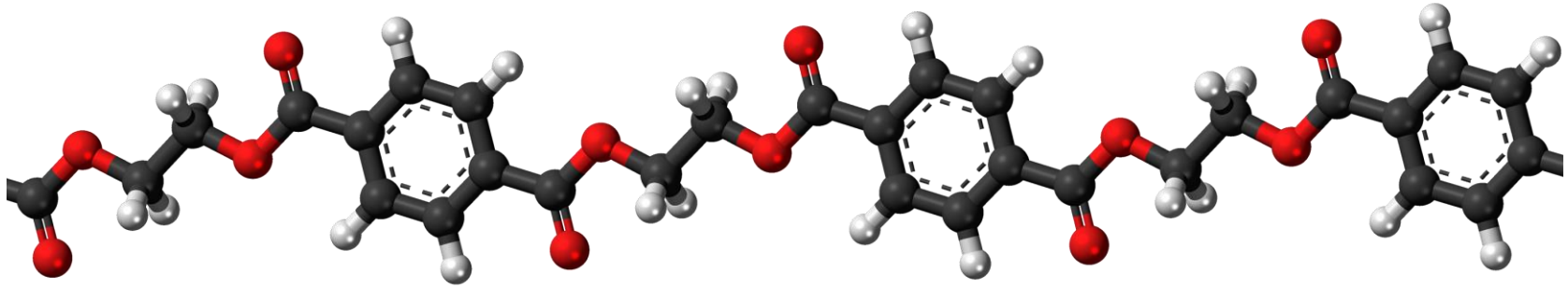
2302106 – Basic Organic Chemistry for ISE – Part II

Lecture 6-2

Polymers – Addition Polymers



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Recommended Textbook:

Chapter 26 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Addition Polymers

- Many **alkenes** undergo chain-growth polymerization when treated with small amounts of **suitable initiators**
- The chain-growth mechanism involves addition of the reactive end of the growing chain across the double bond of the monomer
- Depending on the monomer and the initiator used, the reactive intermediates may be **free radicals**, **carbocations**, or **carbanions**

free radicals

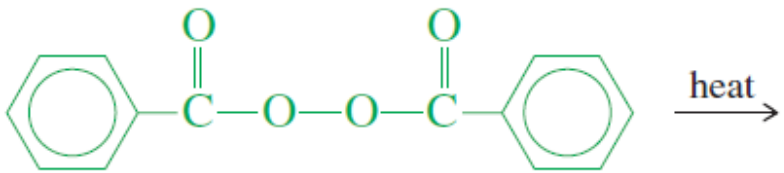
carbocations

carbanions

1) Free-Radical Polymerization

- Results when a suitable alkene is heated with a **radical initiator**
- **Radical initiator: Benzoyl peroxide** cleaves when heated to give two carboxyl radicals, which quickly decarboxylate to give phenyl radicals

Step 1: Initiation step (the **initiator** forms a radical that reacts with the **monomer** to start the chain)



benzoyl peroxide

1) Free-Radical Polymerization

Step 2: Propagation step (another molecule of monomer adds to the chain)

Step 3: Termination step

1) Free-Radical Polymerization

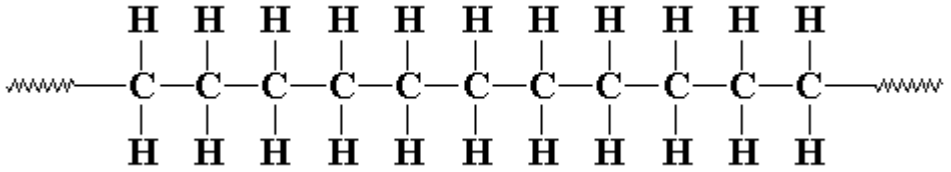
Extra: Chain Branching

- Results from **abstraction of a hydrogen atom in the middle** of a chain by the free radical at the end of a chain

- A **new chain grows** from the point of the free radical in the middle of the chain

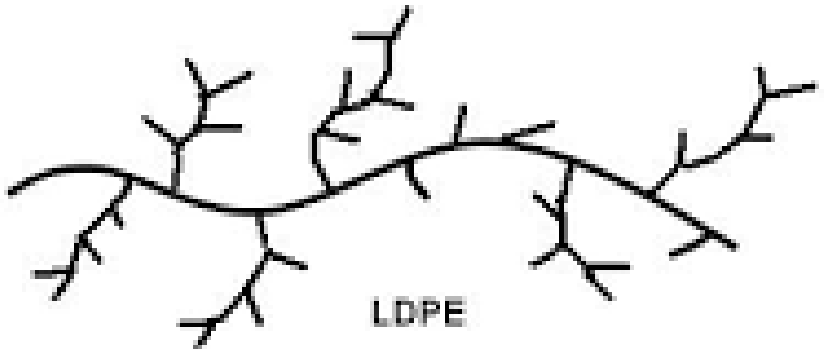
Extra: Chain Branching

Polyethylene (PE)



- **High Density PE (HDPE)**

Stronger due to the orderly structure of **unbranched** linear polymer chains



- **Low Density PE (LDPE)**

Soft and flimsy because it has a highly **branched**, amorphous structure

2) 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 as a co-catalyst**

Step 1: Initiation step

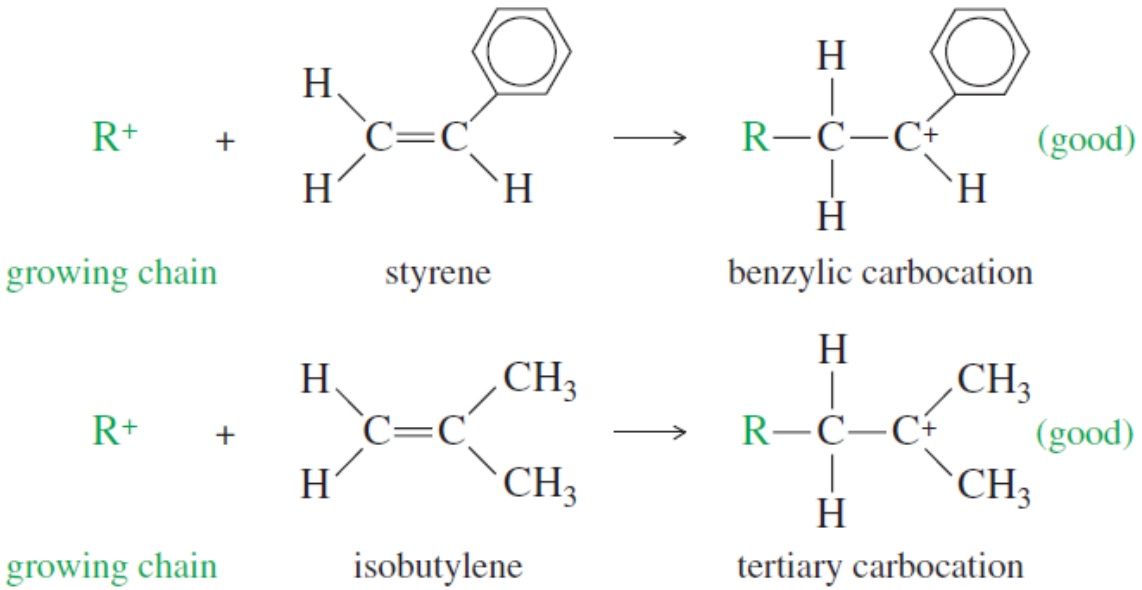
Step 2: Propagation step

Step 3: Termination step

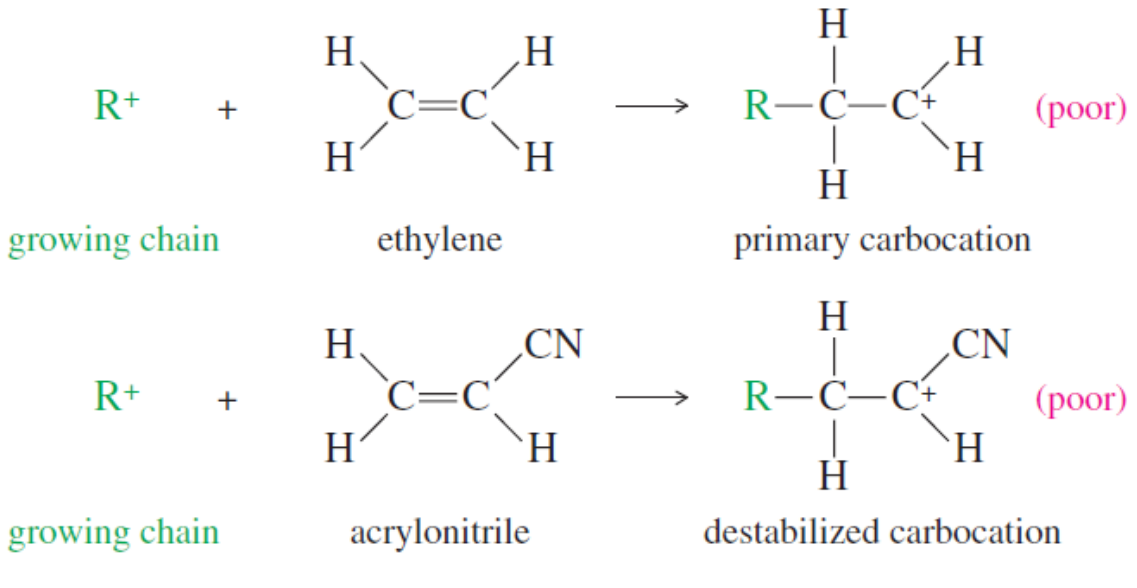
2) Cationic Polymerization

Cationic process needs a monomer that forms a relatively **stable carbocation**

Good monomers for cationic polymerization



Poor monomers for cationic polymerization



3) Anionic Polymerization

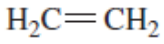
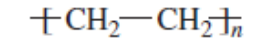
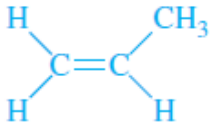
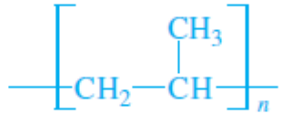
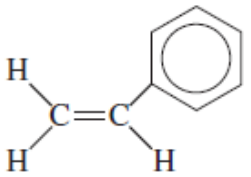
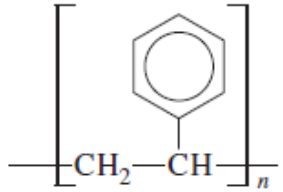
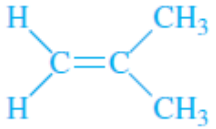
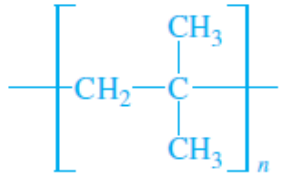
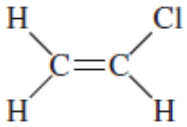
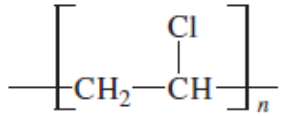
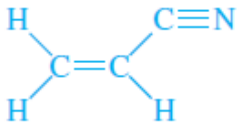
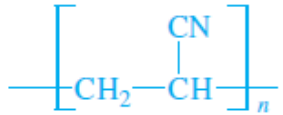
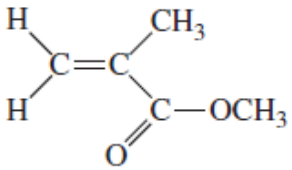
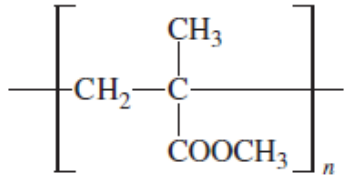
- Occurs through **carbanion intermediates**
- Effective anionic polymerization requires a monomer that gives a **stabilized carbanion** (contain at least one strong **electron-withdrawing group** such as a **carbonyl** group, a **cyano** group, or a **nitro** group)
- Initiated by a **strong carbanion-like reagent** such as an **organolithium** or **Grignard reagent**

Step 1: Initiation step

Step 2: Propagation step

Step 3: Termination step

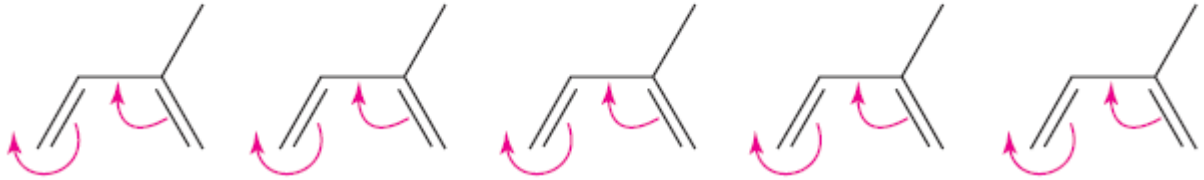
Examples of Addition Polymers

Polymer	Polymer Uses	Monomer Formula	Polymer Repeating Unit
polyethylene	bottles, bags, films		
polypropylene	plastics, olefin fibers		
polystyrene	plastics, foam insulation		
poly(isobutylene)	specialized rubbers		
poly(vinyl chloride)	vinyl plastics, films, water pipes		
poly(acrylonitrile)	Orlon®, Acrilan® fibers		
poly(methyl α-methacrylate)	acrylic fibers, Plexiglas®, Lucite® paints		

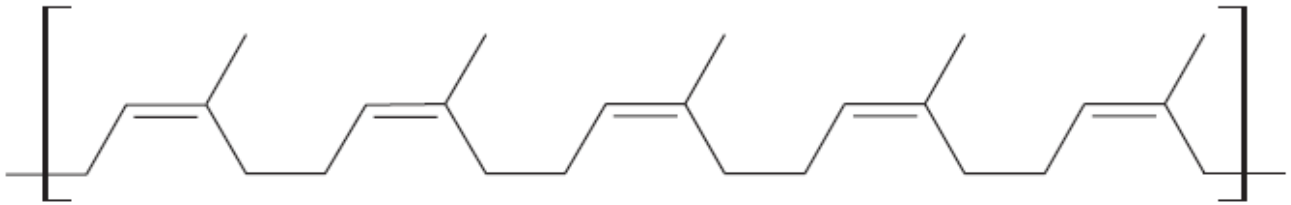
Addition Polymers – Natural Rubbers

- Natural rubber is a **terpene** composed of **isoprene** units
- results from **1,4-addition** to each isoprene molecule, with all the double bonds in the ***cis*** configuration

Imaginary polymerization of isoprene units



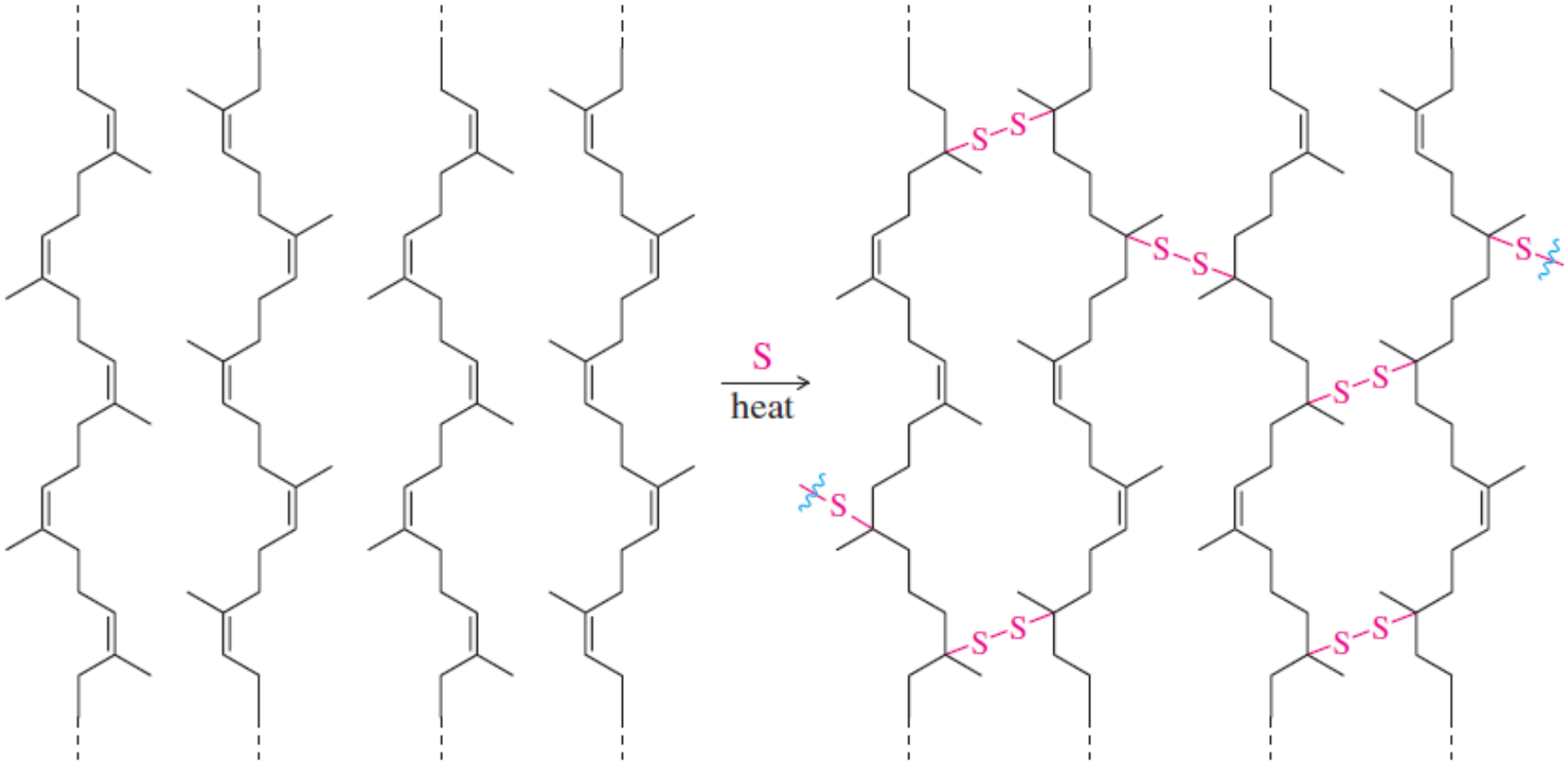
Natural rubber



Latex from a rubber tree

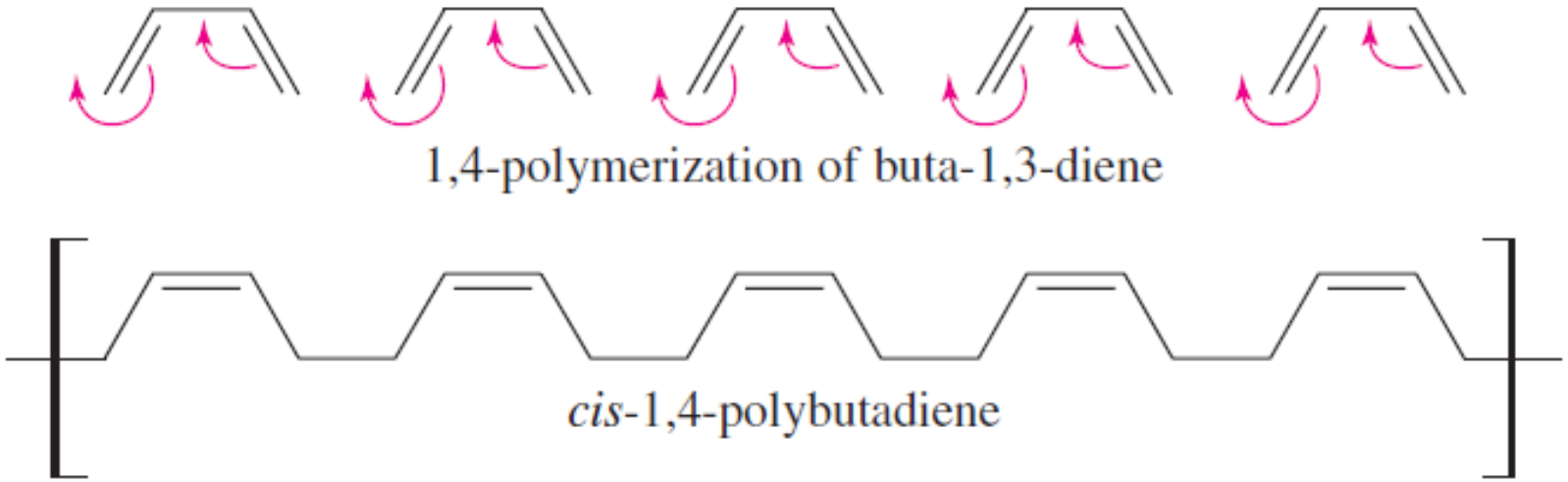
Addition Polymers – Natural Rubbers

- **Vulcanization:** Heating rubber with **sulphur** leads to cross-linking of rubber; it becomes **stronger** and **more elastic**, allows the casting of complicated shapes such as rubber tires



Addition Polymers –Synthetic Rubbers

- There are many different formulations for synthetic rubbers, but the simplest is a polymer of **buta-1,3-diene**

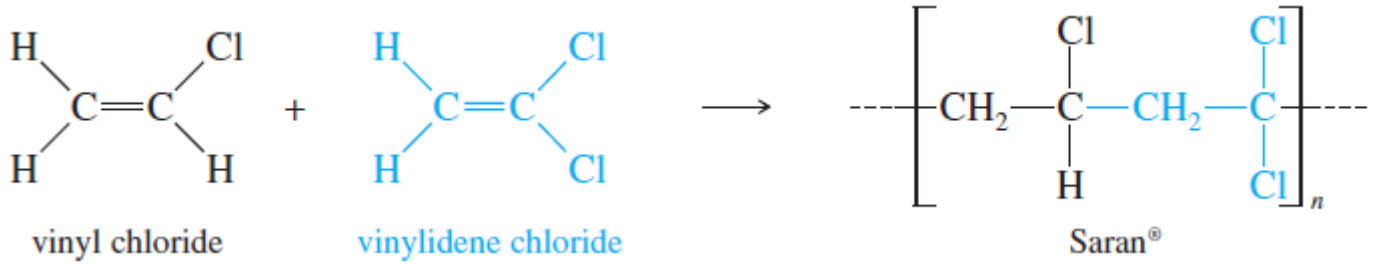


- Specialized catalysts can produce buta-1,3-diene polymers where 1,4-addition has occurred on each butadiene unit and the remaining double bonds are all ***cis***

- This polymer has properties similar to those of natural rubber, and it can be vulcanized in the same way

Addition Polymers – Copolymers

- Made by polymerizing two or more different monomers together
- In many cases, monomers are chosen so that they add selectively in an **alternating manner**, giving the **alternating copolymer**



Two different copolymers, formed from monomers ● and ●

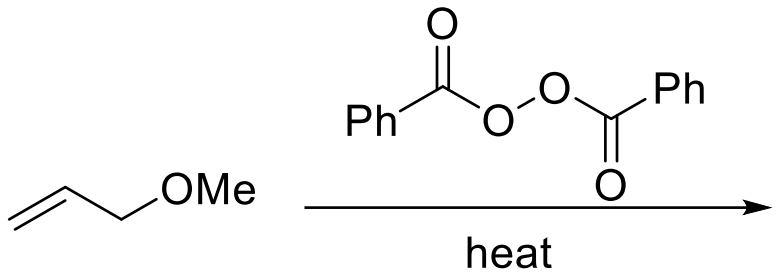
alternating copolymer **random copolymer**

X = ● Y = ●

- An *alternating copolymer* is formed when X and Y alternate regularly along the chain.
- A *random copolymer* is formed when X and Y are randomly distributed along the chain.

Addition Polymers – Examples

- Suggest the product of the following reaction



Addition Polymers – Examples

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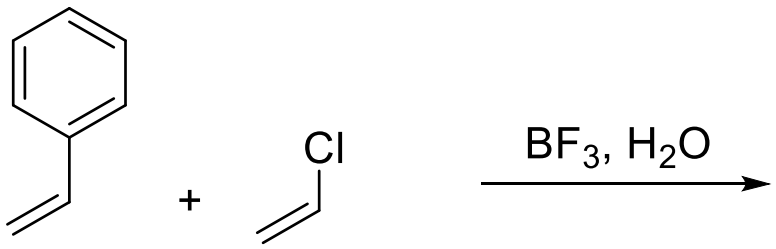

Addition Polymers – Examples

- Suggest the product of the following reaction