

# CYI101

## Common CHEMISTRY(Organic)

**Macromolecules:** Polymerization techniques, Natural and Synthetic polymer

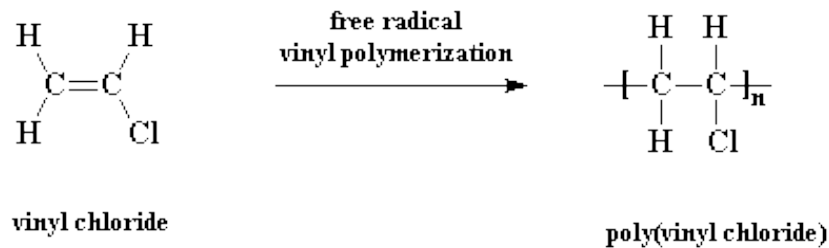
7<sup>th</sup> February 2022/Sec G & H

## Some Common Addition Polymers

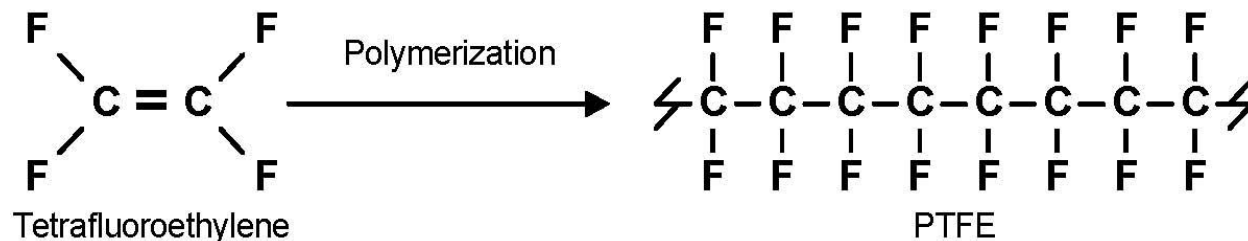
Name(s)	Formula	Monomer	Properties	Uses
<b>Polyethylene</b> low density (LDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	<b>ethylene</b> $\text{CH}_2=\text{CH}_2$	<b>soft, waxy solid</b>	<b>film wrap, plastic bags</b>
<b>Polyethylene</b> high density (HDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	<b>ethylene</b> $\text{CH}_2=\text{CH}_2$	<b>rigid, translucent solid</b>	<b>electrical insulation bottles, toys</b>
<b>Polypropylene</b> (PP) different grades	$-\text{[CH}_2-\text{CH}(\text{CH}_3)]_n-$	<b>propylene</b> $\text{CH}_2=\text{CHCH}_3$	<u>atactic</u> : soft, elastic solid <u>isotactic</u> : hard, strong solid	<b>similar to LDPE carpet, upholstery</b>
<b>Poly(vinyl chloride)</b> (PVC)	$-(\text{CH}_2-\text{CHCl})_n-$	<b>vinyl chloride</b> $\text{CH}_2=\text{CHCl}$	<b>strong rigid solid</b>	<b>pipes, siding, flooring</b>
<b>Poly(vinylidene chloride)</b> (Saran A)	$-(\text{CH}_2-\text{CCl}_2)_n-$	<b>vinylidene chloride</b> $\text{CH}_2=\text{CCl}_2$	<b>dense, high-melting solid</b>	<b>seat covers, films</b>
<b>Polystyrene</b> (PS)	$-\text{[CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n-$	<b>styrene</b> $\text{CH}_2=\text{CHC}_6\text{H}_5$	<b>hard, rigid, clear solid</b> soluble in organic solvents	<b>toys, cabinets packaging (foamed)</b>
<b>Polyacrylonitrile</b> (PAN, Orlon, Acrilan)	$-(\text{CH}_2-\text{CHCN})_n-$	<b>acrylonitrile</b> $\text{CH}_2=\text{CHCN}$	<b>high-melting solid</b> soluble in organic solvents	<b>rugs, blankets clothing</b>
<b>Polytetrafluoroethylene</b> (PTFE, Teflon)	$-(\text{CF}_2-\text{CF}_2)_n-$	<b>tetrafluoroethylene</b> $\text{CF}_2=\text{CF}_2$	<b>resistant, smooth solid</b>	<b>non-stick surfaces electrical insulation</b>
<b>Poly(methyl methacrylate)</b> (PMMA, Lucite, Plexiglas)	$-\text{[CH}_2-\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3]_n-$	<b>methyl methacrylate</b> $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	<b>hard, transparent solid</b>	<b>lighting covers, signs skylights</b>
<b>Poly(vinyl acetate)</b> (PVAc)	$-(\text{CH}_2-\text{CHOCOCH}_3)_n-$	<b>vinyl acetate</b> $\text{CH}_2=\text{CHOCOCH}_3$	<b>soft, sticky solid</b>	<b>latex paints, adhesives</b>
<b>cis-Polyisoprene</b> natural rubber	$-\text{[CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2]_n-$	<b>isoprene</b> $\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$	<b>soft, sticky solid</b>	<b>requires vulcanization for practical use</b>
<b>Polychloroprene</b> (cis + trans) (Neoprene)	$-\text{[CH}_2-\text{CH}=\text{CCl}-\text{CH}_2]_n-$	<b>chloroprene</b> $\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}_2$	<b>tough, rubbery solid</b>	<b>synthetic rubber oil resistant</b>

**Polyvinyl chloride (PVC)** is a solid plastic made from vinyl chloride. Polyvinyl chloride is the world's third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene

**PVC** is used to make pipes, vinyl flooring and siding, hoses, cable coatings, medical devices, and plumbing and automotive parts.



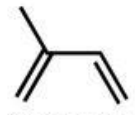
**Teflon** is polytetrafluoroethene (PTFE). PTFE is used as a **non-stick coating** for pans and other cookware. It is nonreactive, partly because of the strength of carbon–fluorine bonds, and so it is often used in **containers and pipework** for reactive and corrosive chemicals. Where used as a lubricant, PTFE reduces friction, wear, and energy consumption of machinery. It is commonly used as a graft material in **surgical interventions**. It is also frequently employed as coating on **catheters**; this interferes with the ability of bacteria and other infectious agents to adhere to catheters and cause hospital-acquired infections.



**Natural polymers** (also called biopolymers) include rubber, cellulose,, keratin, starch and DNA,

## Natural Polymers

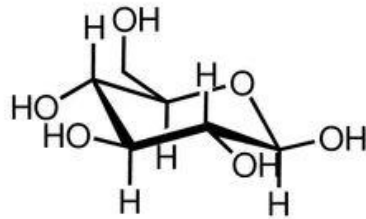
### Monomer



Isoprene



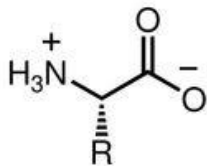
Polyisoprene:  
Natural rubber



$\beta$ -D-glucose



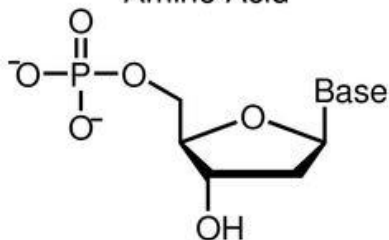
Poly( $\beta$ -D-glycoside):  
cellulose



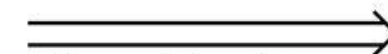
Amino Acid



Polyamino acid:  
protein

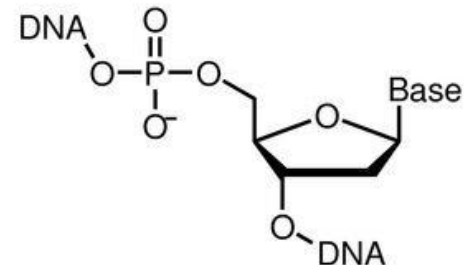
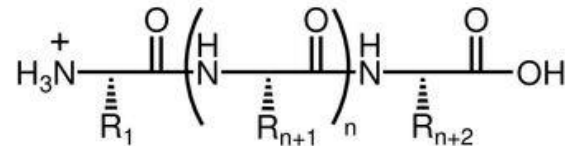
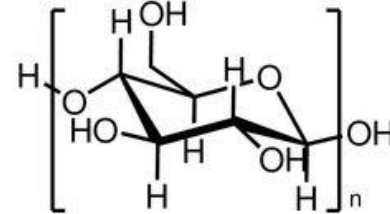
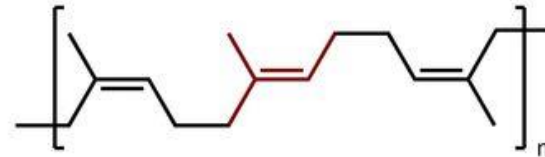


Nucleotide  
Base = C, G, T, A



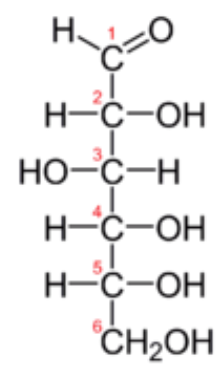
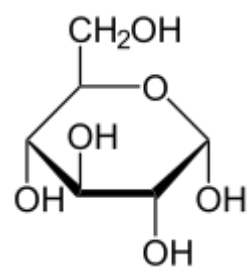
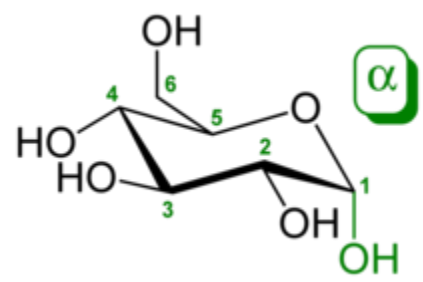
oligonucleic acid  
DNA

### Polymer

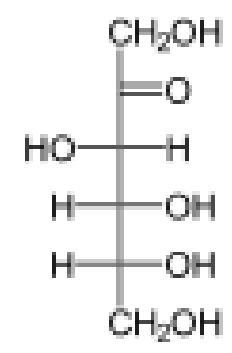
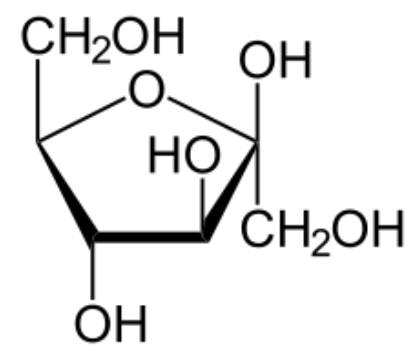


Cellulose and starches are both made from **sugars** - so they're called **polysaccharides** (meaning "**many sugars**")

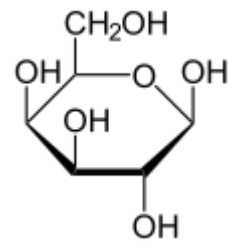
**Glucose**



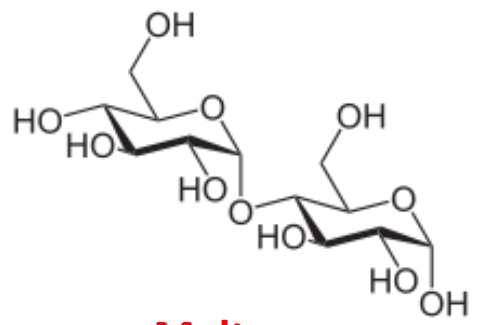
**Fructose**



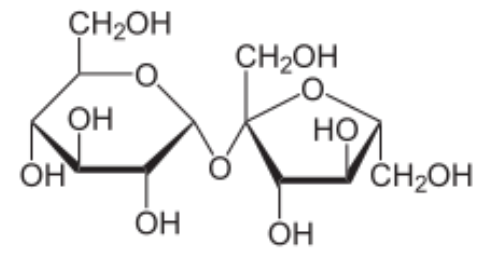
**Galactose**



**Disaccharide**

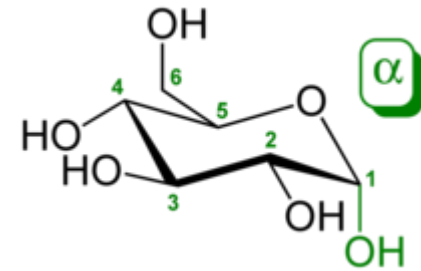
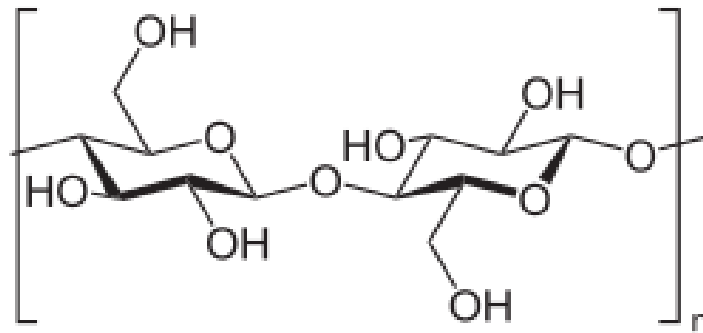


**Maltose**

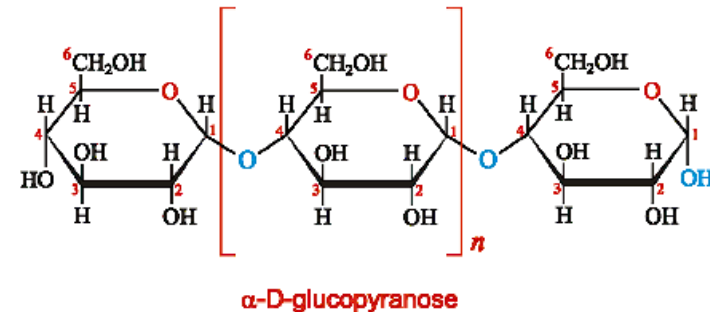


**Sucrose**

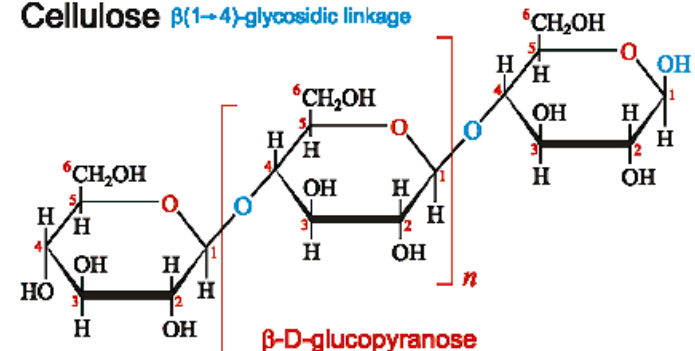
**Cellulose** is an organic compound with the formula  $(C_6H_{10}O_5)_n$ , a polysaccharide consisting of a linear chain of **several hundred to many thousands** of  **$\beta(1\rightarrow4)$  linked D-glucose** units.



**Starch**  $\alpha(1\rightarrow4)$ -glycosidic linkage



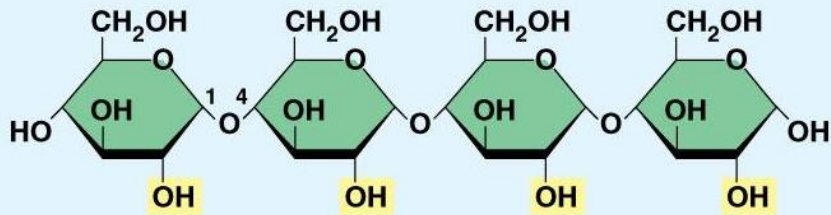
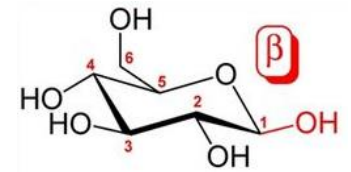
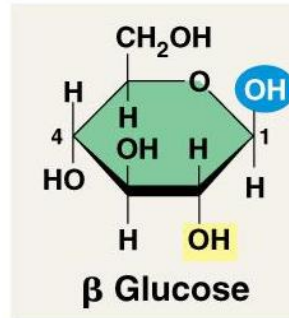
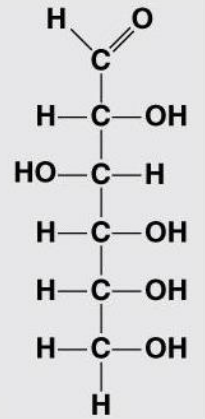
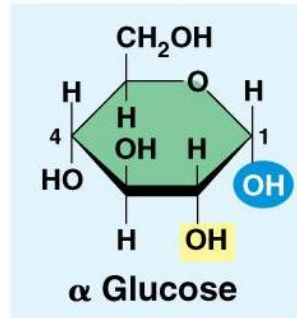
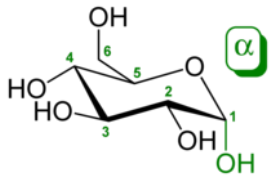
**Cellulose**  $\beta(1\rightarrow4)$ -glycosidic linkage



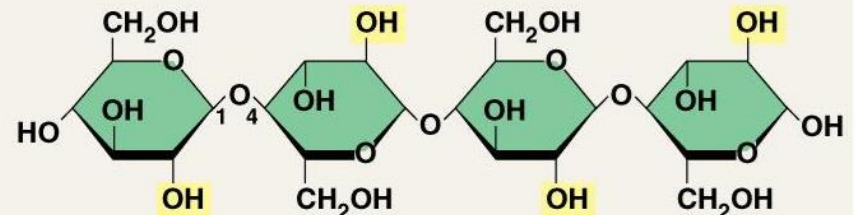
Cellulose is mainly used to produce paperboard and paper.  
Cellulose is the most abundant organic polymer on Earth.  
Cotton fibres represent the purest natural form of cellulose.

**Starch** or amylum is a polymeric carbohydrate consisting of numerous glucose units joined by **glycosidic bonds**. This **polysaccharide** is produced by most **green plants as energy storage**. It is the most common carbohydrate in human diets and is contained in large amounts in staple foods like **potatoes, wheat, maize (corn), rice**.

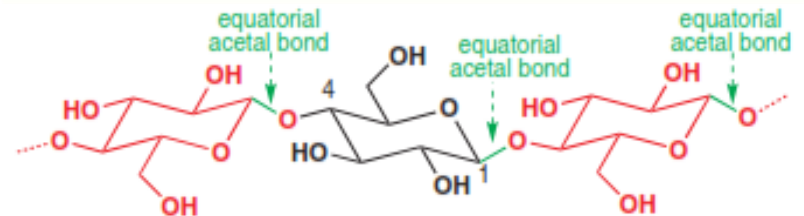
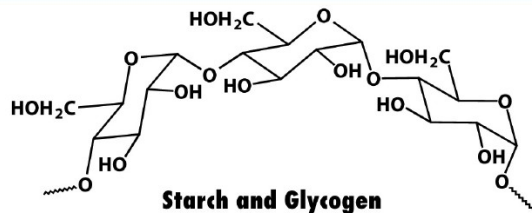
## $\alpha$ and $\beta$ glucose ring structures



**(b) Starch: 1–4 linkage of  $\alpha$  glucose monomers**

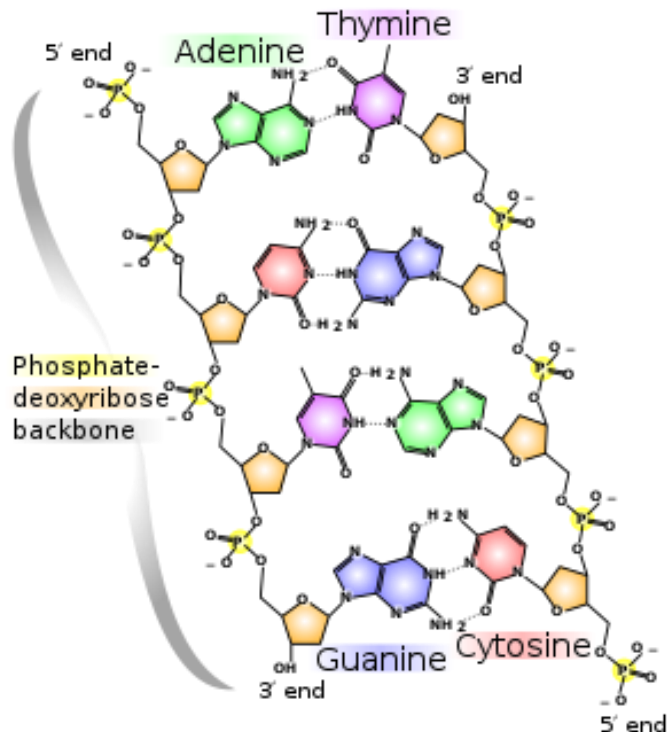


**(c) Cellulose: 1–4 linkage of  $\beta$  glucose monomers**

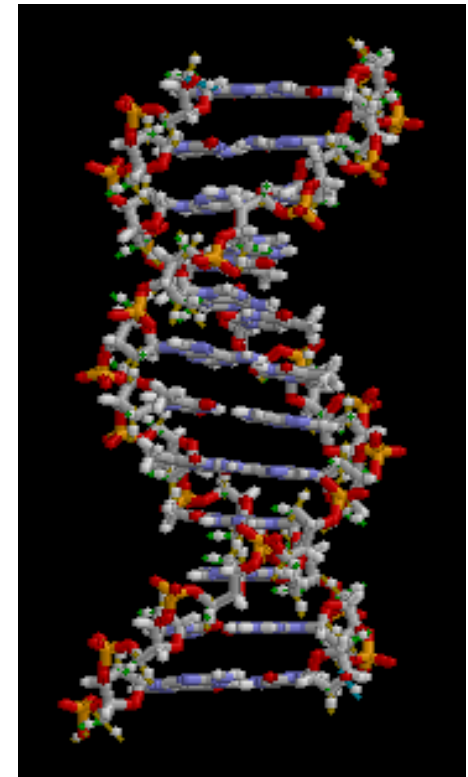




The two **DNA strands** are also known as **polynucleotides** as they are composed of simpler monomeric units called nucleotides. Each nucleotide is composed of one of four nitrogen-containing nucleobases (**cytosine [C], guanine [G], adenine [A] or thymine [T]**), a sugar called deoxyribose, and a phosphate group. The nucleotides are joined to one another in a chain by covalent bonds between the sugar of one nucleotide and the phosphate of the next, resulting in an alternating sugar-phosphate backbone. The nitrogenous bases of the two separate polynucleotide strands are bound together, according to base pairing rules (A with T and C with G), with hydrogen bonds to make double-stranded DNA. The complementary nitrogenous bases are divided into two groups, pyrimidines and purines. In DNA, the pyrimidines are thymine and cytosine; the purines are adenine and guanine.



**DNA double helix**





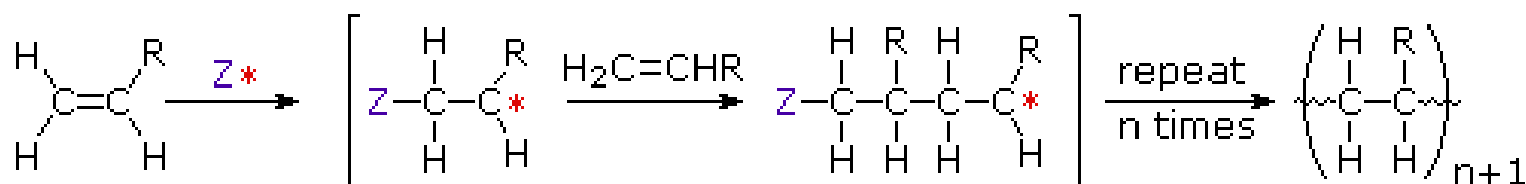
The **Degree of Polymerization**, or DP, is the number of **monomeric** units in a macromolecule or **polymer** or oligomer molecule. ...

Divide the molecular weight of the **polymer** by the molecular weight of the monomer unit to **calculate** the **degree of polymerization**. If the molecular mass of tetrafluoroethylene is 120,000, its **degree of polymerization** is  $120,000 / 100 = 1,200$ .

$$\text{Degree of polymerisation} = \frac{\text{Molecular weight of polymer}}{\text{Molecular weight of monomer}}$$

## Synthesis of Polymers

All the monomers from which addition polymers are made are **alkenes** or functionally substituted alkenes. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations.



$\text{Z}^*$  is an initiating species

$*$  may be a radical, a cation or an anion

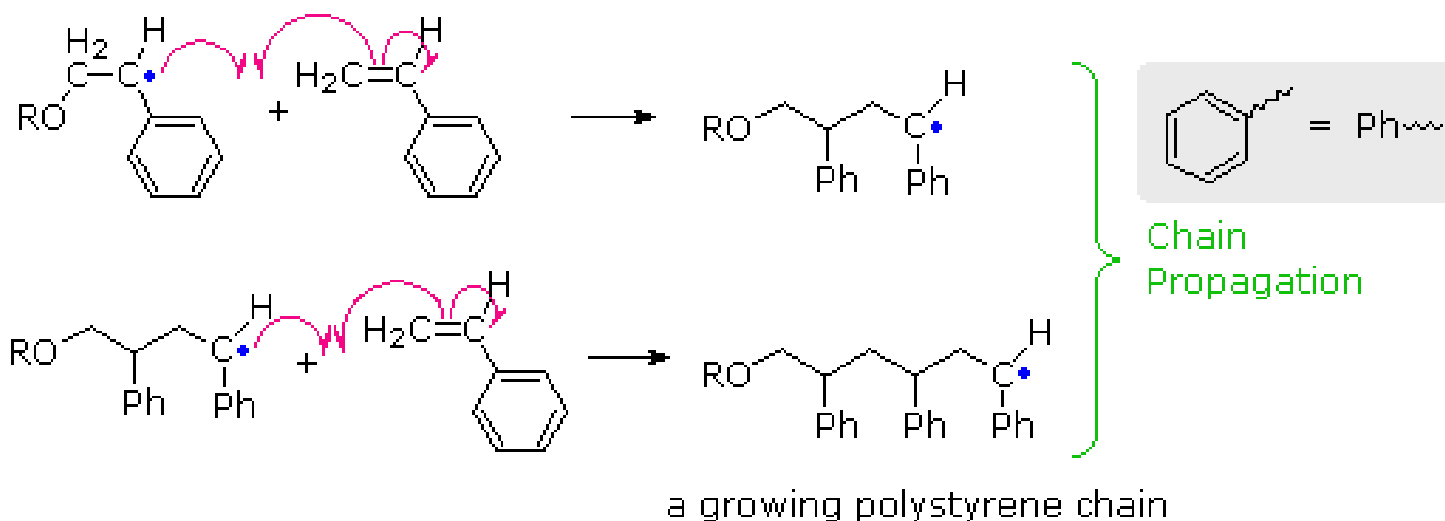
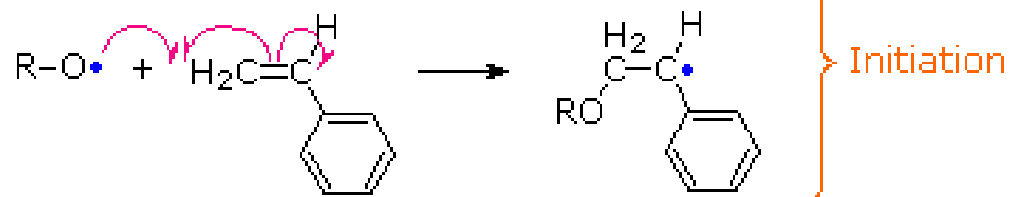
**Radical Polymerization:** The initiator is a radical, and the propagating site of reactivity is a **carbon radical**.

**Cationic Polymerization:** The initiator is an acid, and the propagating site of reactivity is a **carbocation**.

**Anionic Polymerization:** The initiator is a nucleophile, and the propagating site of reactivity is a **carbanion**.

**Coordination Catalytic Polymerization:** The initiator is a transition metal complex, and the propagating site of reactivity is a **terminal catalytic complex**.

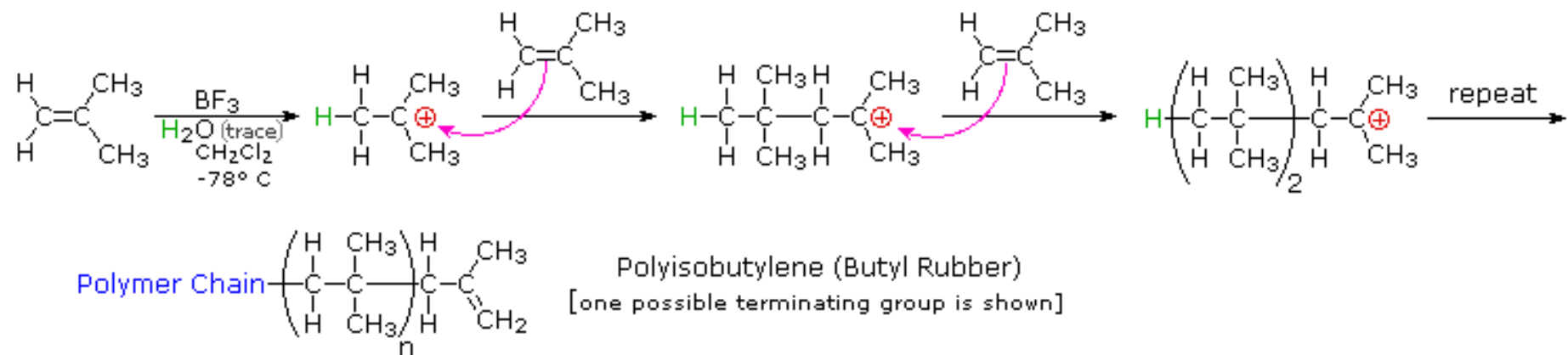
# Radical Chain-Growth Polymerization



When radical polymerization is desired, it must be started by using a **radical initiator**, such as a **peroxide**. The first **two equations** illustrate the **initiation** process, and the **last two equations** are examples of **chain propagation**.

# Cationic Chain-Growth Polymerization

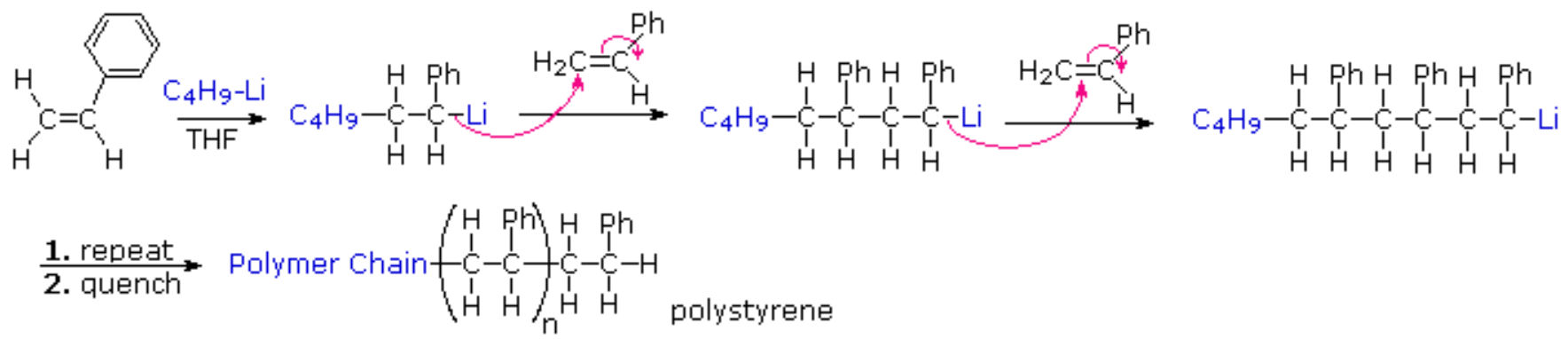
Polymerization of **isobutylene (2-methylpropene)** by traces of strong acids is an example of cationic polymerization. The polyisobutylene product is a **soft rubbery solid**. This process is similar to radical polymerization, as demonstrated by the following equations. Chain growth ceases when the terminal **carbocation combines** with a nucleophile or loses a proton, giving a **terminal alkene** (as shown here).



Monomers bearing **cation stabilizing groups**, such as **alkyl, phenyl or vinyl** can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as  **$\text{HClO}_4$**  , or **Lewis acids** containing traces of water (as shown above) serve as initiating reagents.

# Anionic Chain-Growth Polymerization

Treatment of a cold THF solution of **styrene** with 0.001 equivalents of **n-butyllithium** causes an immediate polymerization. This is an example of **anionic polymerization**, the course of which is described by the following equations. Chain growth may be terminated by **water or carbon dioxide**. Only monomers having anion stabilizing substituents, such as **phenyl, cyano or carbonyl** are good substrates for this polymerization technique.

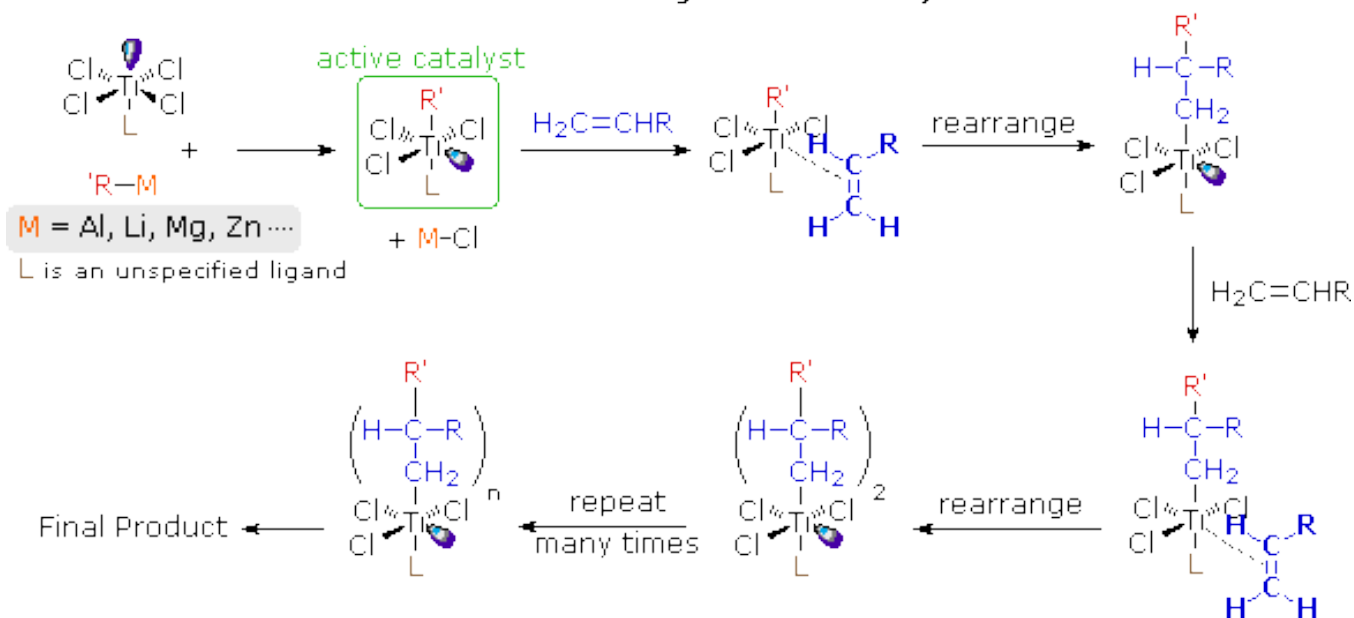


Species that have been used to initiate anionic polymerization include **alkali metals**, alkali amides, **alkyl lithiums** and various electron sources.

# Ziegler-Natta Catalytic Polymerization

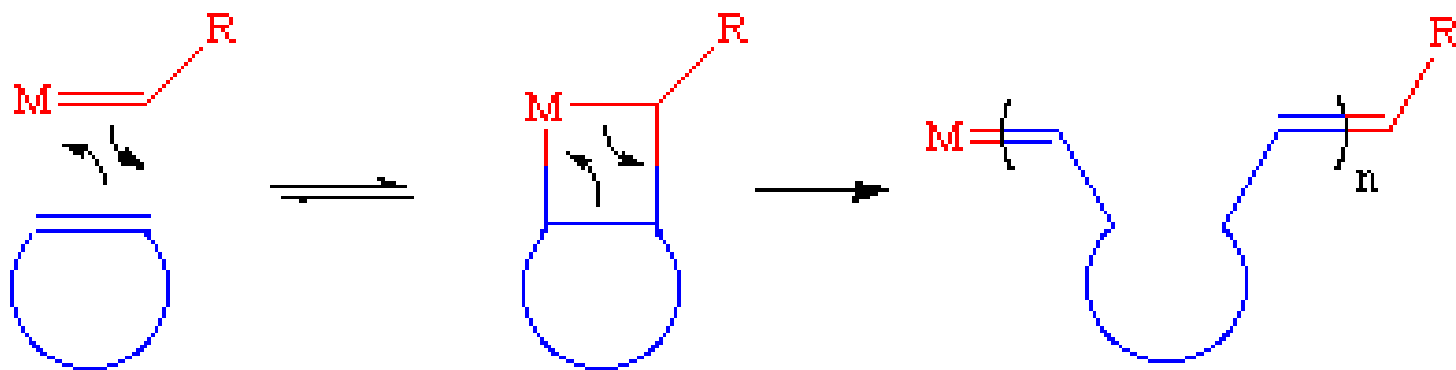
An efficient and stereospecific catalytic polymerization procedure was developed by **Karl Ziegler** (Germany) and **Giulio Natta** (Italy) in the 1950's. Their findings permitted, for the first time, the synthesis of **unbranched, high molecular weight polyethylene (HDPE)**, laboratory synthesis of natural rubber **from isoprene**, and configurational control of polymers from **terminal alkenes** like propene (e.g. pure isotactic and syndiotactic polymers). For this important discovery these chemists received the **1963 Nobel Prize in chemistry**.

## A Mechanism for Ziegler-Natta Catalysis



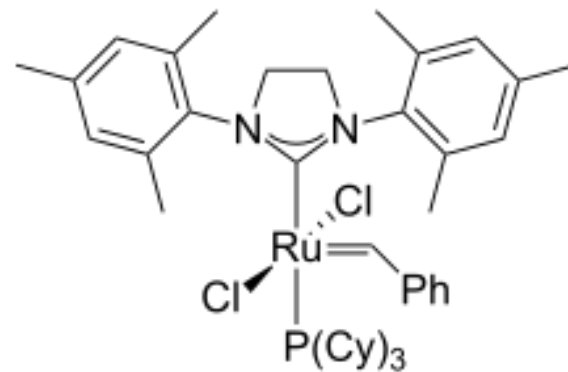
Ziegler-Natta catalysts are prepared by reacting certain transition metal halides with **organometallic reagents** such as **alkyl aluminum**, **lithium and zinc reagents**. The catalyst formed by reaction of **triethylaluminum with titanium tetrachloride** has been widely studied, but other metals (e.g. **V & Zr**) have also proven effective. The above diagram presents one mechanism for this useful reaction.

**Ring-opening metathesis polymerization (ROMP)** is a type of **olefin metathesis** chain-growth polymerization. The driving force of the reaction is relief of ring strain in cyclic olefins (e.g. norbornene or cyclopentene). A variety of heterogeneous and homogeneous catalysts have been developed. Most large-scale commercial processes rely on the former while some fine chemical syntheses rely on the homogeneous catalysts. Catalysts are based on transition metals such as W, Mo, Re, Ru, and Ti.



**Olefin metathesis** is an organic reaction that entails the redistribution of fragments of alkenes (olefins) by the scission and regeneration of carbon-carbon double bonds

**Grubbs**, together with **Richard R. Schrock** and **Yves Chauvin**, won the **Nobel Prize in Chemistry 2005** in recognition of their contributions to the development of **olefin metathesis**.



**Grubbs catalysts**