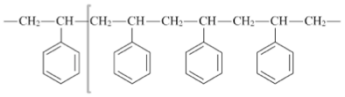
Synthetic Polymers

Introduction

- A polymer is a large molecule composed of many smaller repeating units.
- First synthetic polymers:
  - ⇨ Polyvinyl chloride (PVC) in 1838
  - ⇨ Polystyrene in 1839
- Now, >250 billion pounds produced annually, worldwide.

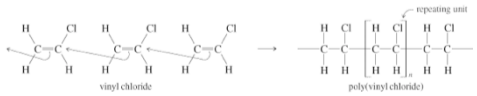
Polystyrene & Others

Addition polymers result from the rapid addition of one molecule at a time to a reactive cation, radical, or anion intermediate at the growing end of the chain. The monomers are usually alkenes. Click on the right-hand edge that defines a single repeat unit of the polymer.

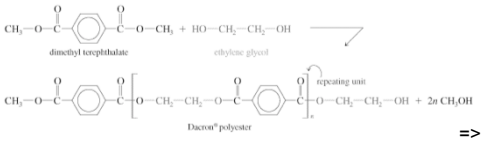


Classes of Polymers

- Addition, or chain-growth, polymers



- Condensation, or step-growth, polymers



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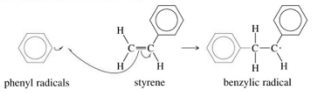
Addition Polymers

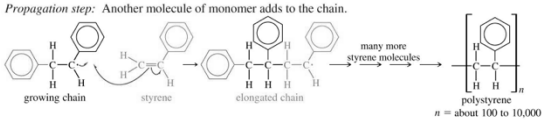
- Three kinds of processes (intermediates):
  - ⇨ Free radicals
  - ⇨ Carbocations
  - ⇨ Carbanions
- Examples of addition polymers:
  - ⇨ polypropylene plastics
  - ⇨ polystyrene foam insulation
  - ⇨ poly(acrylonitrile) Orlon® fiber
  - ⇨ poly(methyl α-methacrylate) Plexiglas ®

Free Radical Polymerization

Initiation step: The initiator reacts with the monomer to start the chain.



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



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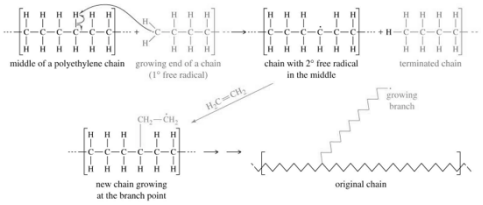
Chain Branching

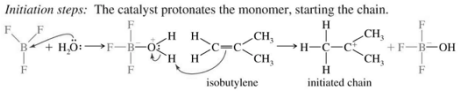
- Low-density polyethylene:
  - ⇨ soft and flimsy
  - ⇨ highly branched, amorphous structure



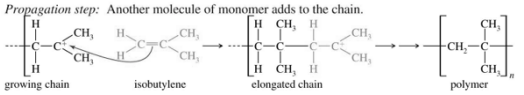
Cationic Polymerization

- Alkene is treated with an acid.
- Intermediate must be a stable carbocation.

Initiation steps: The catalyst protonates the monomer, starting the chain.



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



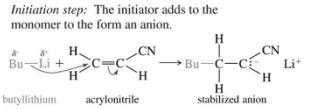
Question

- Of the following monomers, which one would undergo cationic polymerization most readily?
- A) $H_2C{=}CHCH_3$
- B) $H_2C{=}C(CH_3)_2$
- C) $H_2C{=}CHC{\equiv}N$
- D) $H_2C{=}CHCl$

Anionic Polymerization

- Alkene must have an electron-withdrawing group like C=O, C≡N, or NO_2.
- Initiator: Grignard or organolithium reagent.

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



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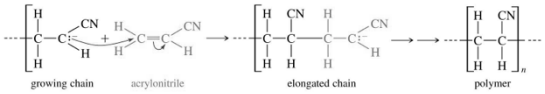
Propagation step: Another molecule of monomer adds to the chain.

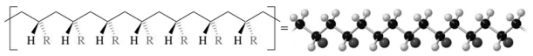


Question

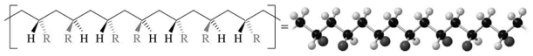
- Which monomer would undergo anionic polymerization most readily?
- A) $H_2C{=}CHCH_3$
- B) $H_2C{=}CHCH{=}CH_2$
- C) $H_2C{=}CHC{\equiv}N$
- D) $H_2C{=}CHCl$

Stereochemistry

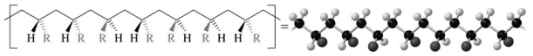
An isotactic polymer (side groups on the same side of the backbone)



A syndiotactic polymer (side groups on alternating sides of the backbone)



An atactic polymer (side groups on random sides of the backbone)



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Properties of Polymers

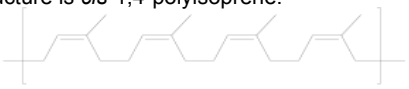
- Isotactic and syndiotactic polymers are stronger and stiffer due to their regular packing arrangement.
- Anionic intermediate usually gives isotactic or syndiotactic polymers.
- Free radical polymerization is nearly random, giving branched atactic polymers.

Ziegler-Natta Catalyst

- Polymerization is completely stereospecific.
- Either isotactic or syndiotactic, depending on catalyst.
- Polymer is linear, not branched.
- Example of catalyst: solution of $TiCl_4$ mixed with solution of $(CH_3CH_2)_3Al$ and heated for an hour.

Natural Rubber

- Soft and sticky, obtained from rubber tree.
- Long chains can be stretched, but then return to original structure.
- Chains slide past each other and can be pulled apart easily.
- Structure is *cis*-1,4-polyisoprene.

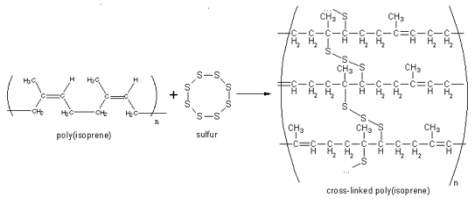


Vulcanization

- Process was discovered accidentally by Goodyear when he dropped rubber and sulfur on a hot stove.
- Sulfur produces cross-linking that strengthens the rubber.
- Hardness can be controlled by varying the amount of sulfur.

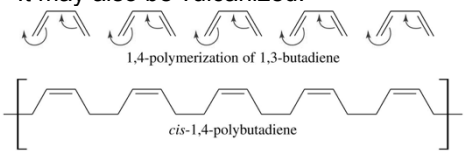
Vulcanized Roller Hockey Ball

Vulcanization



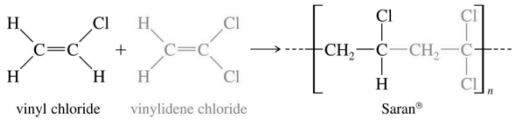
Synthetic Rubber

- With a Ziegler-Natta catalyst, a polymer of 1,3-butadiene can be produced, in which all the additions are 1,4 and the remaining double bonds are all cis.
- It may also be vulcanized.



Copolymers

- Two or more different monomers.
- Saran®: alternating molecules of vinyl choride and 1,1-dichloroethylene.
- ABS plastic: acrylonitrile, butadiene, and styrene.



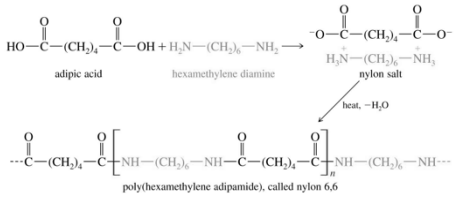
Condensation Polymers

Condensation Polymers

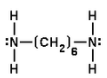
- Polymer formed by ester or amide linkages between difunctional molecules.
- Step growth: Monomers do not have to add one at a time. Small chains may condense into larger chains.
- Common types:
  - Polyamides
  - Polyesters
  - Polycarbonates
  - Polyurethanes

Polyamides: Nylon

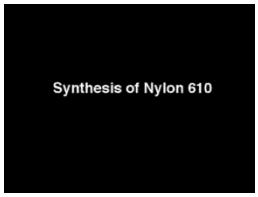
Usually made from reaction of diacids with diamines, but may also be made from a single monomer with an amino group at one end and acid group at other.



Nylon

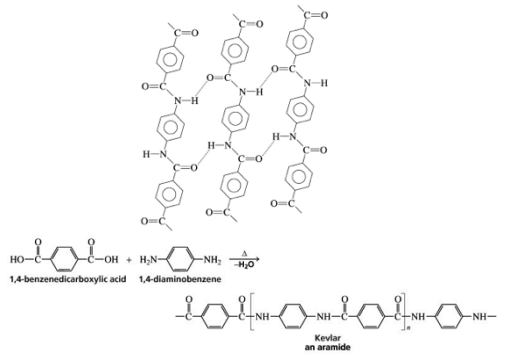


Nylon



Question

- What combination should be used to prepare Nylon 66?
- A) HO_2C-$(CH_2)4$-CO_2H + H_2N-$(CH_2)_6$-NH_2
- B) HO_2C-$(CH_2)6$-CO_2H + H_2N-$(CH_2)_6$-NH_2
- C) HO_2C-$(CH_2)4$-CO_2H + H_2N-$(CH_2)_4$-NH_2
- D) HO_2C-$(CH_2)6$-CO_2H + H_2N-$(CH2)_4$-NH_2

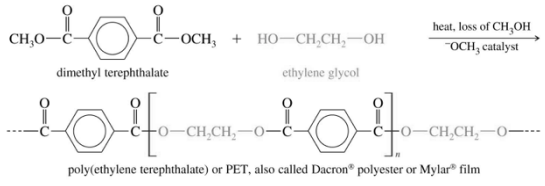


Question

- The reaction of 1,4-diaminobenzene with the acyl chloride of benzene-1,4-dicarboxylic acid to produce the polymer Kevlar and HCl is an example of a(n)
- A) condensation reaction.
- B) elimination reaction.
- C) substitution reaction.
- D) addition reaction.

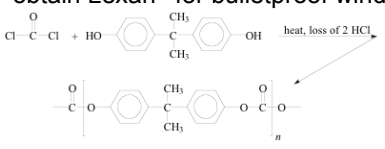
Polyesters

- Dacron® and Mylar®: polymer of terephthalic acid and ethylene glycol.
- Made by the transesterification of the methyl ester.



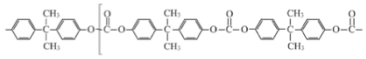
Polycarbonates

- Esters of carbonic acid.
- Carbonic acid is in equilibrium with CO_2 and water, but esters are stable.
- React phosgene with bisphenol A to obtain Lexan® for bulletproof windows.



Step-growth Polymers

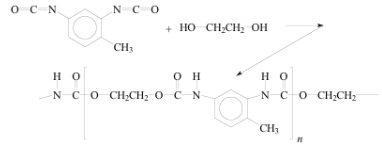
Step-growth polymers are formed by the intermolecular reaction of monomers with two functional groups. Click on the location that defines the right-hand edge of the monomer for which the left-hand edge is shown in green below.



Lexan
a polycarbonate

Polyurethanes

- Esters of carbamic acid, R-NH-COOH.
- Urethanes are prepared by reacting an alcohol with isocyanate.
- Polyurethanes are prepared by reacting a diol with a diisocyanate.



Plasticizers

- Nonvolatile liquid that dissolves, lowers the attraction between chains, and makes the polymer more flexible.
- Example: Dibutyl phthalate is added to poly(vinyl chloride) to make it less brittle. The plasticizer evaporates slowly, so "vinyl" becomes hard and inflexible over time…..The foggy film that forms on your windshield on a hot day.

Recycling vs. Landfill

250 billion pounds of waste "plastics" are produced annually, worldwide.

http://www.lotfi.net/recycle/plastic.html

Recycling categories for common plastics

Plastic recycling number	Acronym and name of polymer	Original uses	Recycle uses
1	PET Poly(ethylene terephthalate)	Beverage bottles, food and cleanser bottles	Carpet fibers, fiberfill insulation, nonfood containers
2	HDPE High-density polyethylene	Milk, juice, water bottles, grocery bags (crinkly)	Oil and soap bottles, trash cans, grocery bags, pipes
3	PVC (or V) Polyvinyl chloride	Food and water bottles, food wraps, blister packs, construction materials	Drainage pipes, flooring tile, traffic cones
4	LDPE Low-density polyethylene	Flexible bags for trash, bread, milk, groceries; flexible wraps and containers	Bags for trash, groceries; irrigation pipes; oil bottles
5	PP Polypropylene	Handles, bottle caps, lids, wraps, bottles	Auto parts, fibers, pails, refuse containers
6	PS Polystyrene	Foam cups, packaging; cutlery; furniture; appliances	Insulation, toys, trays, packaging "peanuts"
7	Other	Various	Plastic "lumber," posts, fencing, pallets