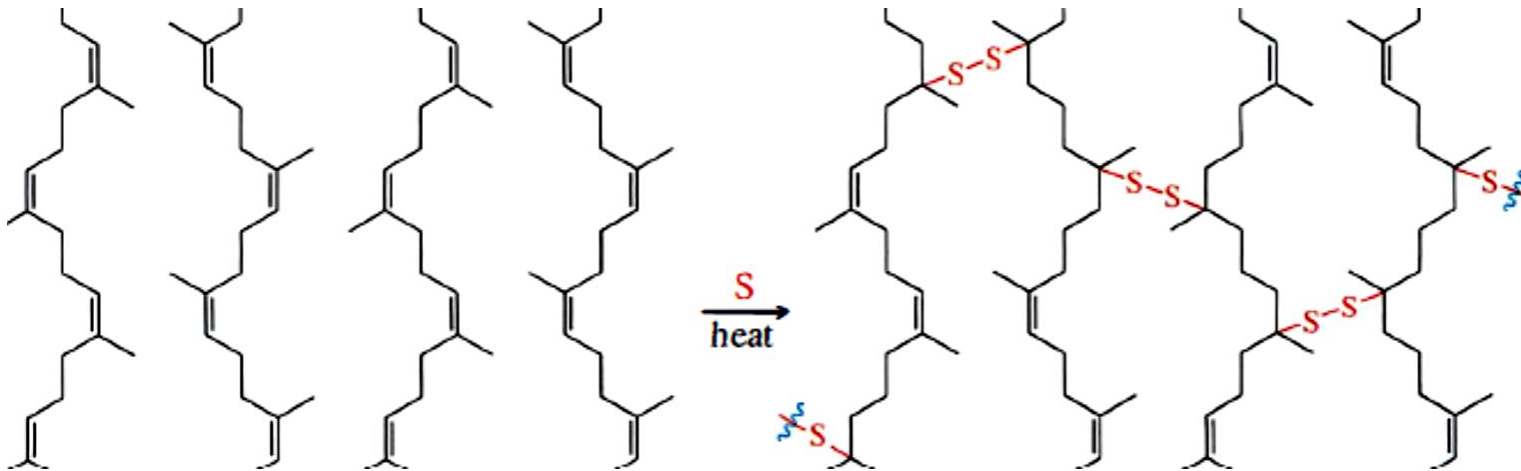
Natural Rubber



isoprene units

cis-poly(2-methyl-1,3-butadiene)
natural rubber

Vulcanization of rubber introduces disulfide cross-links between the polyisoprene chains. Cross-linking forms a stronger, elastic material that does not pull apart when it is stretched.



Copolymers of Two or More Monomers

When two or more different monomers are used to form a polymer, the resulting product is called a **copolymer**.

There are four types of copolymers.

In an **alternating copolymer**, the two monomers alternate.

In a **block copolymer**, there are blocks of each kind of monomer.

In a **random copolymer**, the distribution of monomers is random.

A **graft copolymer** contains branches derived from one monomer grafted onto a backbone derived from another monomer.

an alternating copolymer	ABABABABABABABABABABA
a block copolymer	AAAAABBBBBBAAAAABBBBBBAAA
a random copolymer	AABABABBBABAABBABABBAAAB
a graft copolymer	AAAAAAAAAAAAAAAAAAAAAAAAA B B B B B B B B B B B B B B B B B B

Ref: Paula Y. Bruce, Organic Chemistry, 3rd Ed

Monomer	Copolymer name	Uses
$\text{CH}_2=\text{CH}-\text{Cl}$ vinyl chloride	Saran	film for wrapping food
$\text{CH}_2=\text{CCl}-\text{Cl}$ vinylidene chloride		
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ styrene	SAN	dishwasher-safe objects, vacuum cleaner parts
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ acrylonitrile		
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ acrylonitrile	ABS	bumpers crash helmets, telephones, luggage
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-butadiene		
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$ styrene	butyl rubber	inner tubes, balls, inflatable sporting goods
$\text{CH}_2=\text{C}(\text{CH}_3)_2$ isobutylene		
$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$ isoprene		

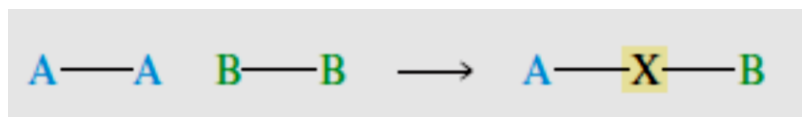
Step-Growth Polymers

Step-growth polymers are formed by the intermolecular reaction of bifunctional molecules. When the functional groups react, in most cases a small molecule such as alcohol, or HCl is lost, hence these polymers are also called *condensation polymers*. There are two types of step-growth polymers.

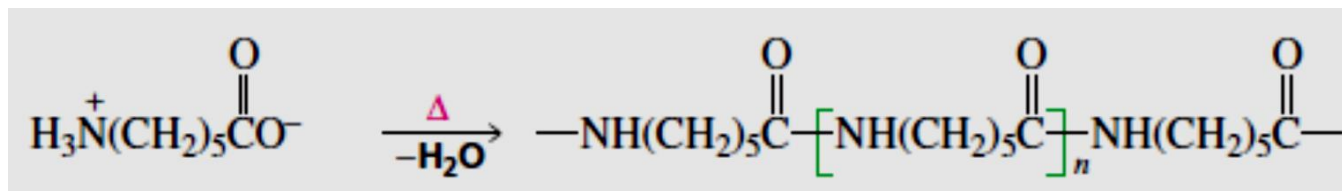
1. One type is formed by the reaction of a single monomer that possesses two different functional groups A and B. Functional group A of one monomer reacts with functional group B of another monomer.



2. The other type of step-growth polymer is formed by the reaction of two different bifunctional monomers. One monomer contains two A functional groups and the other monomer contains two B functional groups.



Nylon is the common name of a synthetic **polyamide**. **Nylon 6** is an example of a step growth polymer formed by a monomer with two different functional groups.

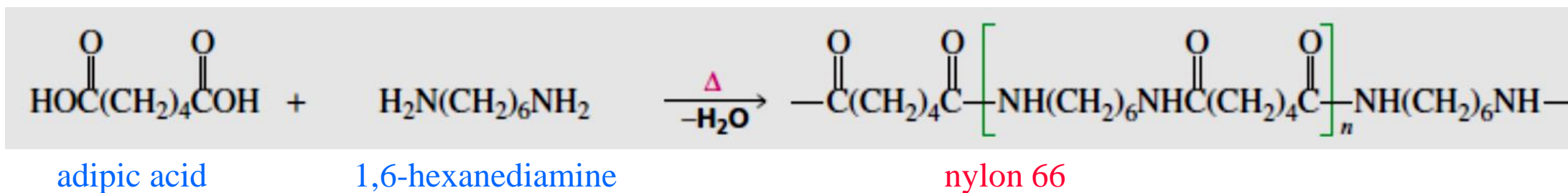


6-aminohexanoic acid

nylon 6
a polyamide

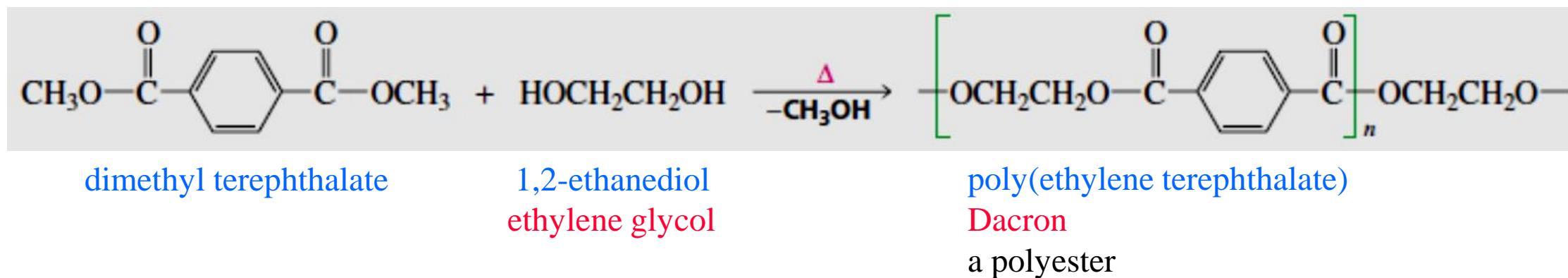
Ref: Paula Y. Bruce, Organic Chemistry, 3rd Ed

Nylon 66 is an example of a step-growth polymer formed by two different bifunctional monomers: adipic acid and 1,6-hexanediamine. It is called nylon 66 because it is a polyamide formed from a six-carbon diacid and a six-carbon diamine.

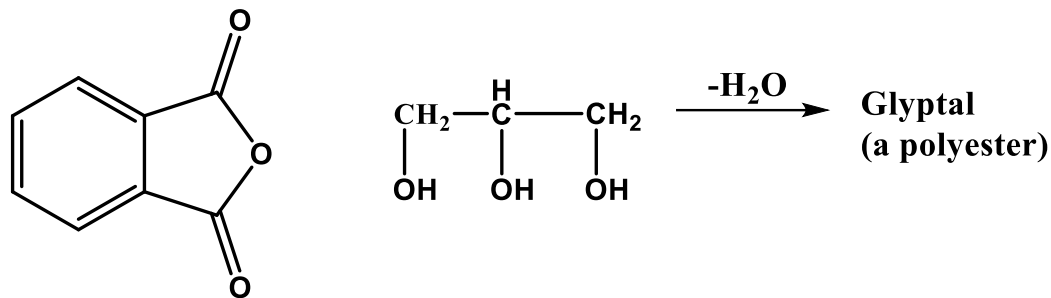


Polyesters

Polyesters are step-growth polymers in which the monomer units are joined together by ester groups. The most common polyester is known by the trade name Dacron® and is made by the transesterification of dimethyl terephthalate with ethylene glycol.



Ref: Paula Y. Bruce, Organic Chemistry, 3rd Ed



If each monomer molecule contains just two functional groups, growth can occur in only two directions, and a linear polymer is obtained, as in nylon 66 or Dacron. But if reaction can occur at more than two positions in a monomer, there is formed a highly cross-linked space network polymer, as in Glyptal, an alkyd resin. Dacron and Glyptal are both polyesters, but their structures are quite different and, as we shall see, so are their uses.