

COURSE CODE: SC202(CHEMISTRY)

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DEPT. OF SCIENCE AND MATHEMATICS

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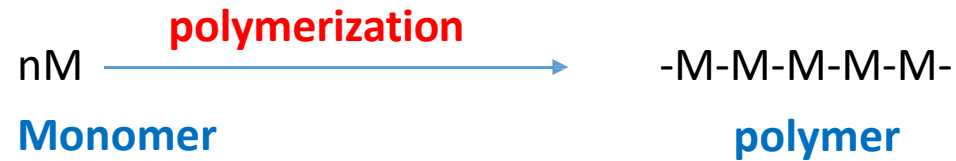
LECTURE-(MACROMOLECULES &

GREEN CHEMICAL PROCESSES)

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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**.

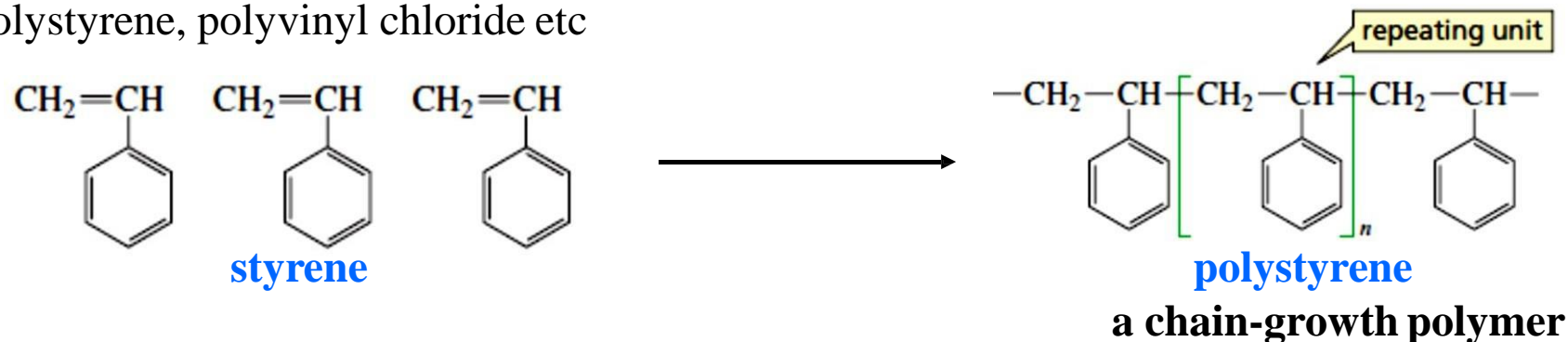


Polymers can be divided into two broad groups: **synthetic polymers** and **biopolymers** (natural polymers). Synthetic polymers are synthesized by scientists, whereas biopolymers are synthesized by organisms. Examples of biopolymers are DNA, RNA etc.

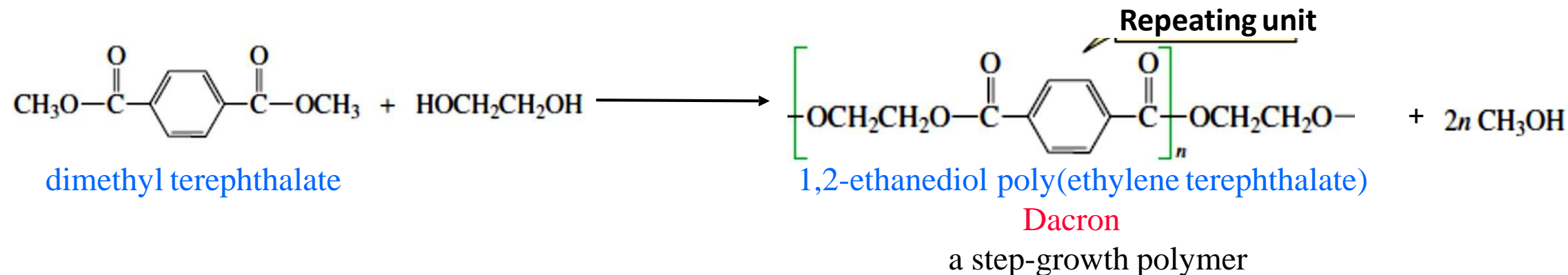
Classes of Synthetic Polymers

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

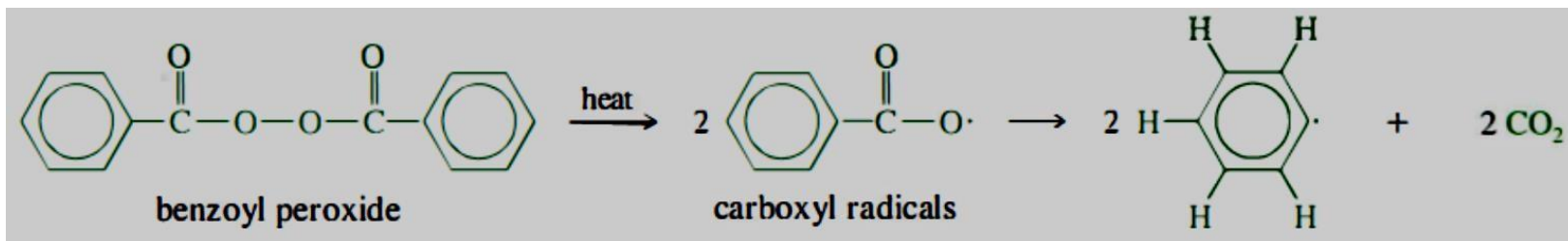
Chain-growth polymerization proceeds by one of three mechanisms: **radical polymerization**, **cationic polymerization**, or **anionic polymerization**. Each mechanism has three distinct phases: an *initiation step* that starts the polymerization, *propagation steps* that allow the chain to grow, and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

Some Important Chain-Growth Polymers and Their Uses

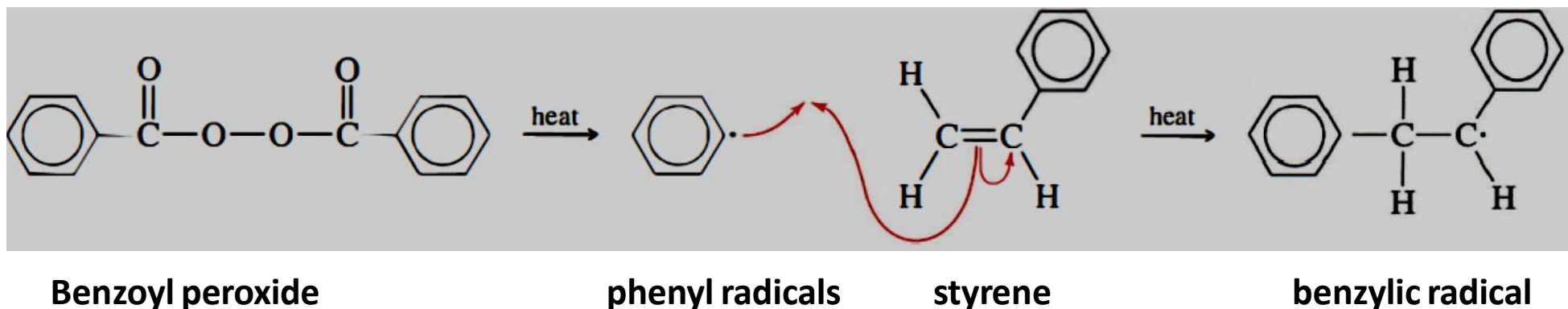
Monomer	Repeating unit	Polymer name	Uses
$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$	polyethylene	film, toys, bottles, plastic bags
$\text{CH}_2=\underset{\text{Cl}}{\text{CH}}$	$-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-$	poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$\text{CH}_2=\text{CH}-\text{CH}_3$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

Free-Radical Polymerization

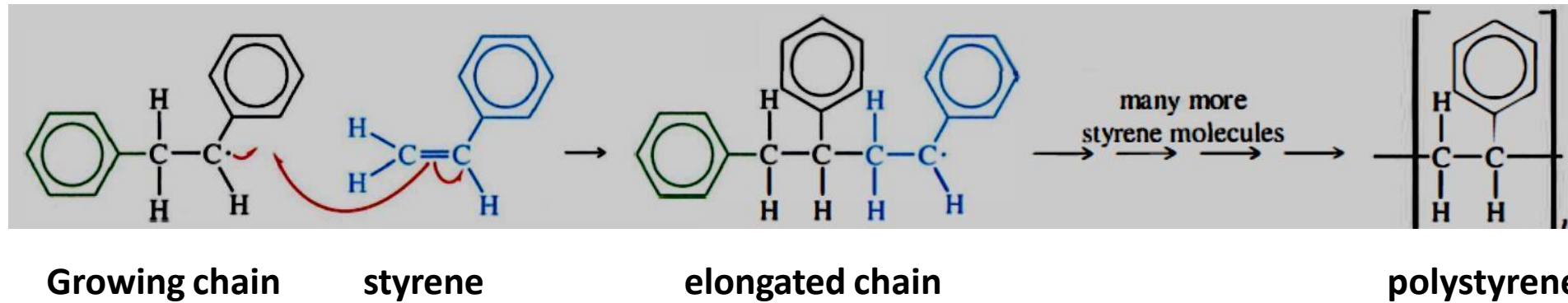
Free-radical polymerization results when a suitable alkene is heated with a radical initiator. For example, styrene polymerizes to polystyrene when it is heated to 100° C in the presence of benzoyl peroxide. This chain-growth polymerization is a free-radical chain reaction. Benzoyl peroxide cleaves when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

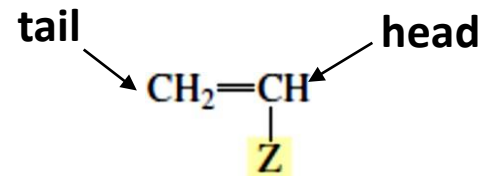


Eventually, the chain reaction stops because the propagating sites are destroyed. Propagating sites can be destroyed when two chains combine at their propagating sites; when two chains undergo *disproportionation*, with one chain being oxidized to an alkene and the other being reduced to an alkane; or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

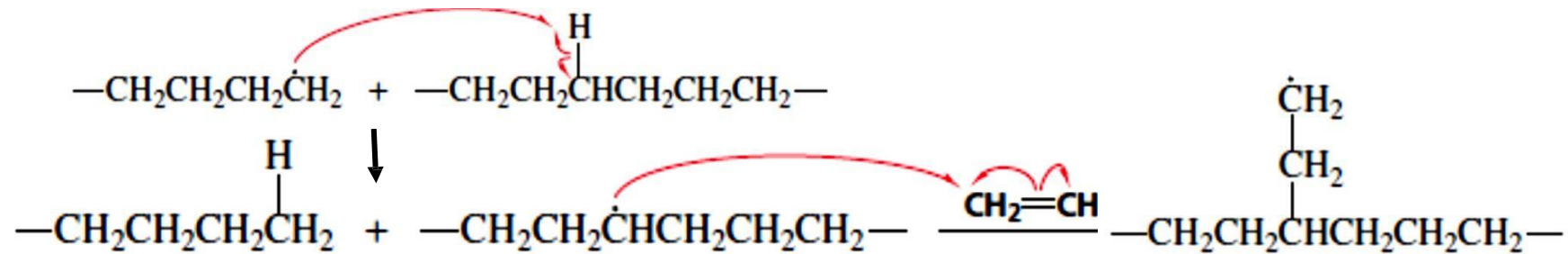


Chain-growth polymerization of monosubstituted ethylenes exhibits a marked preference for **head-to-tail addition**, where the head of one monomer is attached to the tail of another.

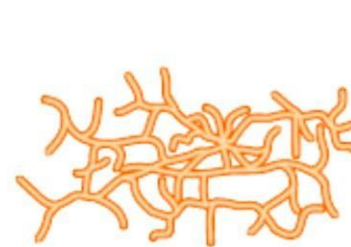


Branching of the Polymer Chain

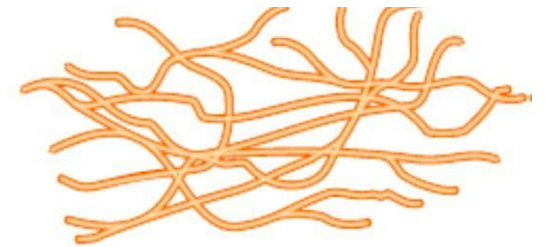
If the propagating site abstracts a hydrogen atom from a chain, a branch can grow off the chain at that point.



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.



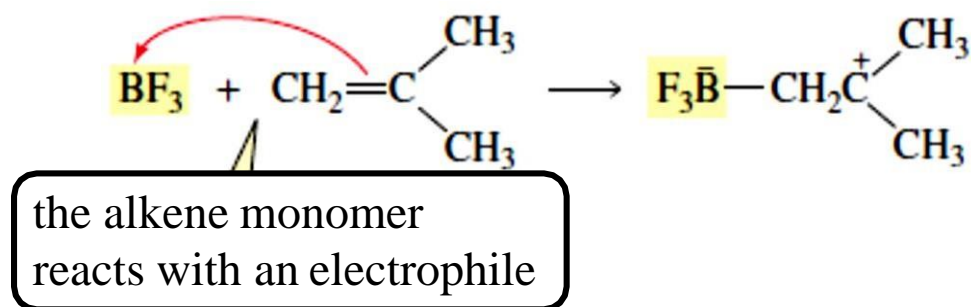
chain with short branches



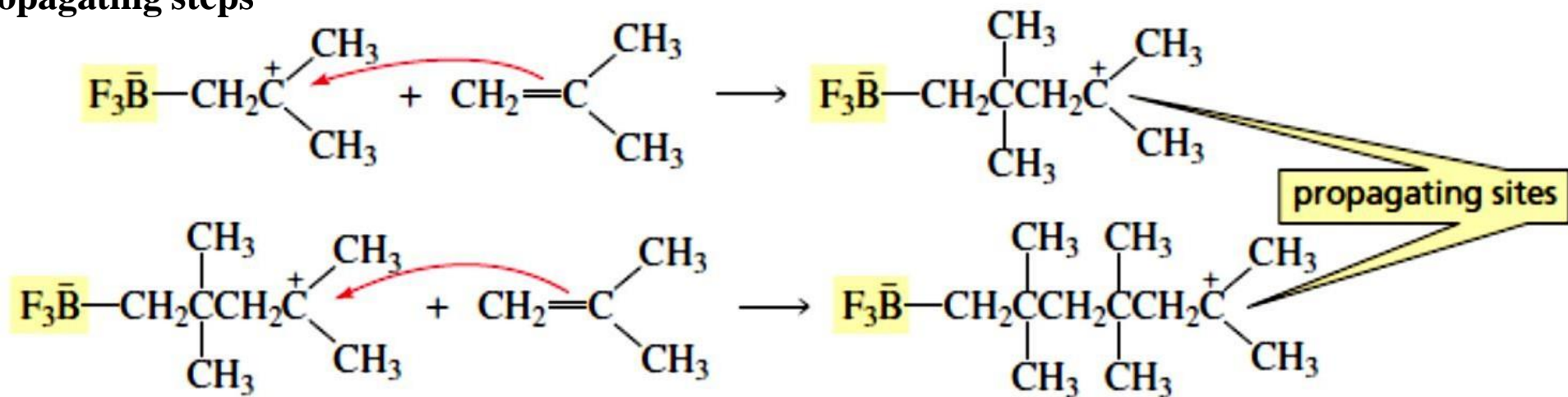
chain with long branches

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.

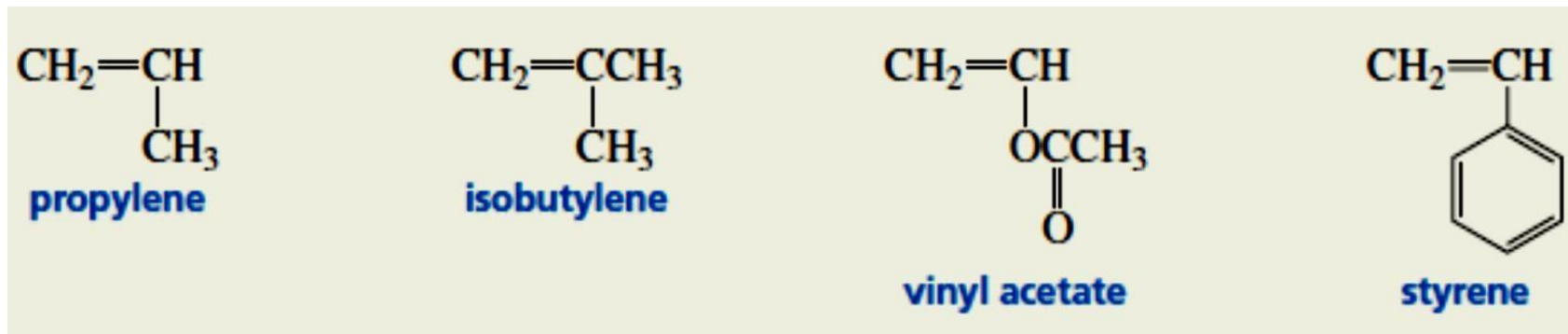
chain-initiating step



chain-propagating steps



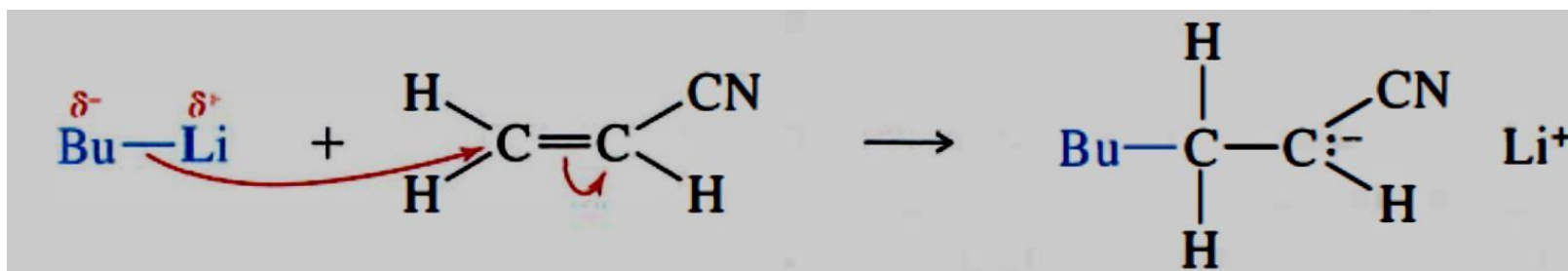
Monomers that are best able to undergo polymerization by a cationic mechanism are those with substituents that can stabilize the positive charge at the propagating site by donating electrons inductively or by resonance.



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.

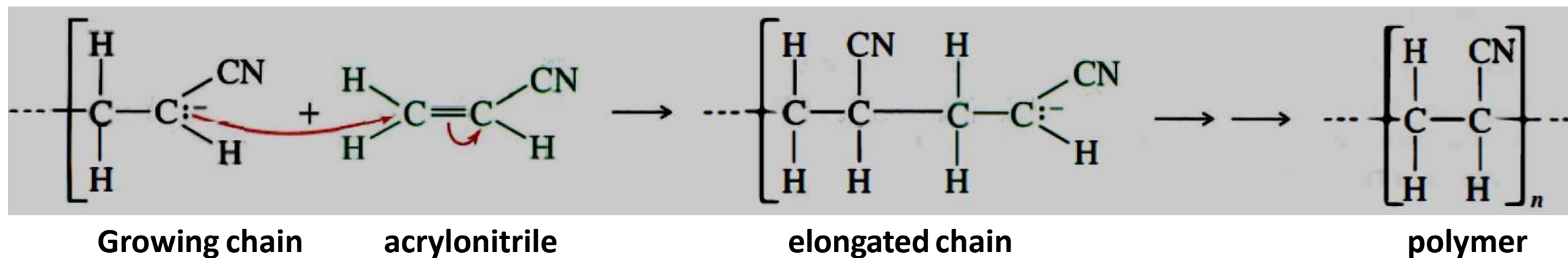
Anionic polymerization is usually initiated by a strong carbanion-like reagent such as an organolithium or Grignard reagent. Conjugate addition of the initiator to a monomer molecule starts the growth of the chain

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

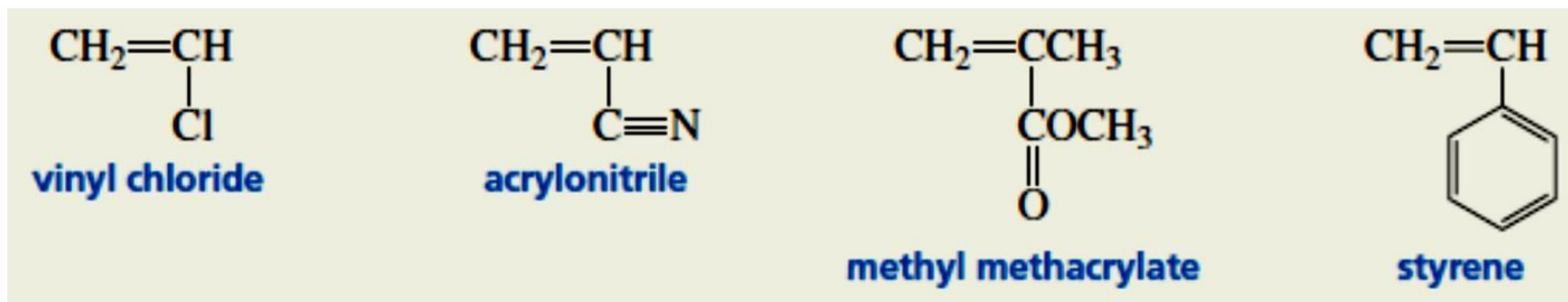


Stabilized anion

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



Examples of Alkenes That Undergo Anionic Polymerization

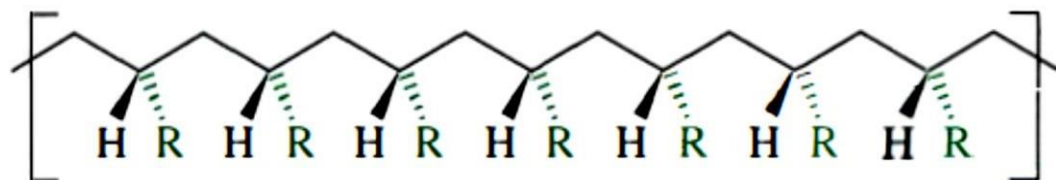


Stereochemistry of Polymers

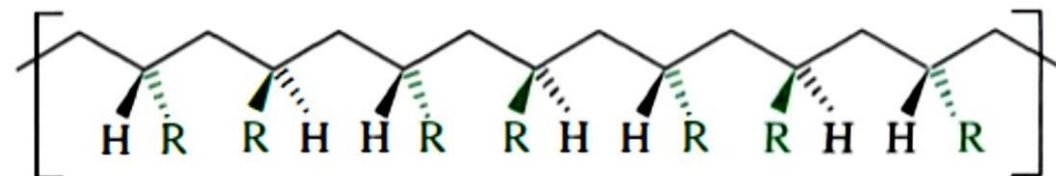
Polymers formed from monosubstituted ethylenes can exist in three configurations: isotactic, syndiotactic, and atactic.

- 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.

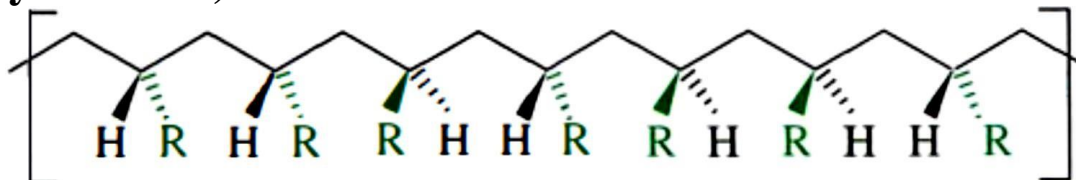
isotactic polymer (same side)



syndiotactic polymer (both sides)



atactic polymer (randomly oriented)

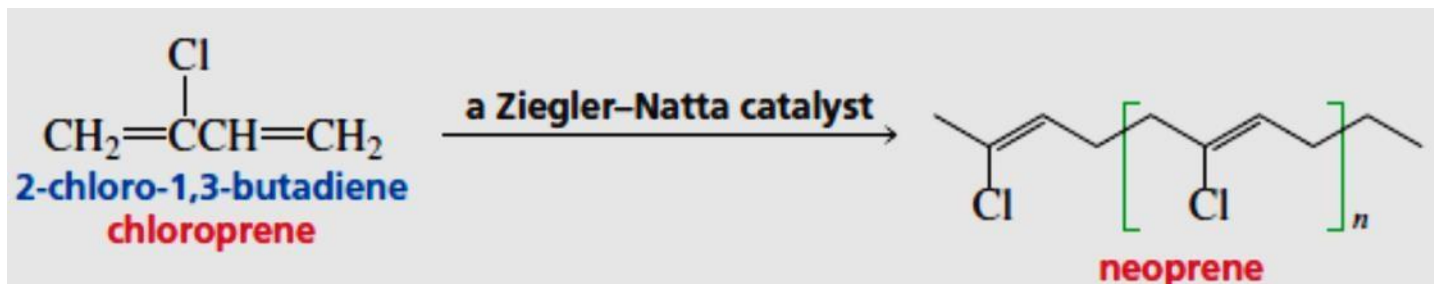
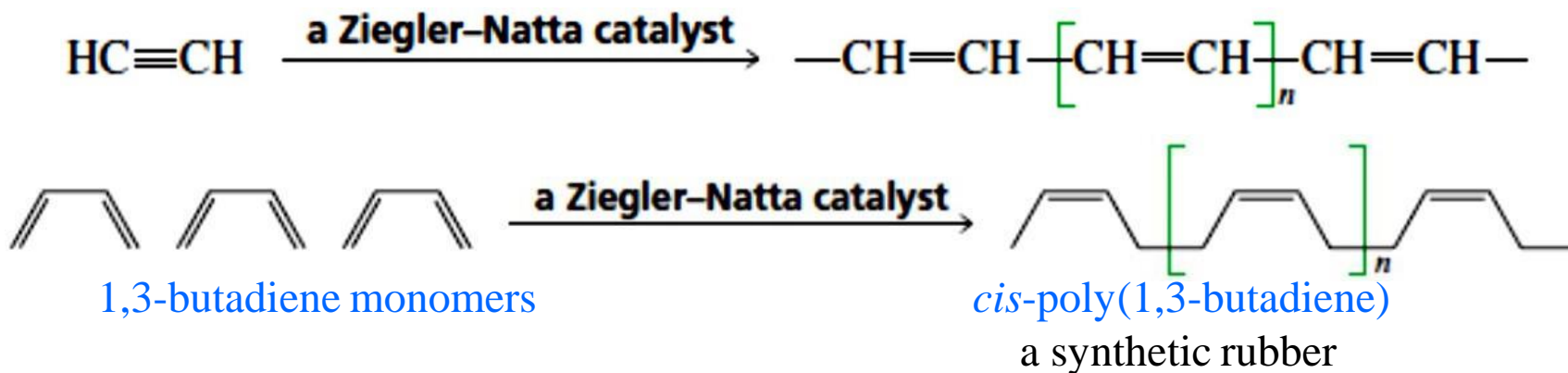


Polymers in the isotactic or syndiotactic configuration are more likely to be crystalline solids because positioning the substituents in a regular order allows for a more regular packing arrangement. Polymers in the atactic configuration are more disordered and cannot pack together as well, so these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

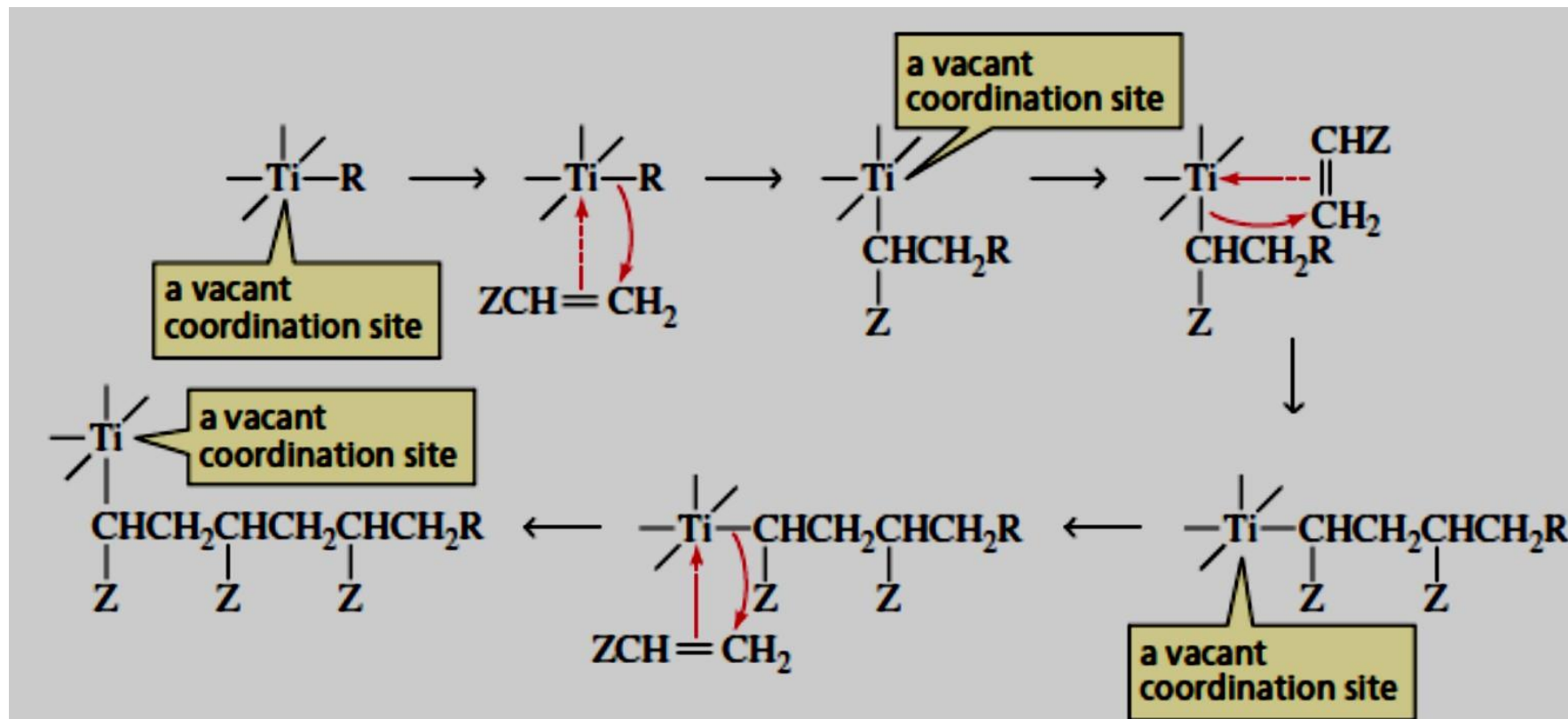
Ziegler-Natta catalyst

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.

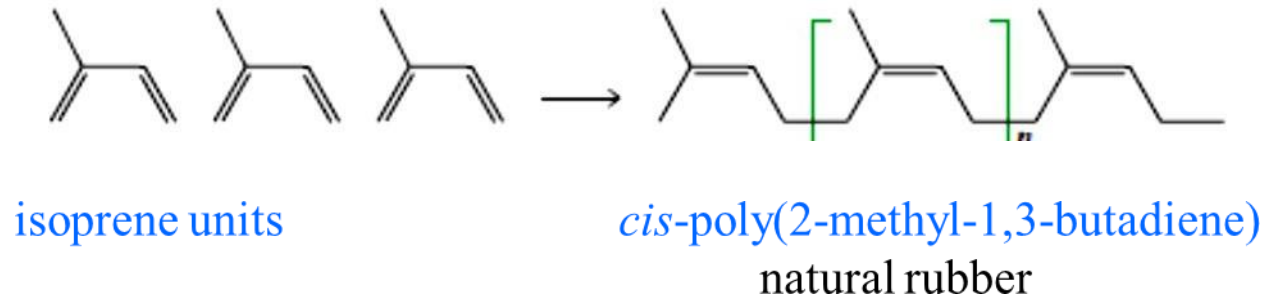


- Coordination polymerization:** The mechanism of the Ziegler–Natta-catalyzed polymerization of a substituted ethylene. A monomer forms a complex with an open coordination site of titanium and then is inserted between the titanium and the growing polymer.

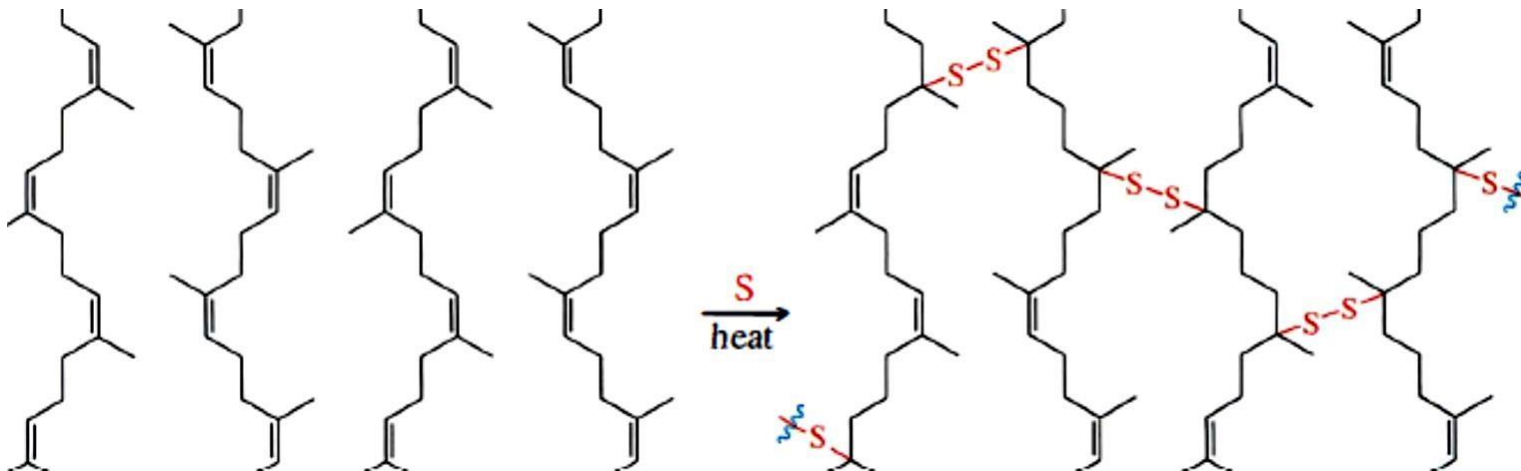


Natural Rubber

An **elastomer** is a polymer that stretches and then reverts to its original shape. When elastomers are stretched, the random chains stretch out. When the stretching force is removed, the chains go back to their random shapes as the van der Waals forces are not strong enough to maintain them in that arrangement. Rubber is an example of an elastomer



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

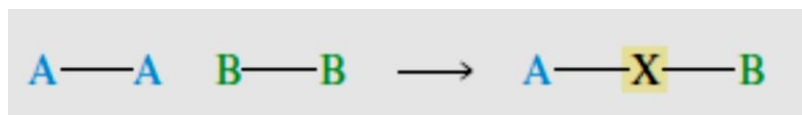
Step-Growth Polymers

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.

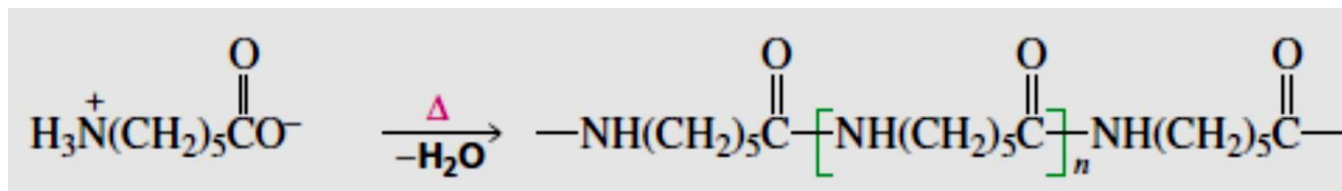
1. One type is formed by the reaction of a single monomer that possesses two different functional groups A and B. Functional group A of one monomer reacts with functional group B of another monomer.



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.

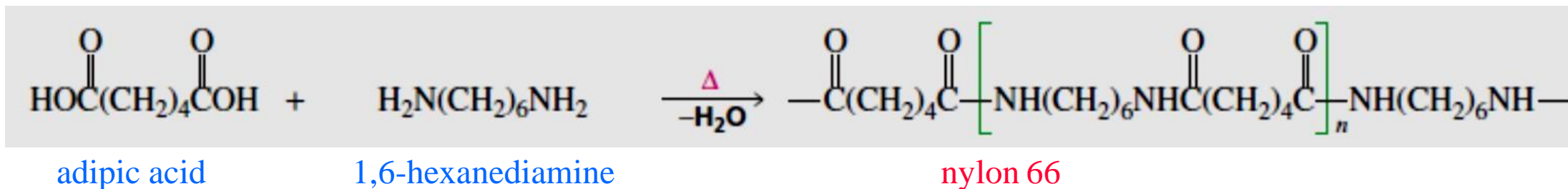


6-aminohexanoic acid

nylon 6
a polyamide

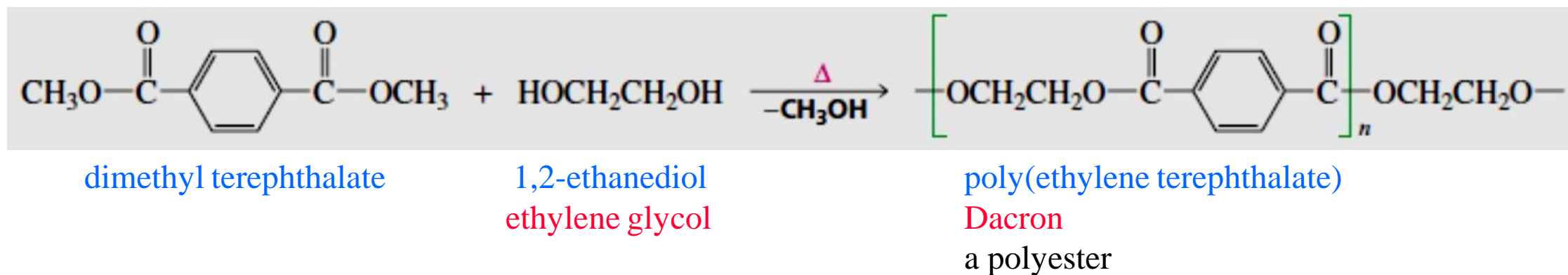
Ref: Paula Y. Bruce, Organic Chemistry, 3rd Ed

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

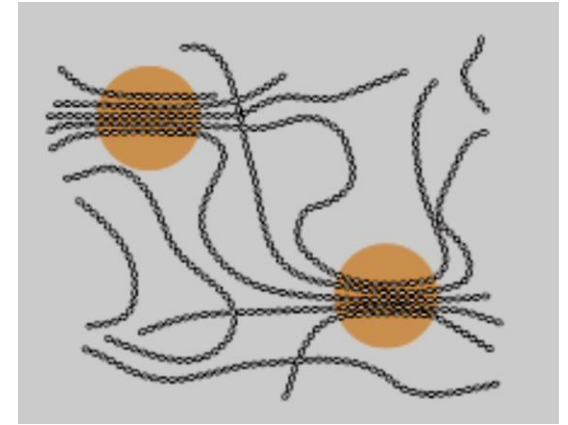
Polyesters are step-growth polymers in which the monomer units are joined together by ester groups. The most common polyester is known by the trade name Dacron® and is made by the transesterification of dimethyl terephthalate with ethylene glycol.



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

Physical Properties of Polymers

A polymer does not exist entirely in crystalline form. The problem is the size of the molecule. As solidification begins, the viscosity of the material rises and the polymer molecules find it difficult to move about and arrange their long chains in the regular pattern needed for crystal formation



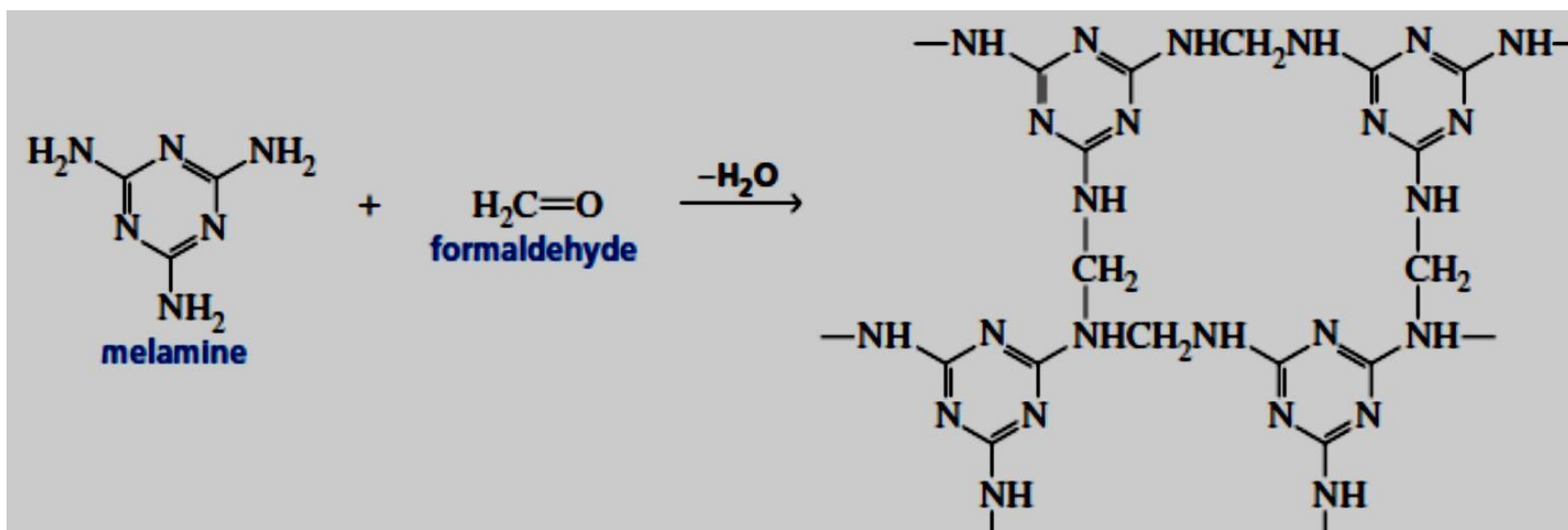
Thermoplastic Polymers

Thermoplastic polymers have both ordered crystalline regions and amorphous noncrystalline regions. Thermoplastic polymers are hard at room temperature, but soft enough to be molded when heated, because the individual chains can slip past one another at elevated temperatures. For example, combs, toys, switch plates, and telephone casings.

Thermosetting Polymers

Polymers which have a high degree of cross-linking are called **thermosetting polymers**. The cross-links are covalent bonds, not intermolecular vander Waals forces so if they are hardened, they cannot be remelted by heating.

Melmac®, a highly cross-linked thermosetting polymer of melamine and formaldehyde, is a hard, moisture-resistant material.



Melmac

Green Chemical Processes

Green chemistry or sustainable chemistry is an interdisciplinary overlap of chemistry and chemical engineering for processes and products for the minimization of the use and generation of hazardous substances.

This comprises of:

1. Use of renewable sources of energy and material feedstock
2. Use of safe and environmentally benign substances including solvents such as water.
3. Design of energy efficient processes.
4. Avoiding the production of waste.
5. Design of efficient methods of synthesis to maximize the amount of raw material that ends up in the product.

Principles of Green Chemistry

1. It is always better to prevent waste than to treat and clean up the waste after its generation.
2. Synthetic methods should be used to maximize the incorporation of all the substances used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess least toxicity to human health and environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

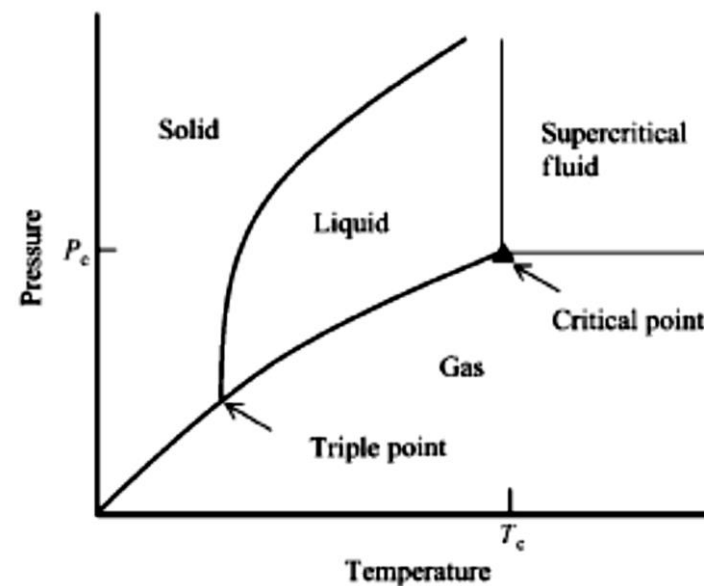
5. The use of auxiliary substances such as solvents, separating agents etc. should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure wherever possible.
7. Raw material should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives- unnecessary derivatization (blocking group, protection/deprotection, temporary modification) should be avoided wherever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and are biodegradable.
11. Analytical methods need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

Three key developments in green chemistry in the field of organic synthesis are:

1. Use of supercritical CO₂ as green solvent.
2. Aqueous H₂O₂ for oxidations
3. The use of hydrogen in asymmetric synthesis.

Applied green chemistry also includes supercritical H₂O oxidation, reactions in water and neat/dry medium reactions. Another branch contributing to green chemistry is biotechnology/bioengineering. In addition, the class of cascade, multicomponent and domino reactions also have positive effect on the reduction of pollutants.

A supercritical fluid (SCF) can be defined as a compound which is above its critical pressure (P_c), and above its critical temperature (T_c).

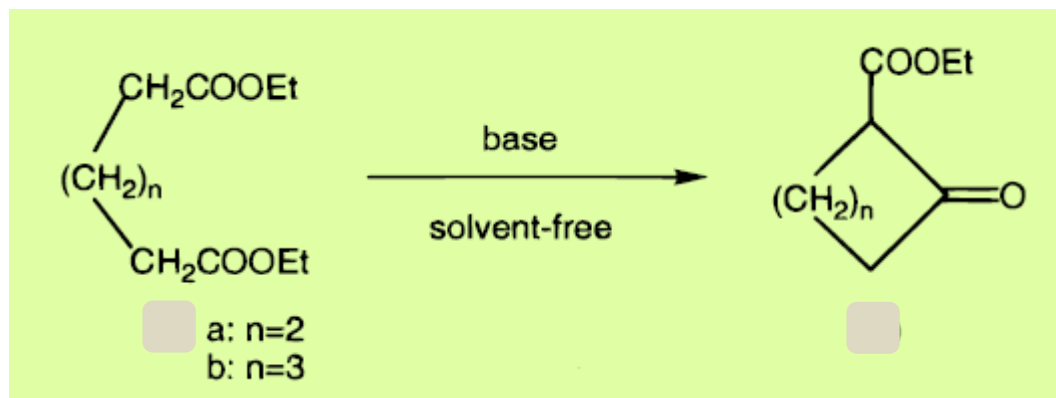


Phase diagram showing supercritical fluid region

Examples of Green Chemical Processes

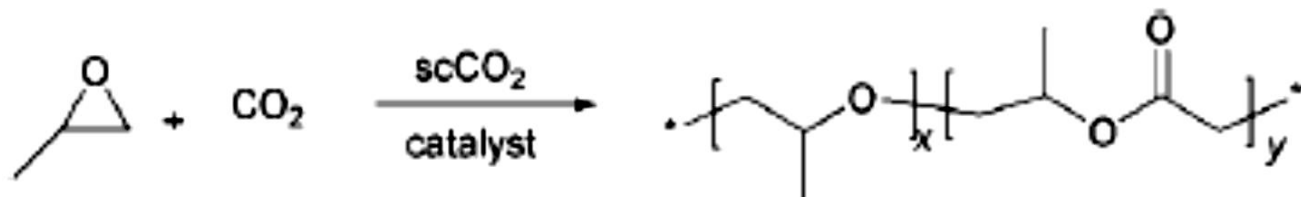
1. Dieckmann Condensation Reaction

- In general Dieckmann condensation reactions of diesters have been carried out in dried solvent under high-dilution conditions in order to avoid intermolecular reaction.
- Recently, Dieckmann condensation reactions of diethyl adipate and pimelate were found to proceed efficiently in the absence of solvent, and the reaction products were collected by a direct distillation of the reaction mixture.

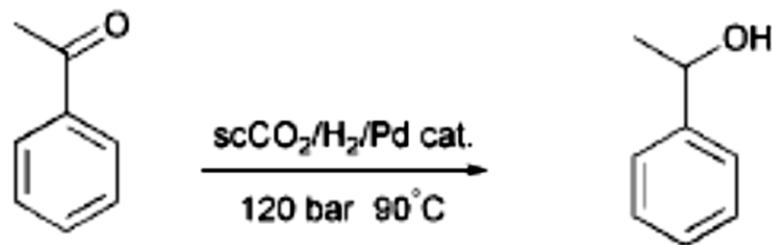
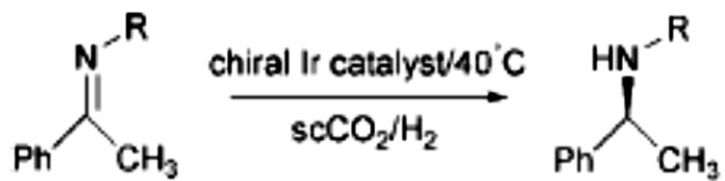


2. Supercritical CO₂ as a Reaction Solvent

a. Polyether–polycarbonate synthesis in scCO₂

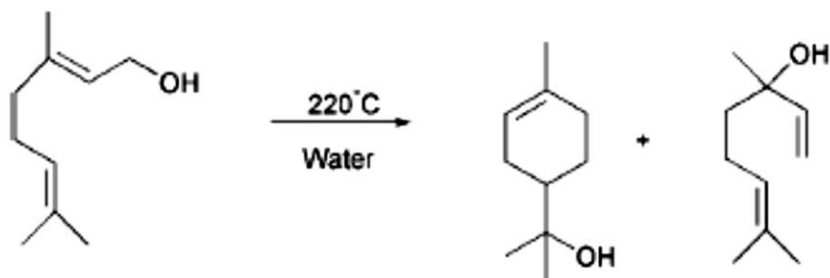


b. Some high yielding hydrogenation reactions carried out in scCO₂

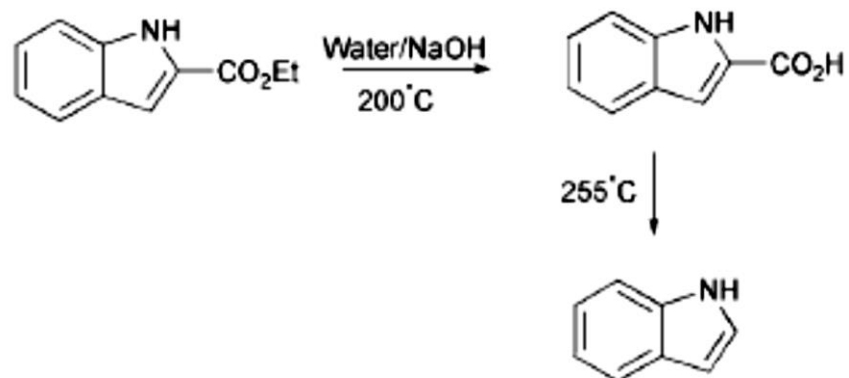


3. Water as a Reaction Solvent

a. Isomerization of geraniol in water



b. Indole synthesis in high temperature water



References:

1. Paula Y. Bruce, Organic Chemistry, 3rd Ed
2. R. T. Morrison, R. N. Boyd, S. K. Bhattacharjee. Organic Chemistry, 7th Edition, Pearson Education, 2011
3. Green Chemistry: An Introductory Text, Mike Lancaster