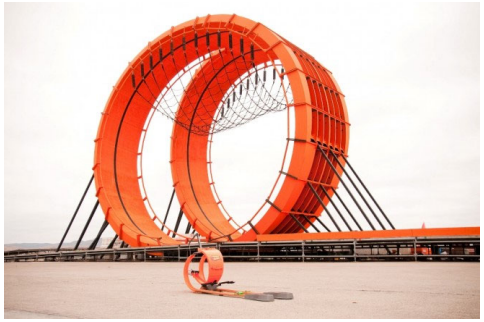
Materials

1. Plastics and Polymers

Plastic: material that can be ***molded*** or ***shaped***

Polymer: ***macromolecule*** = material of high molecular weight, formed from many repeating units

- Mostly from petrochemicals
- Widely used: rubber, insulation material, fibers, paint, foams, adhesives, molds, structural material



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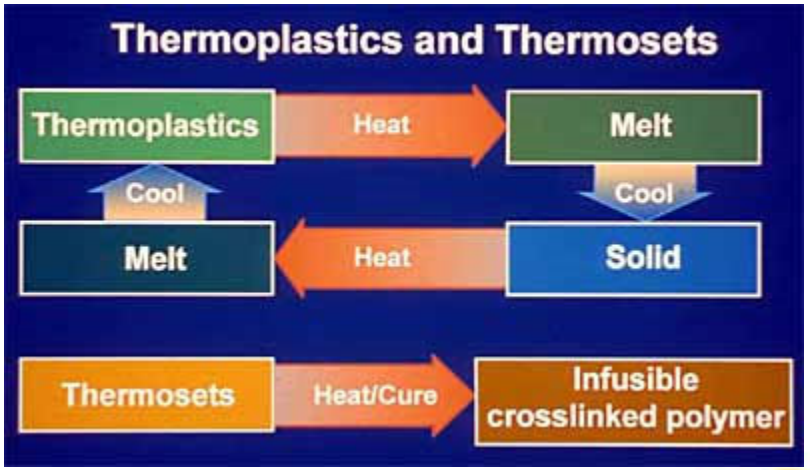
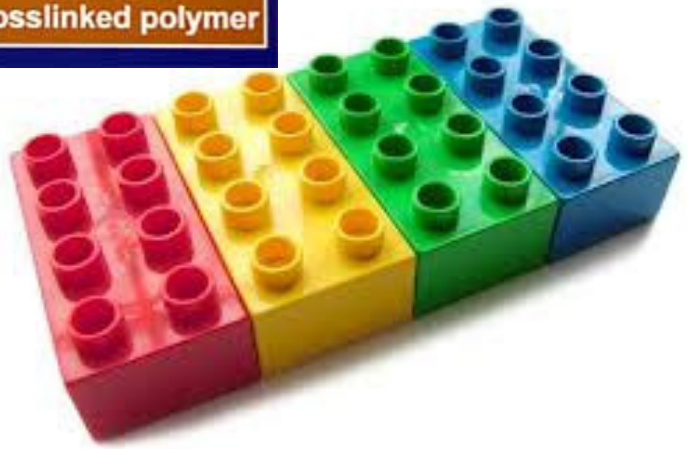
Thermoplastic: material that ***softens when heated***, sets when cool

Thermoset: material that is soft enough to be molded when made but ***permanently sets on heating***





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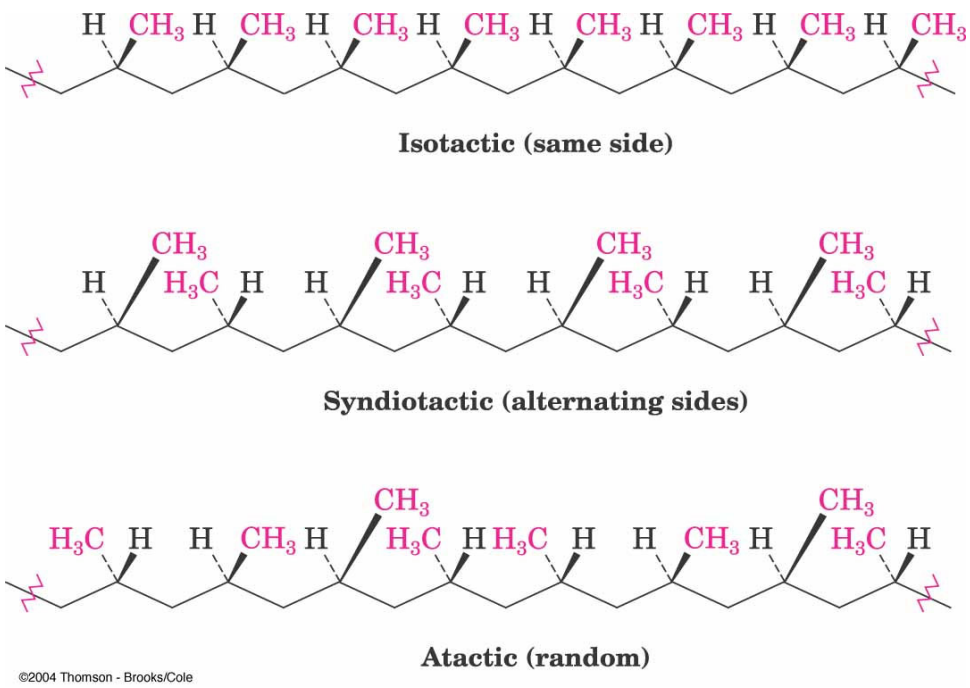
Properties of Polymers depend on their molecular structure

Order in which the monomers are arranged:

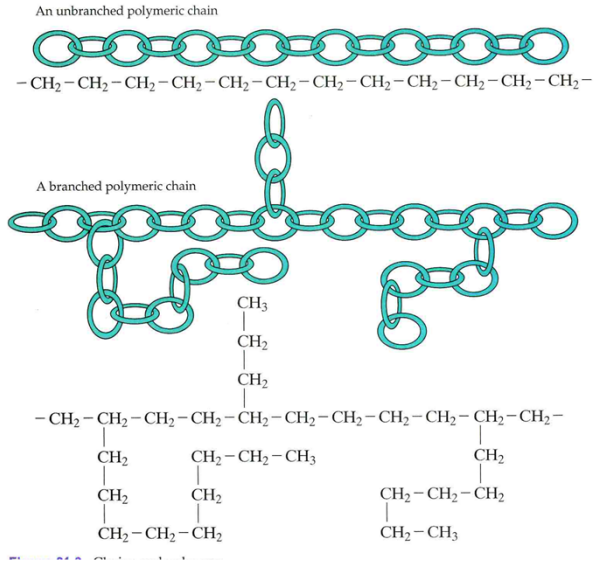
Homopolymers: A-A-A-A-A-A-A-A-A-A

Copolymers: A-B-A-B-A-B or A-A-A-A-B-B-B-B-A-A-A-A

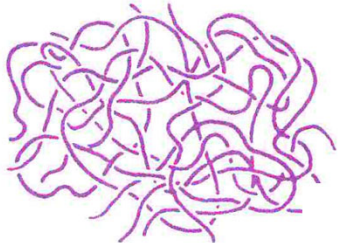
Three-dimensional arrangement within the chain:



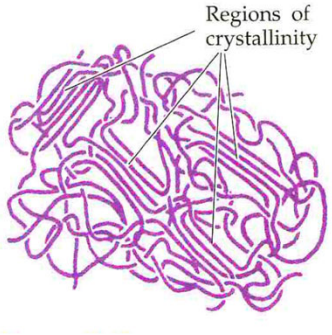
Linear vs. branched



Low density polymer
low melting flexible plastic



High density polymer
denser and more rigid plastic



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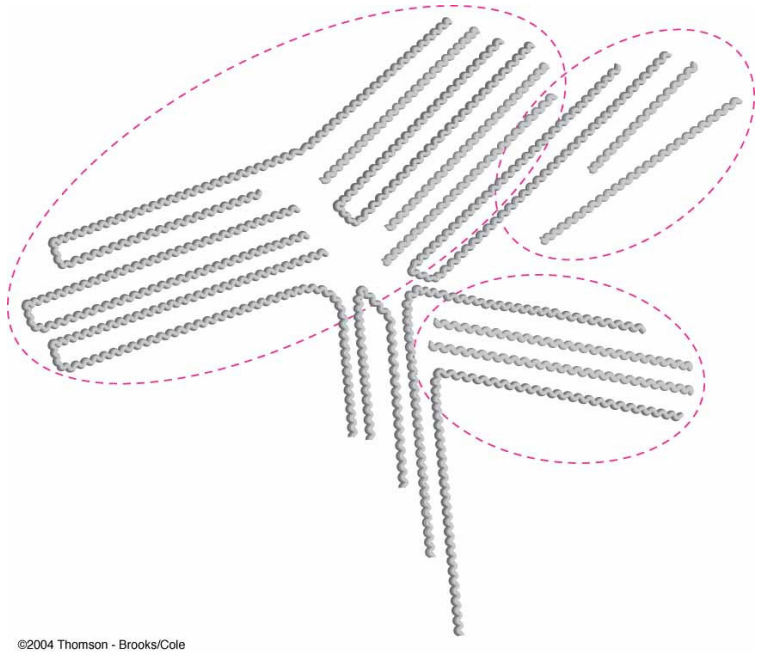
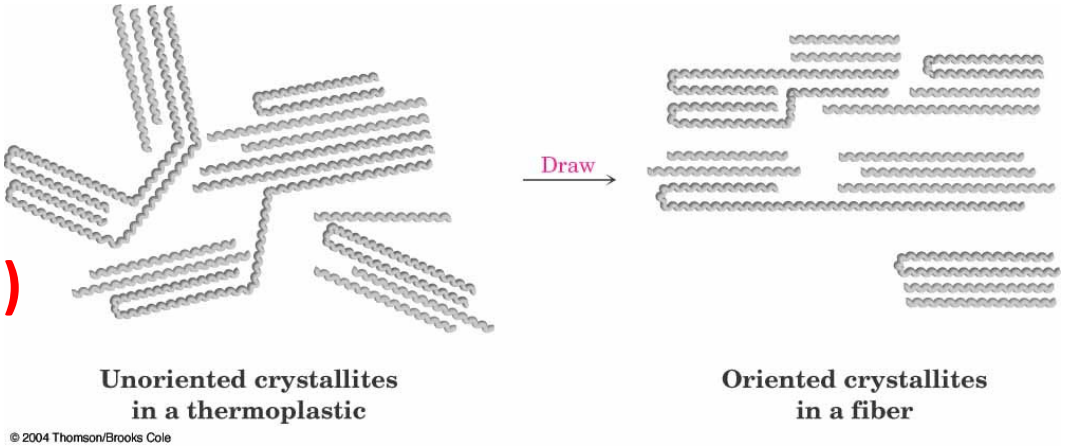
Rigidity is provided by crystalline region



Fibers can be draw by extruding molten polymers (Nylon, Dacron, polyethylene)



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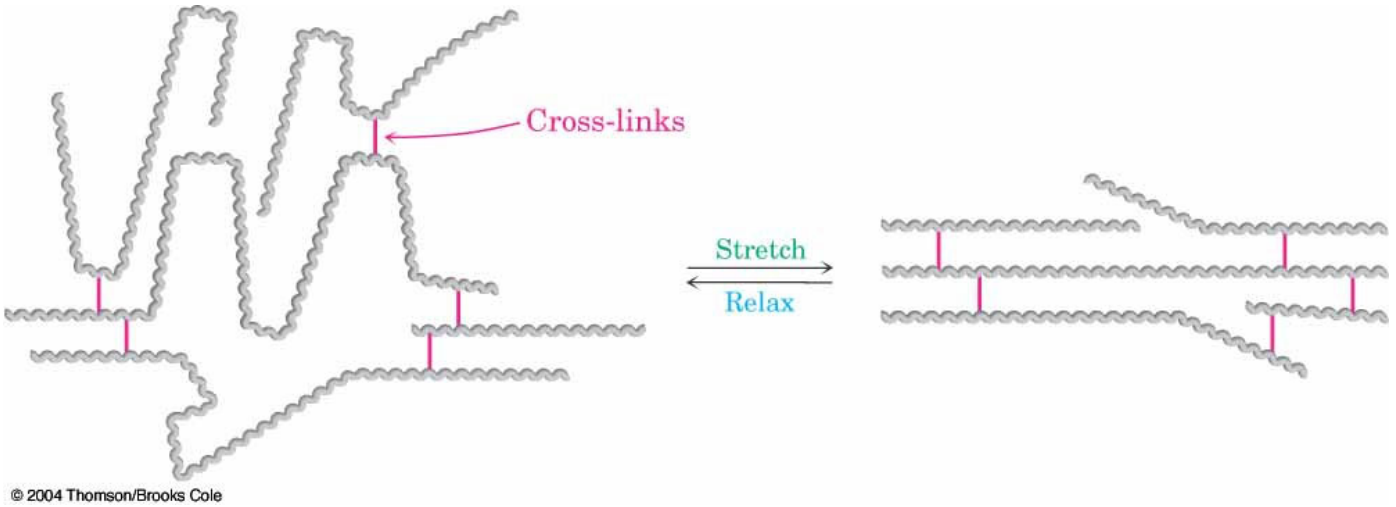
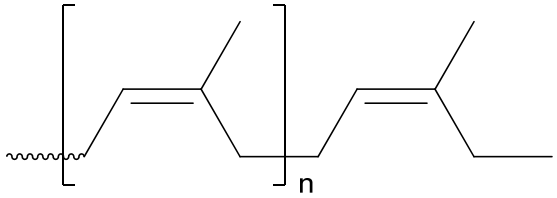
Elastomers: **materials that can be deformed and revert back to original form when deformation force is removed**

E.g. rubber





cis-polyisoprene (natural rubber)

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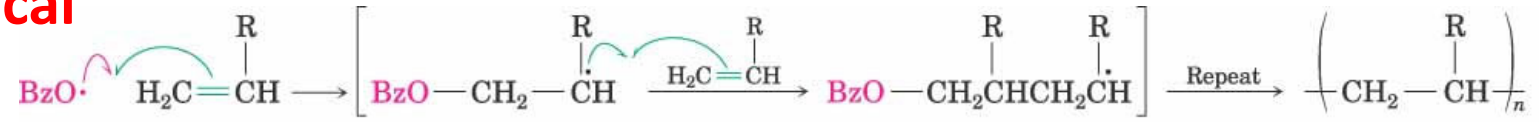
Types of synthesis to bring monomers together

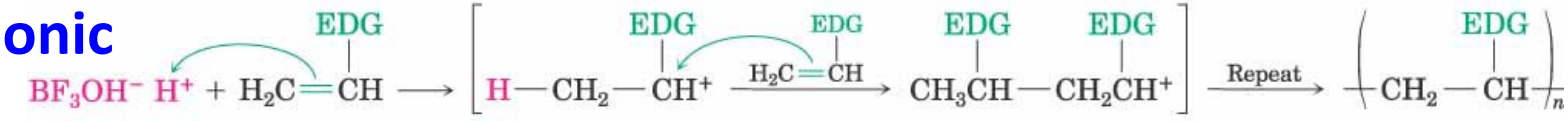
Addition reaction: A• + A –> A-A• + A -> A-A-A•

radical

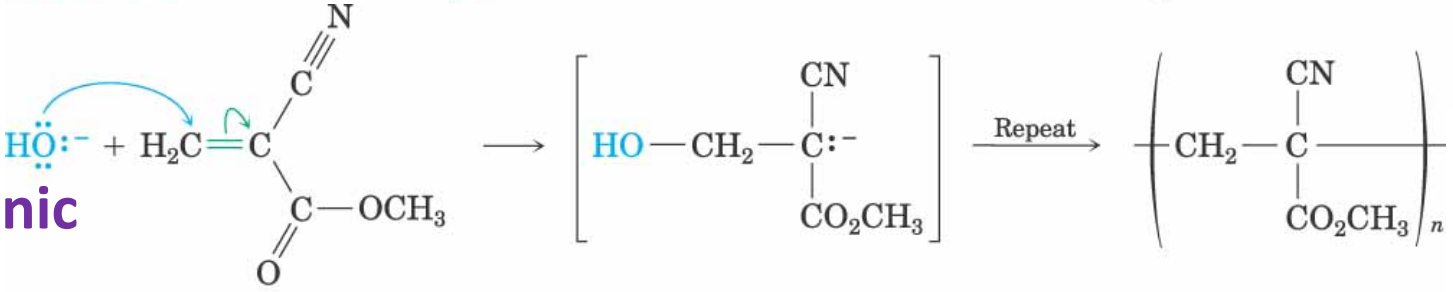


where BzO· = Benzoyloxy, $PhCO_2$·

cationic



anionic



Methyl α-cyanoacrylate
(Super glue)

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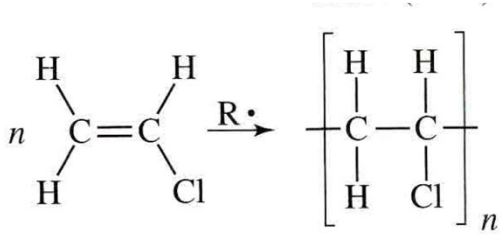
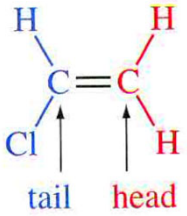
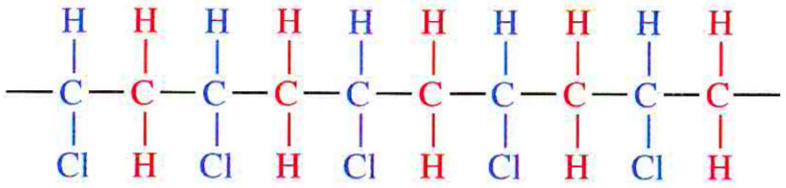
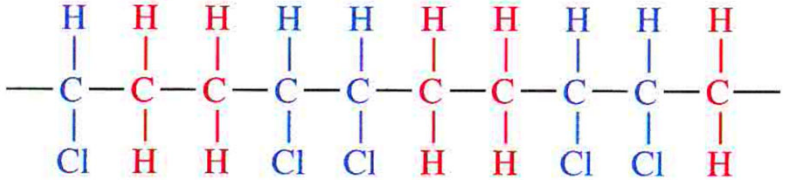
Addition reactions: different products if monomer is non-symmetrical



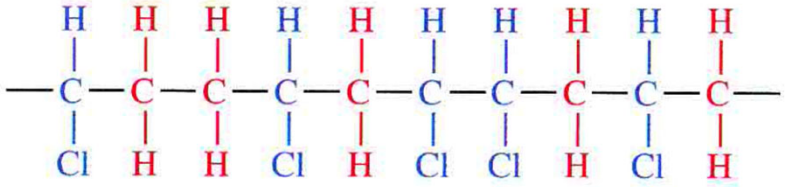




Head-to-tail, Head-to-tail **dominant**



Head-to-head, tail-to-tail



Random

Polyvinyl chloride (PVC)

- **tough**
- **insulating**
- **heat sensitive**

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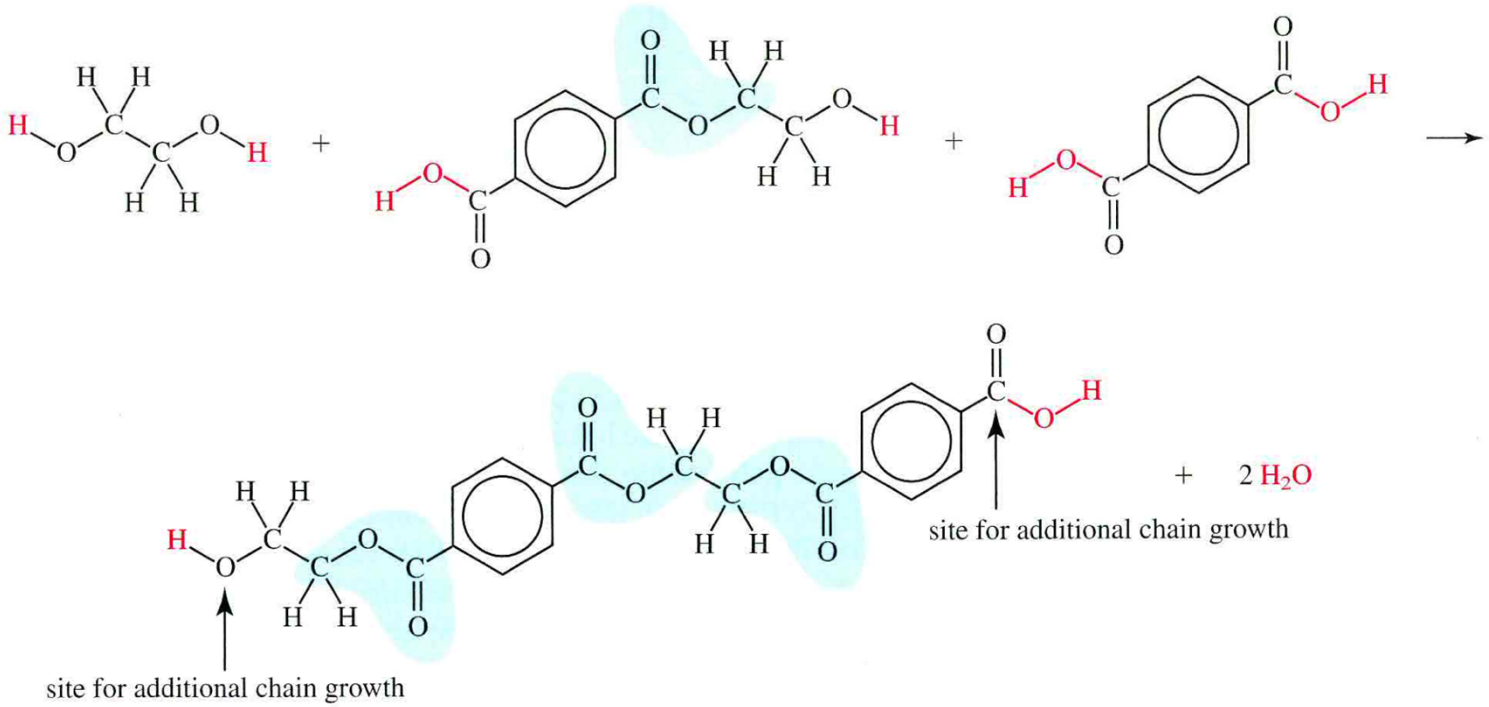
Condensation reactions: X-A-X + Y-B-Y –> X-A-B-Y + XY



PET = Polyester = polyethylene terephthalate

Similar for polyamides like Kevlar: N_2N-Aryl-NH_2 + HO_2C-Aryl-CO_2H

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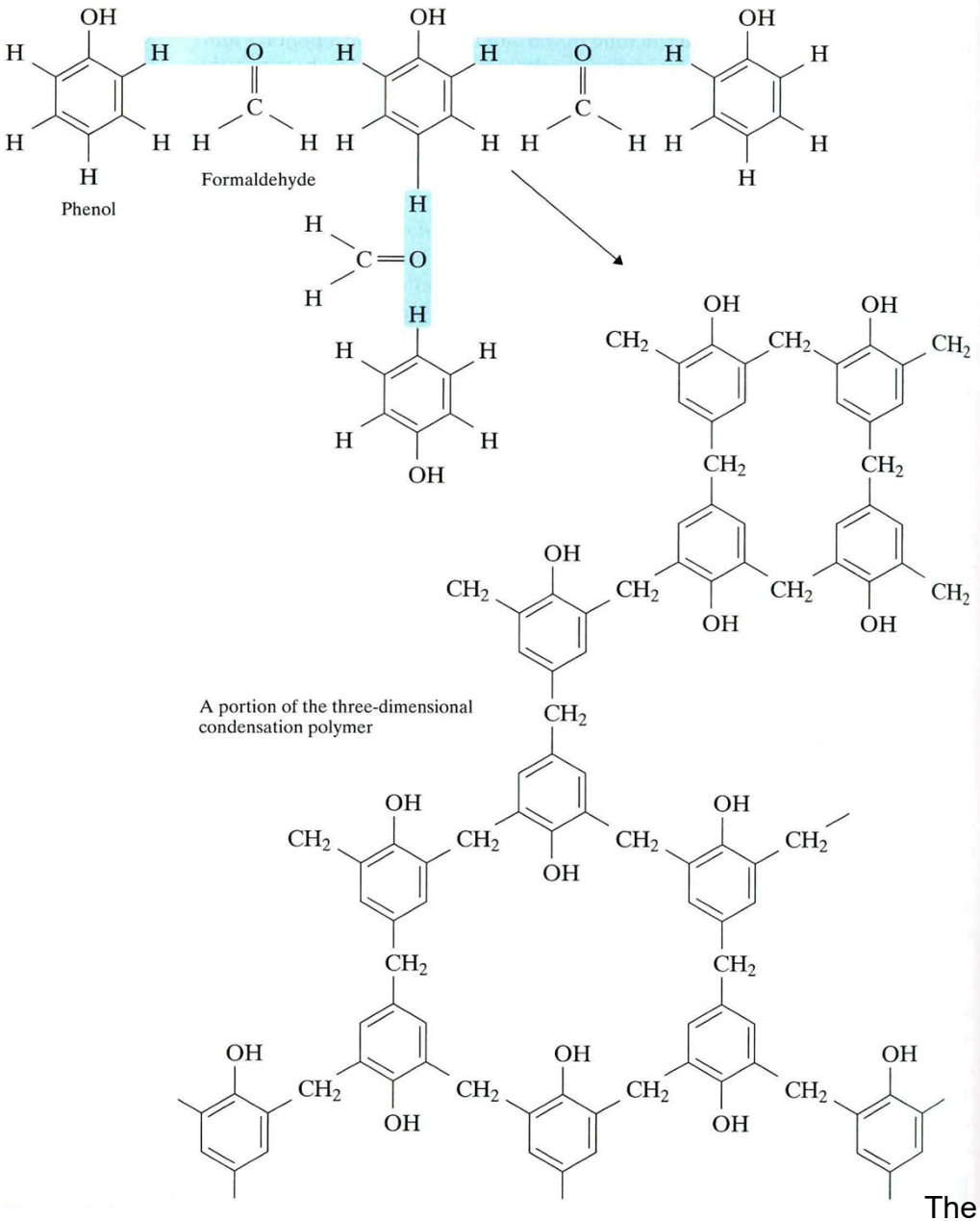

Bakelite (1909):

Phenol-formaldehyde resin with wood ‘flour’ also used to bind plywood layers

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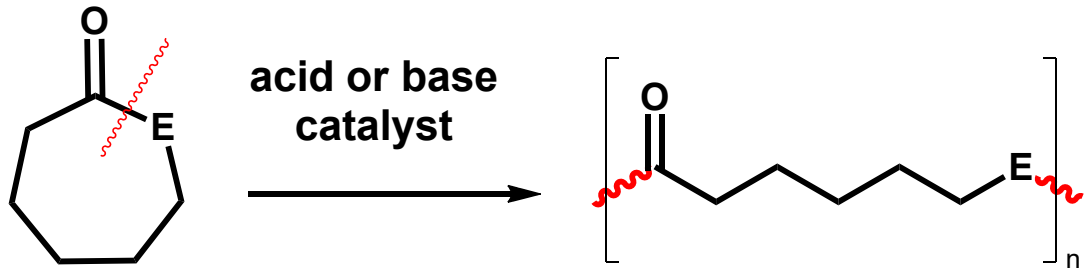
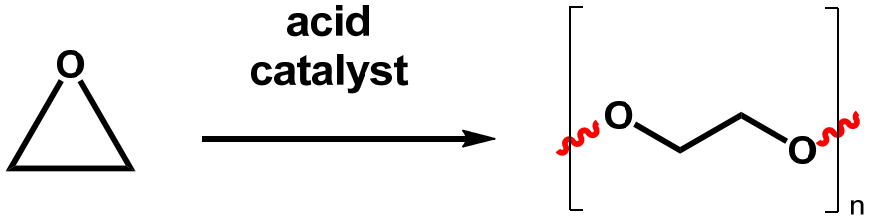
Ring opening polymerizations



E = O = caprolactone
E = NH = caprolactam

E = O = polyester
E = NH = polyamide (nylon-6)



polyethylene glycol (PEG)

Water-soluble

PEG used in surgical applications and can be ingested

Pegylation is attaching PEG polymers to drugs to improve pharmacokinetics

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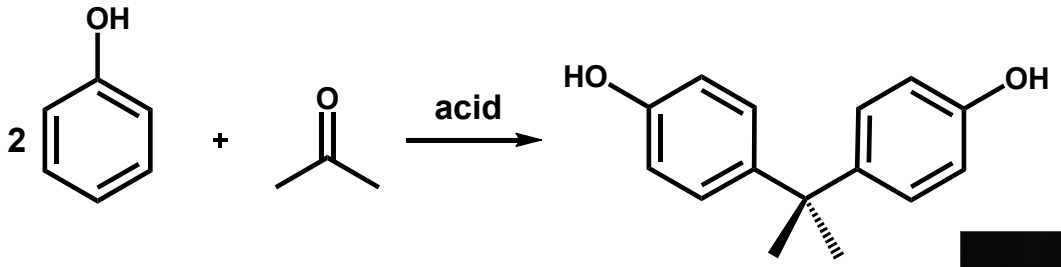
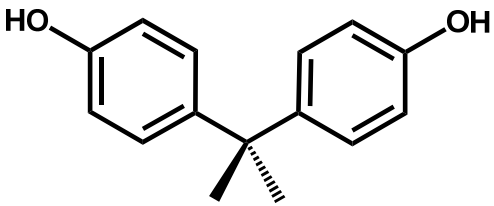
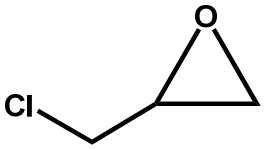
Ring opening polymerizations: Epoxy Resins



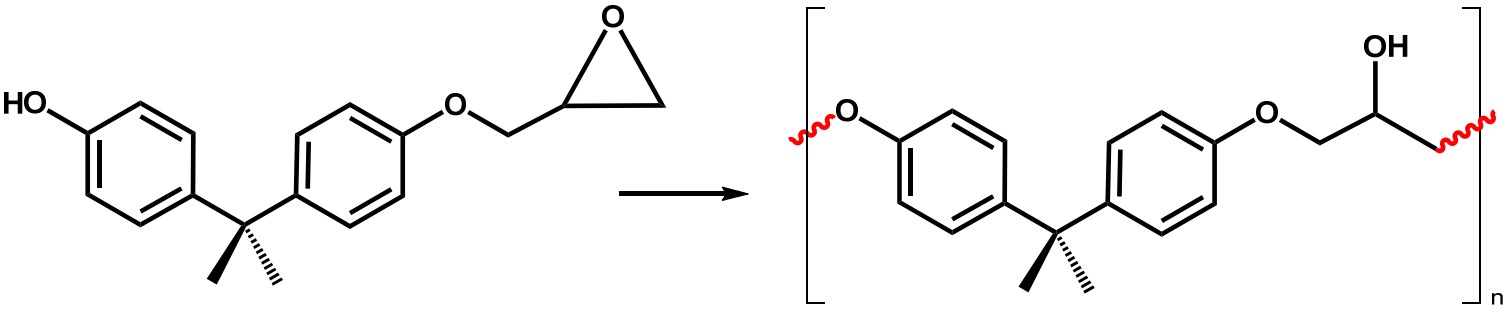
Bisphenol-A



Bisphenol-A



epichlorohydrin



Epoxy resin (a thermoset polymer)

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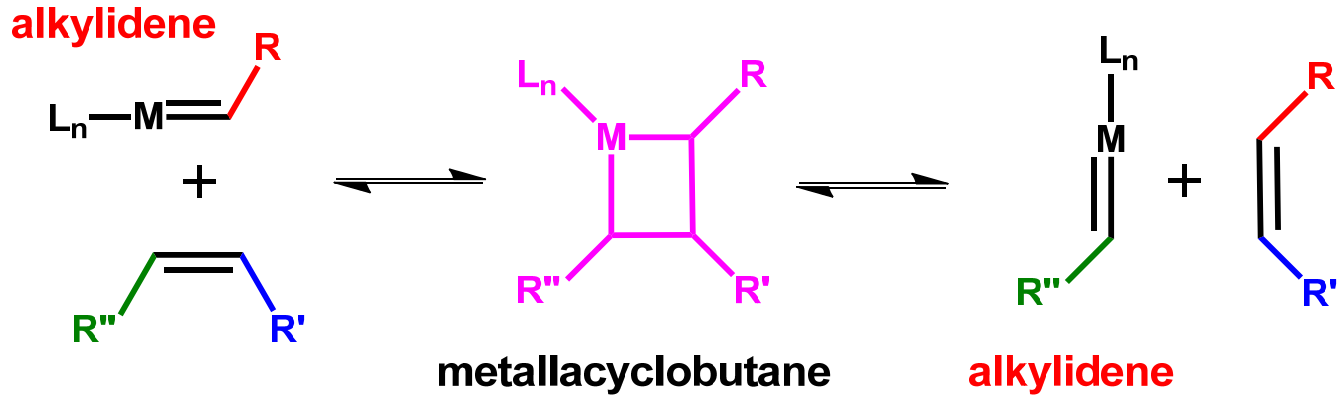
Ring opening polymerizations: Metathesis (ROMP)

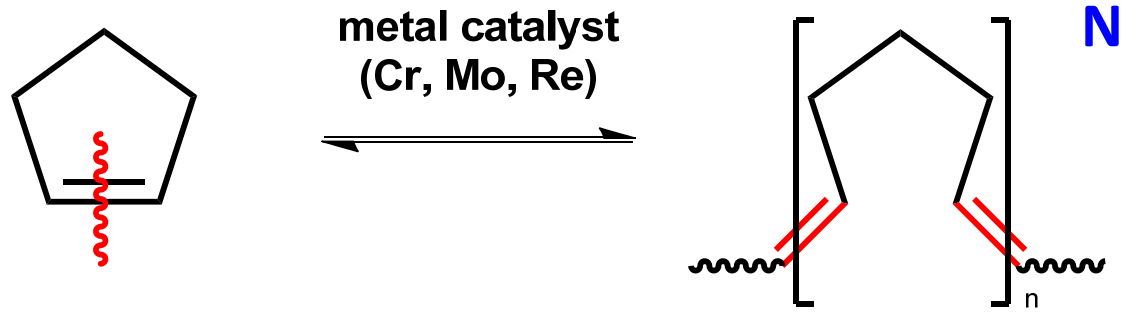
Metal-alkylidenes **are capable of** ***exchanging =CR$_2$*** **ends of alkenes:**



If we use cyclic alkenes we get polymerization:

CD blanks

Non-fog plastics



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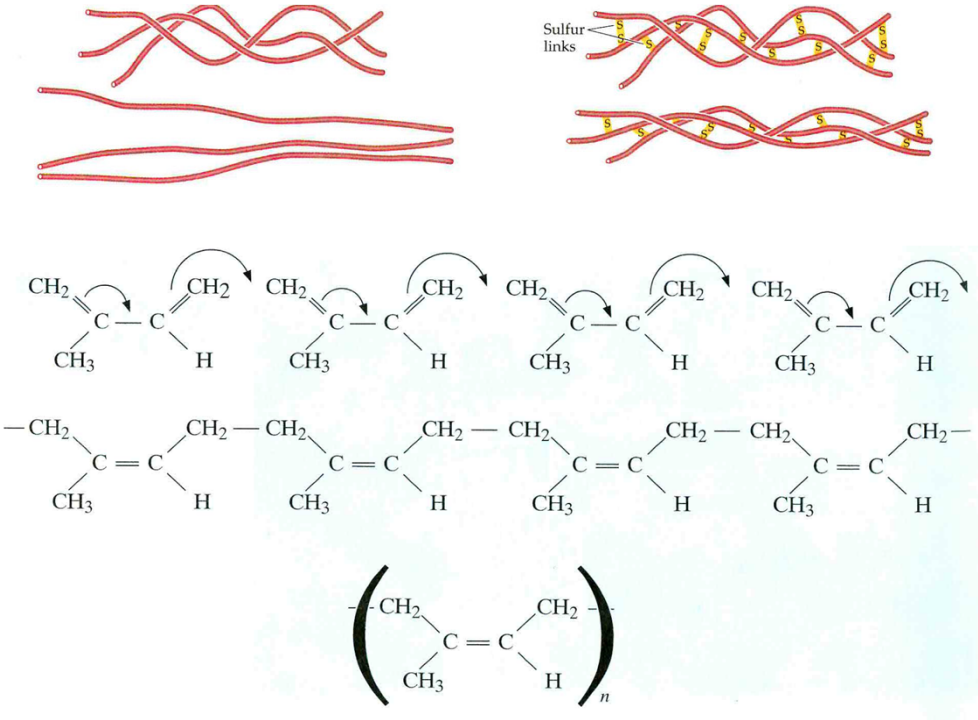
Synthetic Polymers

Synthetic rubber, 1839: Charles Goodyear

accidentally dropped a mixture of rubber and sulfur on a hot stove: mixture was nicely elastic – vulcanized rubber



wikipedia

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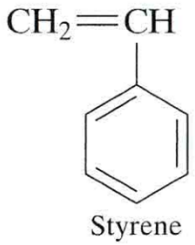
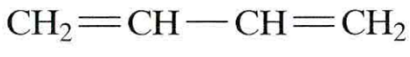
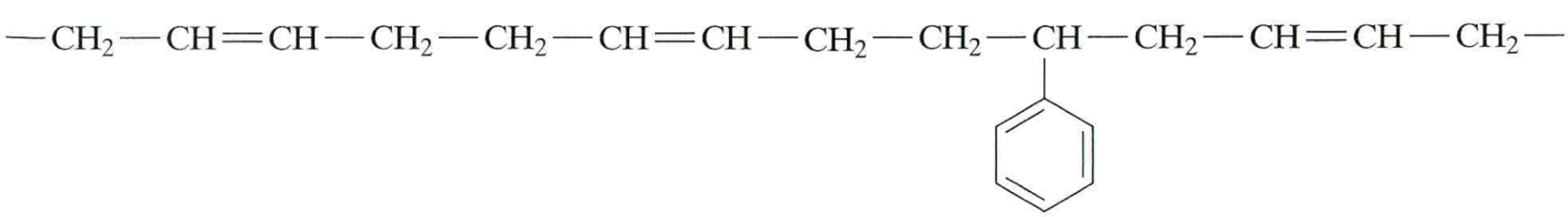
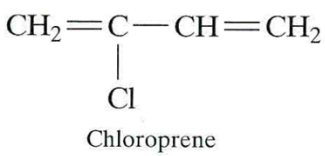
Synthetic elastomers: styrene-butadiene rubber (75:25 btd/sty)

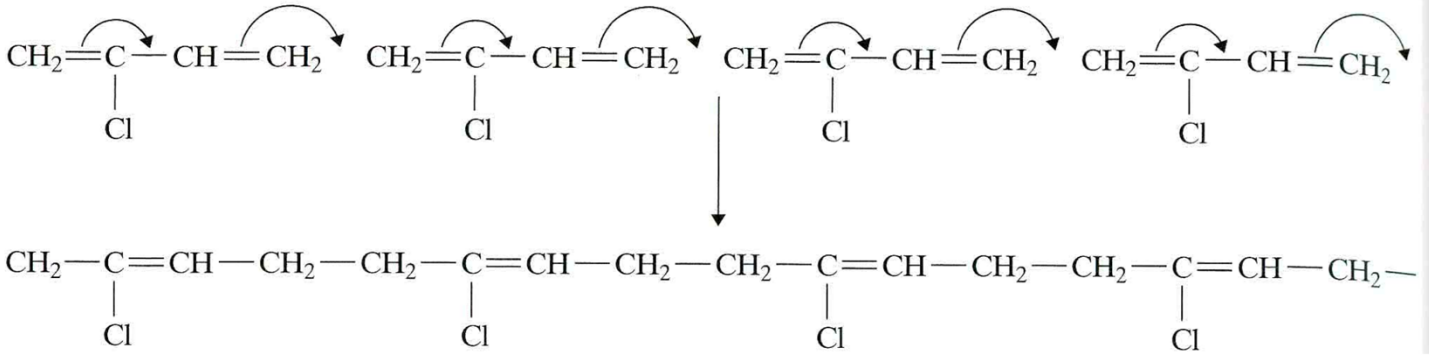






Neoprene





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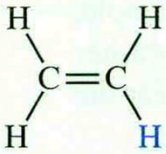
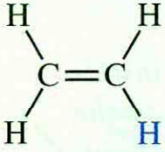
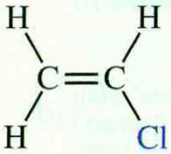
Most popular polymers and their recycling codes: 'The Big Six'

Polymer	Monomer	Properties of Polymer	Uses of Polymer
Polyethylene (LDPE) 4 LDPE	Ethylene 	Translucent if not pigmented. Soft, and flexible. Unreactive to acids and bases. Strong and tough.	Bags, films, sheets, bubble wrap, toys, wire insulation.
Polyethylene (HDPE) 2 HDPE	Ethylene 	Similar to LDPE. More rigid, tougher, slightly more dense.	Opaque milk, juice, detergent, and shampoo bottles. Buckets, crates, and fencing.
Polyvinyl chloride 3 PVC, or V	Vinyl chloride 	Variable. Rigid if not softened with a plasticizer. Clear and shiny, but often pigmented. Resistant to oils, acids, bases, and most chemicals.	Rigid: Plumbing pipe, house siding, charge cards, hotel room keys. Softened: Garden hoses, waterproof boots, shower curtains, IV tubing.

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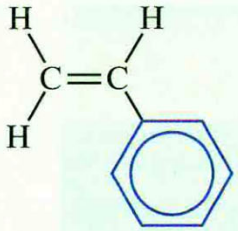
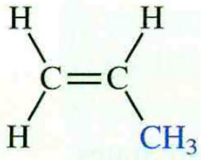
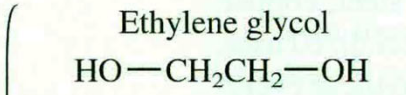
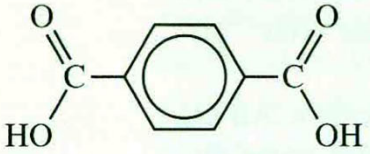
Most popular polymers and their recycling codes: 'The Big Six'

Polystyrene 6 PS	Styrene 	Variable. "Crystal" form transparent, sparkling, somewhat brittle. "Expandable" form lightweight foam. Both forms rigid and dissolve in many organic solvents. 	"Crystal" form: Food wrap, CD cases, transparent cups. "Expandable" form: Foam cups, insulated containers, food packaging trays, egg cartons, packaging peanuts.
Polypropylene 5 PP	Propylene 	Opaque, very tough, good weatherability. High melting point. Resistant to oils. 	Bottle caps. Yogurt, cream, and margarine containers. Carpeting, casual furniture, luggage.
Polyethylene terephthalate 1 PETE, or PET	Ethylene glycol  Terephthalic acid 	Transparent, strong, shatter-resistant. Impervious to acids and atmospheric gases. Most costly of the six. 	Soft-drink bottles, clear food containers, beverage glasses, fleece fabrics, carpet yarns, fiber-fill insulation.

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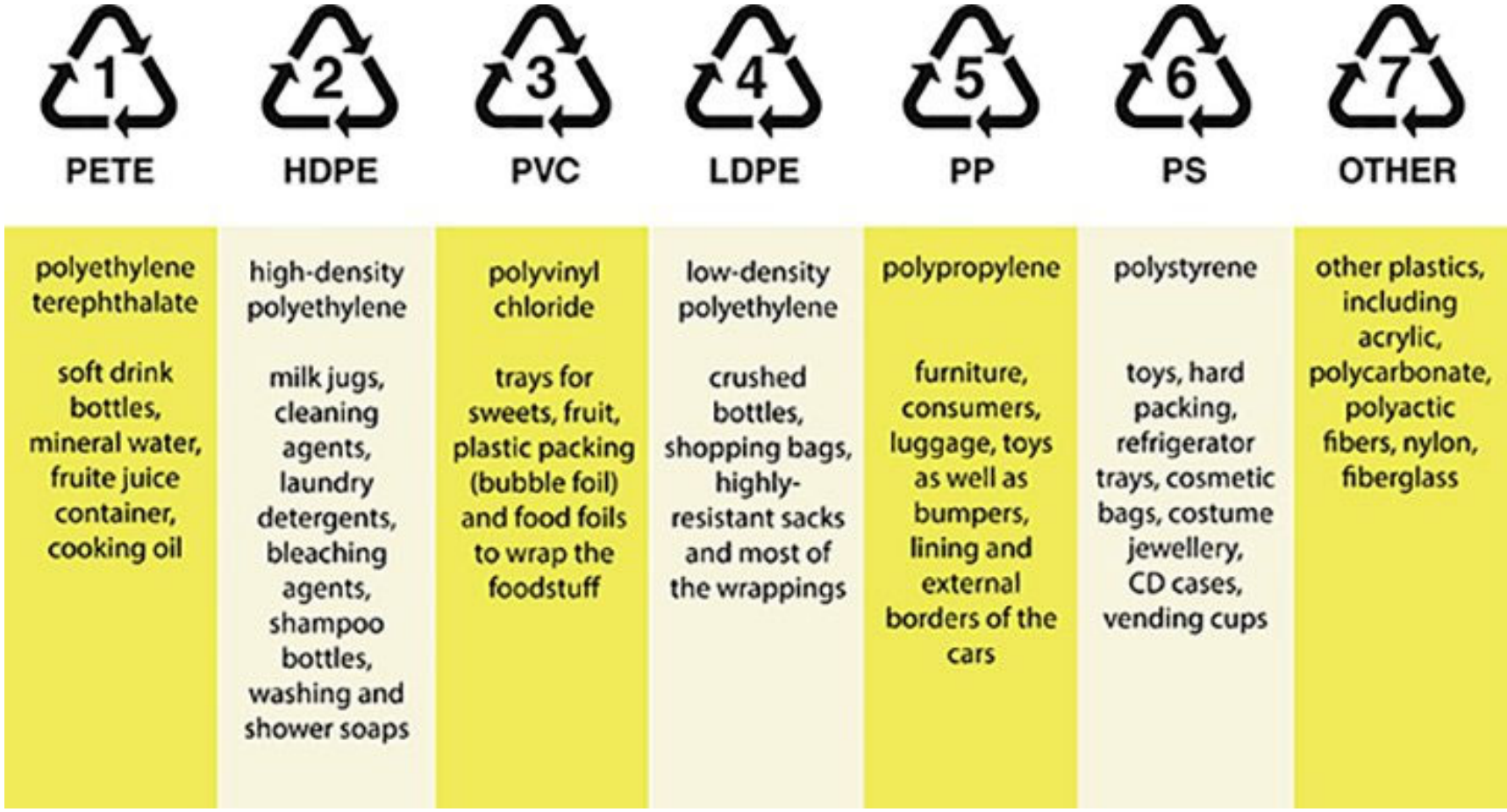
Plastic recycling codes in summary



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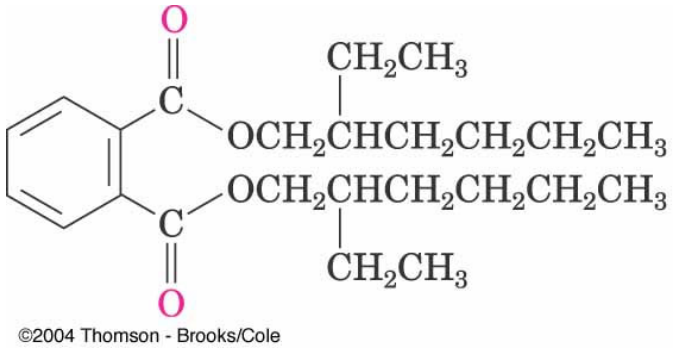
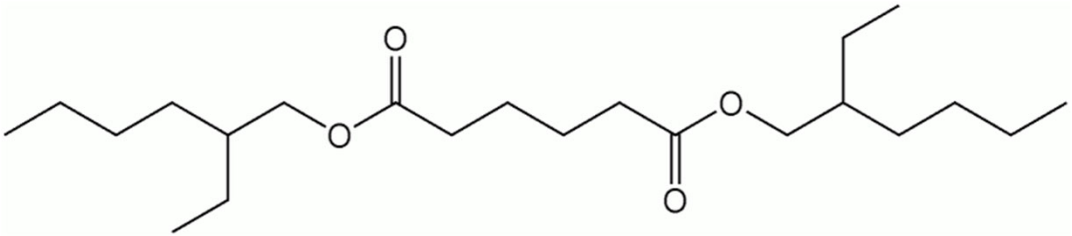
Plasticizers: *lubricants between the chains* to soften polymers: PVC



Di(2-ethylhexyl) phthalate, a plasticizer

PVC food wraps contain other plasticizers such as adipates and citrates



Bis(2-ethylhexyl) adipate – DEHA

Shown to induce liver cancer in mice but not rats: controversial

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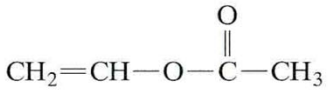
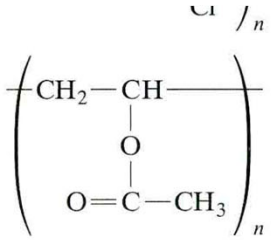
Other major polymers

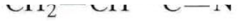
Vinyl acetate



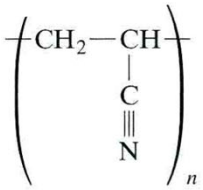
poly(vinyl acetate)
polyvinyl acetate
PVA



Acrylonitrile

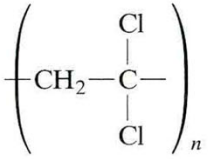


Orlon
Acrilan
Creslan

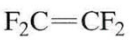


Vinylidine chloride

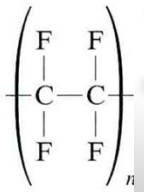
poly(vinylidine chloride)
Saran



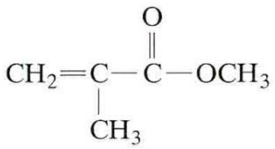
Tetrafluoroethylene



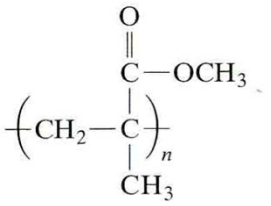
polytetrafluoroethylene
Teflon



Methyl methacrylate



poly(methyl
methacrylate)
Lucite
Plexiglas



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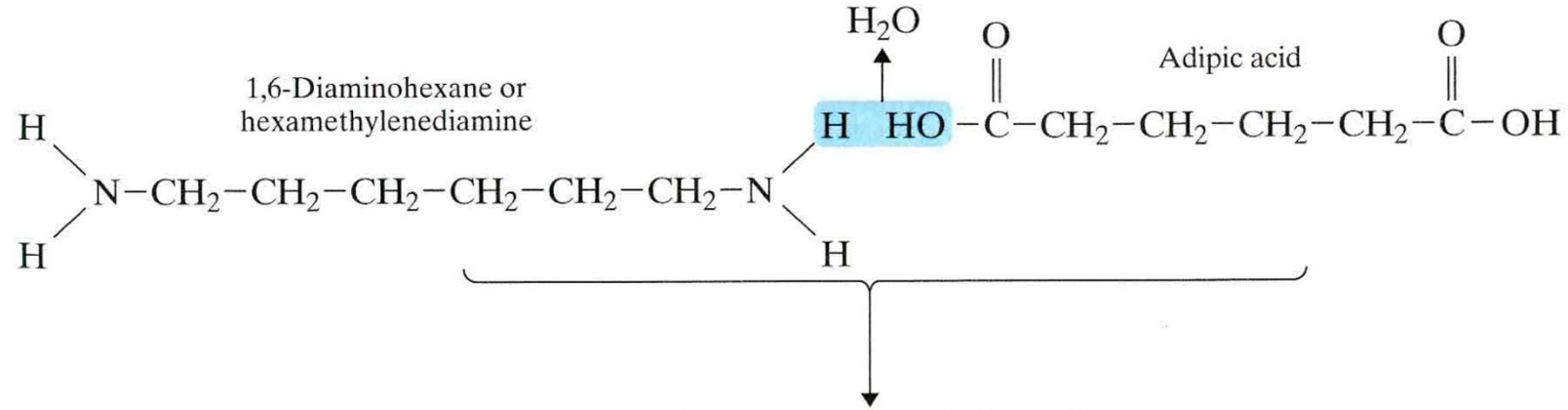
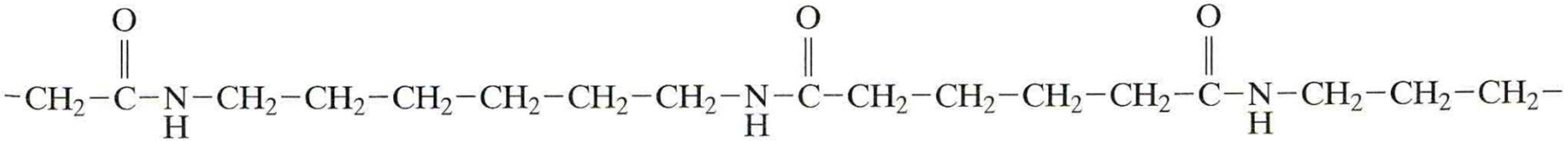
Nylon 6,6





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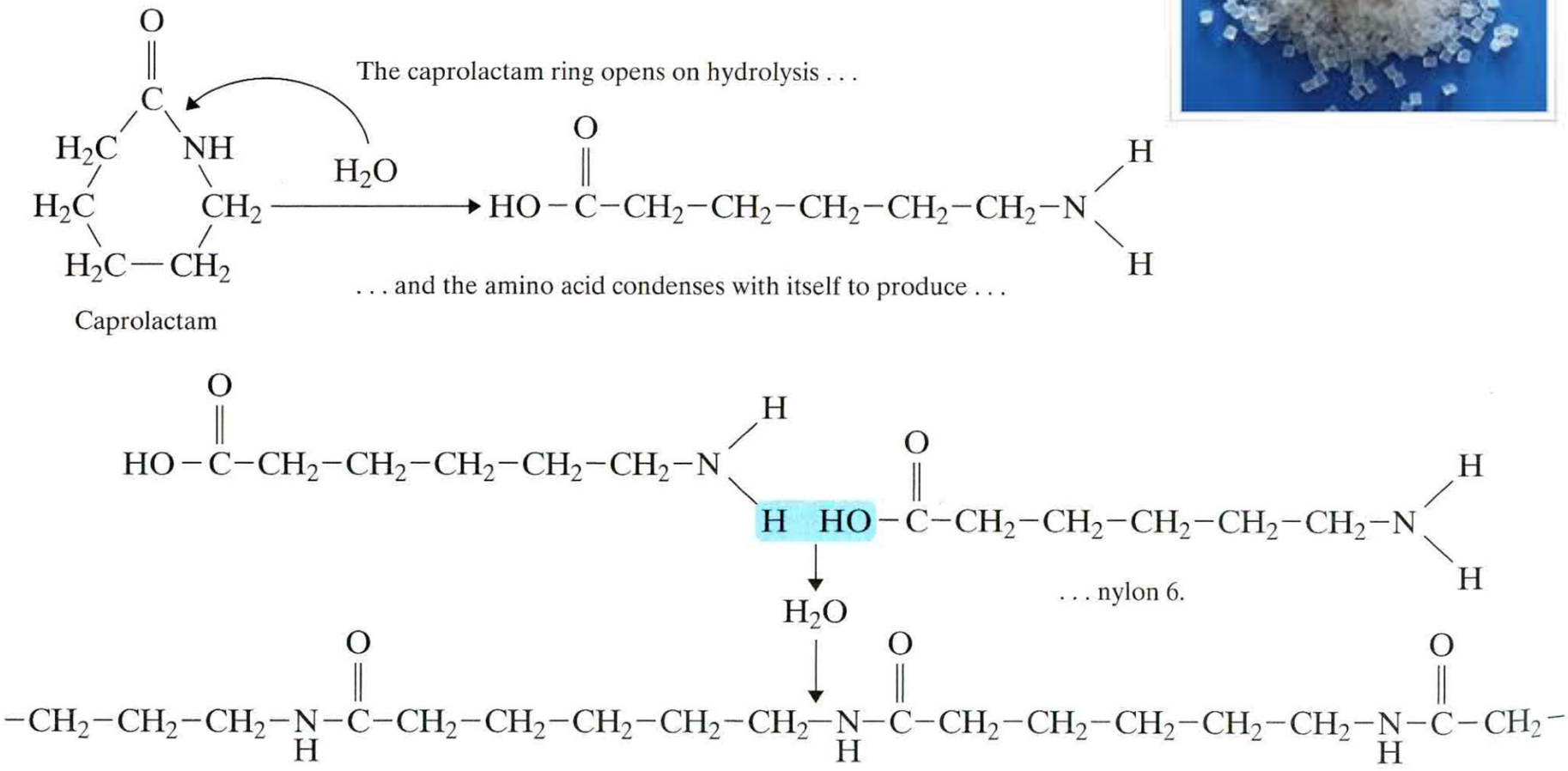
Nylon 6



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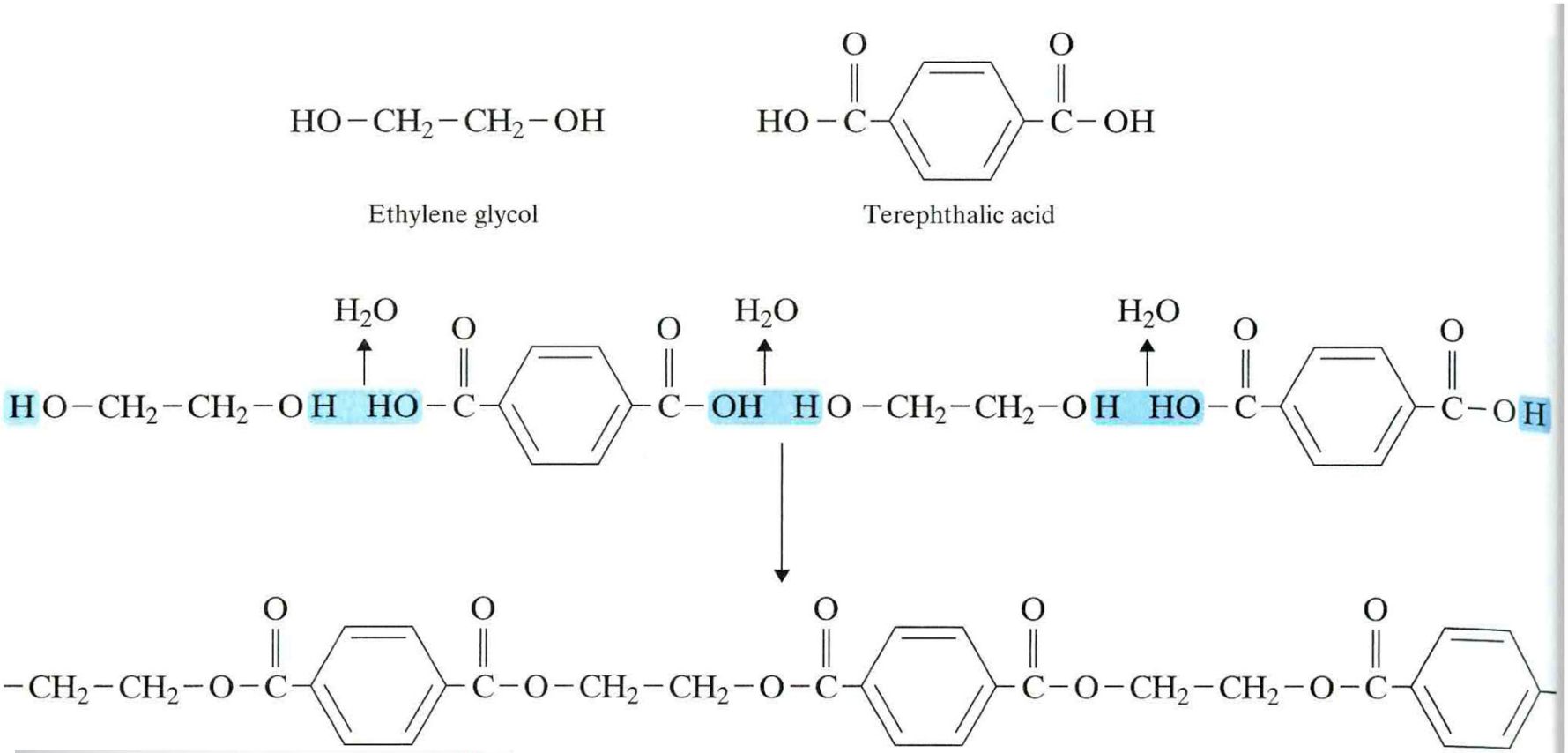
Polyethylene terephthalate: PET



Poly(ethylene terephthalate), a polyester

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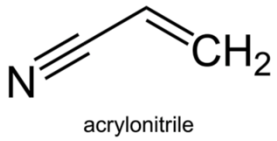
ABS - $A_xB_yS_z$

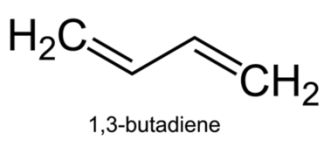
15% - 35% - acrylonitrile

5% - 30% - 1,3-butadiene

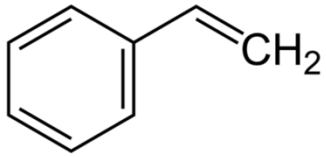
40% - 60% - styrene



acrylonitrile



1,3-butadiene



styrene

- **Tough**
- **Insulating**
- **Injection moldable**
- **Used in: protective equipment, car parts, bottle caps, etc.**

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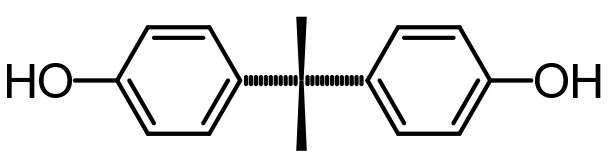
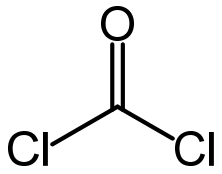
Polycarbonates

Usually with bisphenol-A

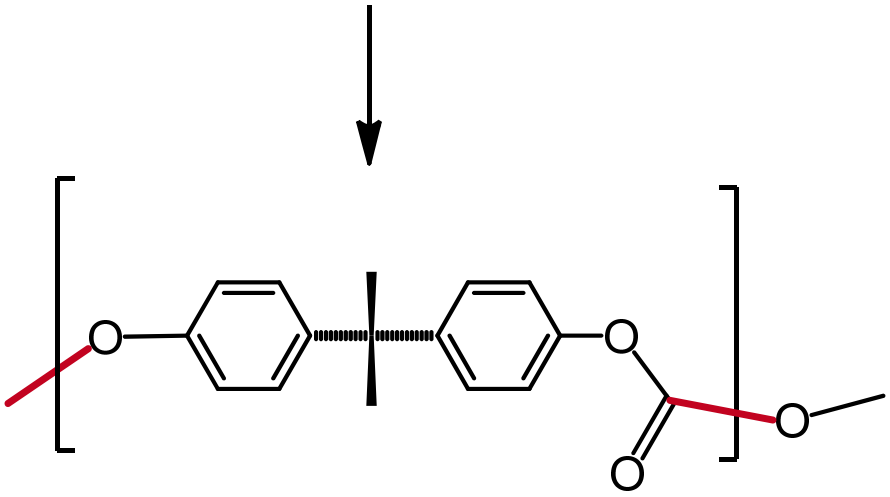


bisphenol-A

+



phosgene



polycarbonate

- **Heat resistant**
- **Insulating**
- **Flame retardant**
- **Used in: circuit boards, CD blanks, formerly water bottles, containers**

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Food packaging: not biodegradable and not recyclable – yet?

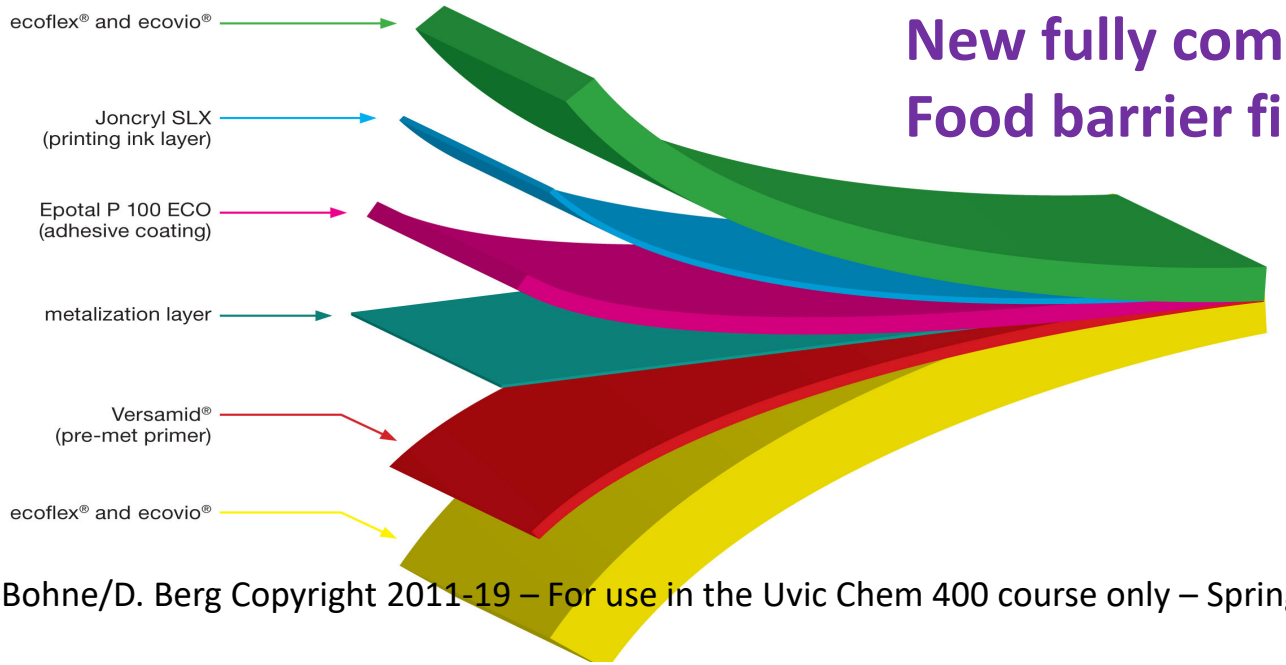
Barrier films are laminates of many layers: 7 or more common

Each layer has its purpose:

- **Low oxygen permeability (nylon)**
- **Low moisture permeability**
- **Toughness (polypropylene, HDPE)**
- **Printable**

6 Layers

BASF
The Chemical Company



New fully compostable Food barrier film from BASF

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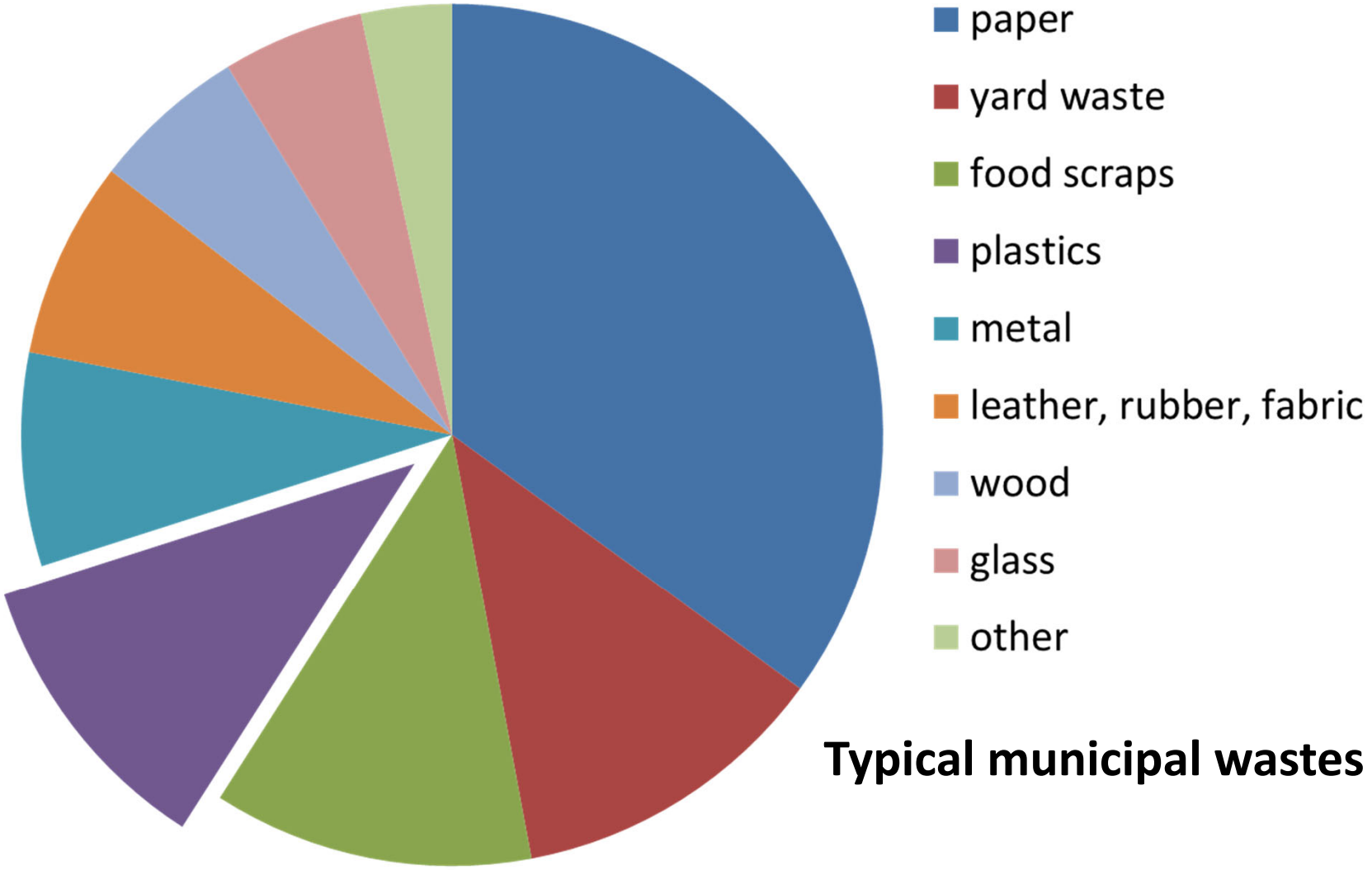
Recycling



Typical municipal wastes US

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2015 World Recycling Data

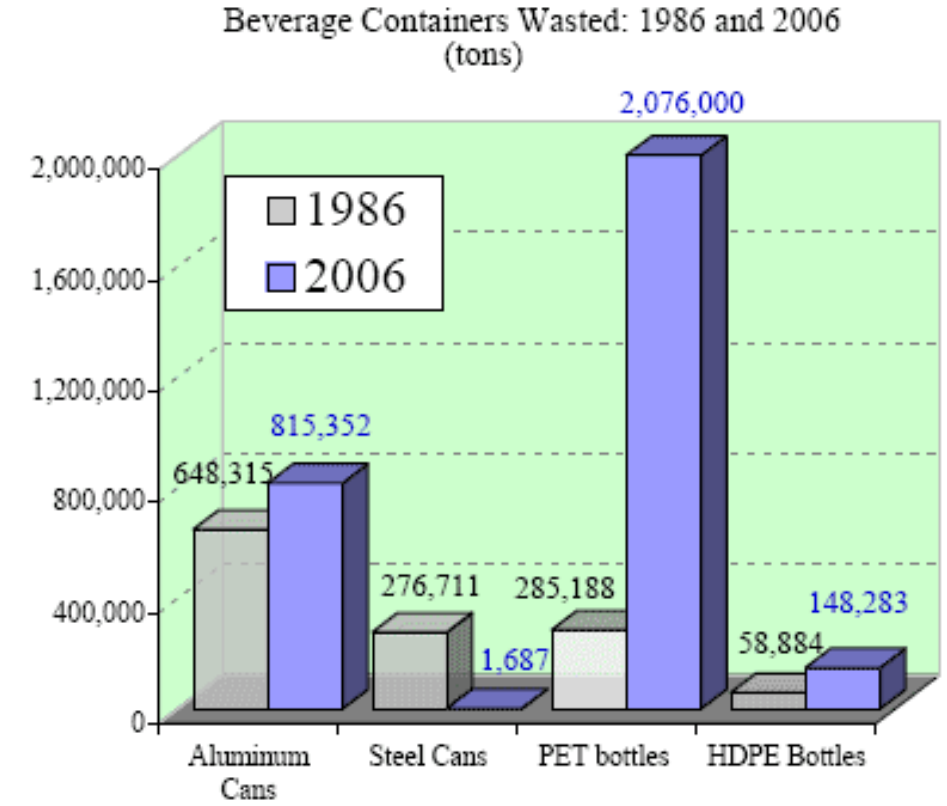
(Source: OECD (2015), "Municipal Waste", OECD Environment Statistics)

Canada 24% recycling rate (places us in the bottom 1/3)

US 35%

Europe 40%

Germany 65%



Dairy beverages excluded. Glass bottles are not shown here due to differences in scale. CRI estimates of glass wasting 1986 and 2006 were almost identical: 6.91 million and 6.96 million tons, respectively.

© Container Recycling Institute, 2008

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Fate of the non-recycled plastics: dump or incineration

Potential solutions:

Biodegradable plastic *(see next slides)*

- monomers that decompose over time (e.g. with moisture)
- smaller chains are degraded by bacteria to $CO_2 + H_2O$

Incineration

- plastics account for up to 30% of waste energy content = fuel?

Issues:

- chlorine based polymers release HCl
- toxic chemicals
- metals in ink in ash (Pb, Cd)

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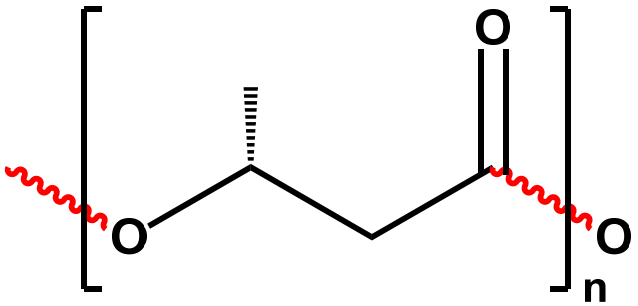
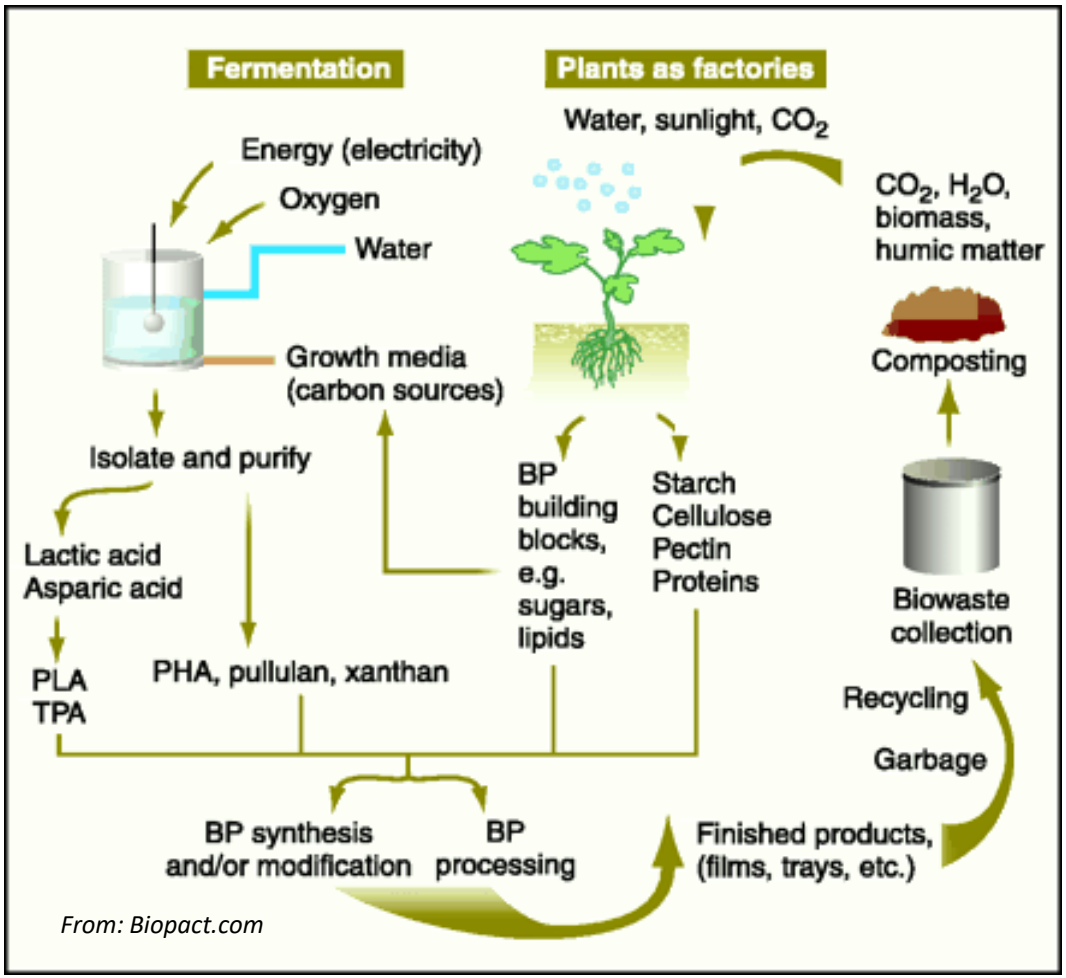
Biodegradable Polymers: *the way forward?*

Alkyl esters: much more easily hydrolyzed than PET

Polyhydroxyalkanoates (PHA)

- **Monomers from bacterial fermentation of sugars**





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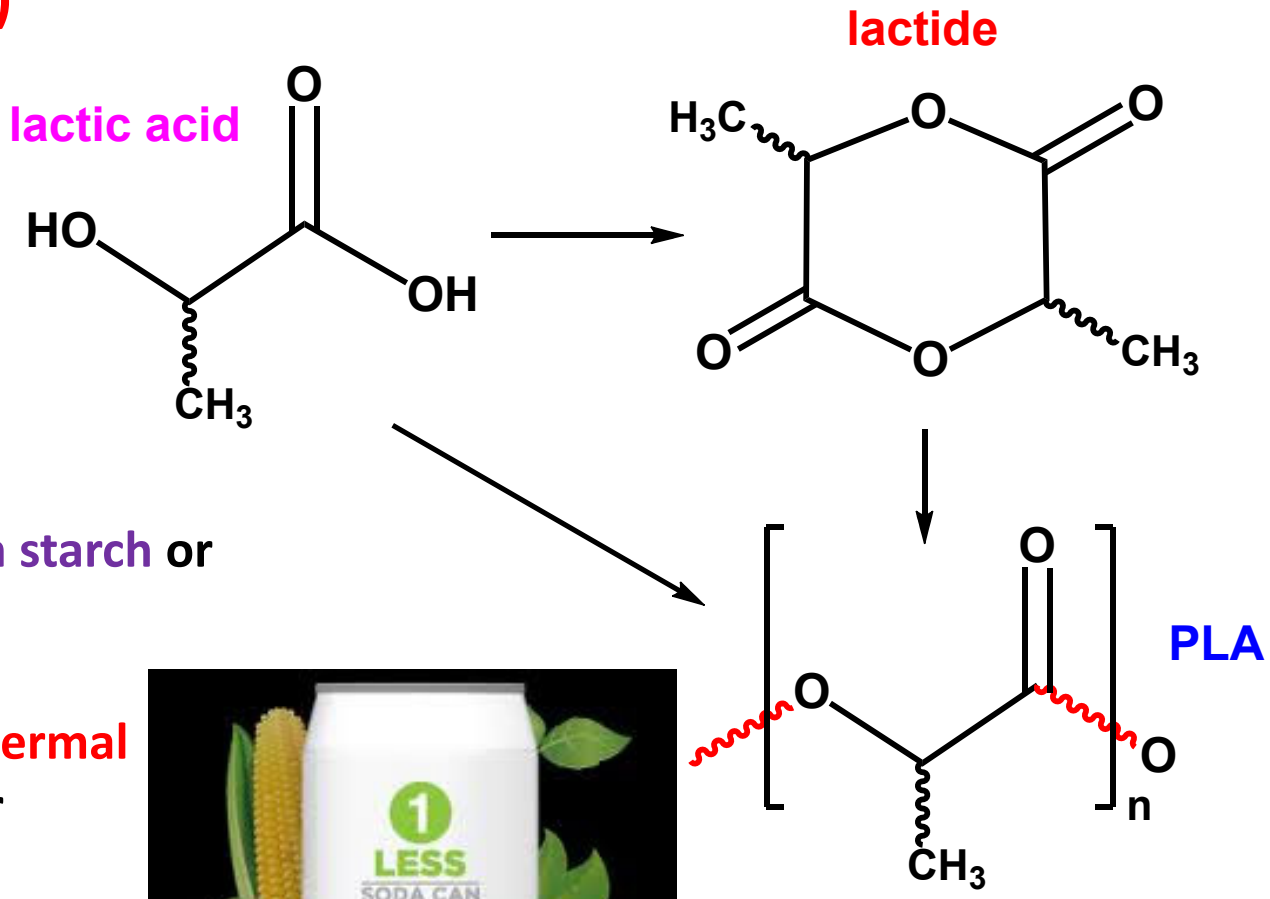
Polylactic acid (PLA)



- Monomer from corn starch or sugarcane
- Degrades quickly
- Easily recycled by thermal depolymerization or hydrolysis

Largest manufacturer in US:
NatureWorks (Cargill)

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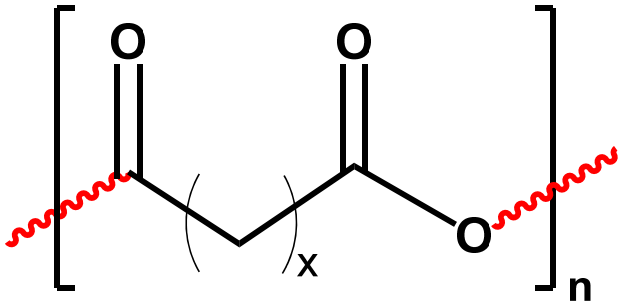
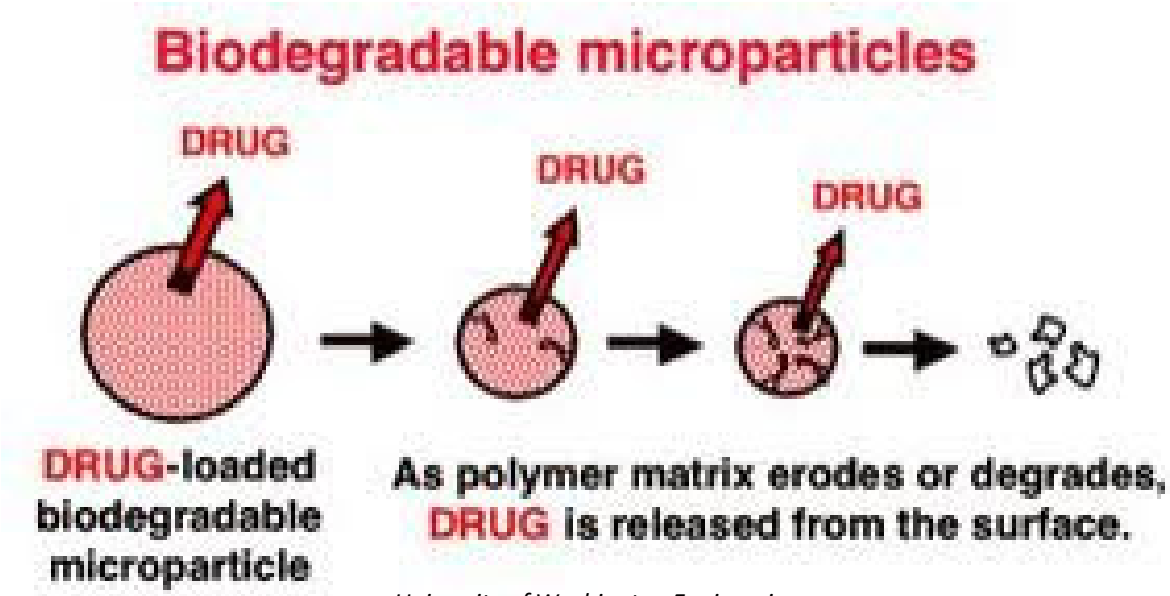
Polyanhydrides

- Anhydrides are quite easy to hydrolyze
- Rapid breakdown in wet environs
- Biocompatible: drug delivery





University of Washington Engineering

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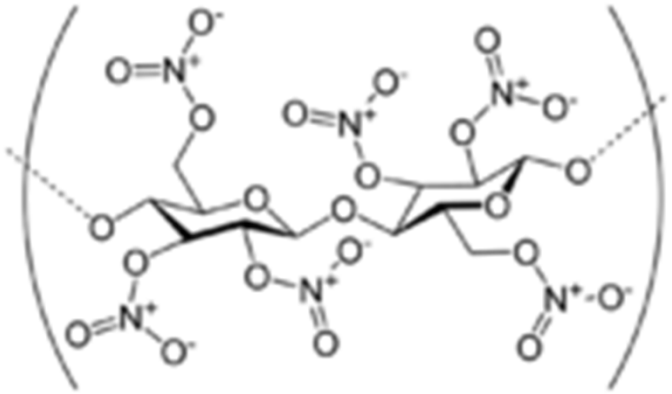
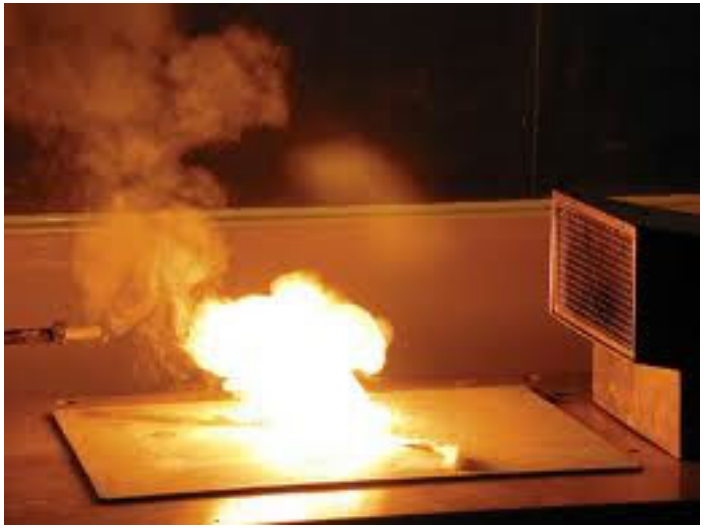
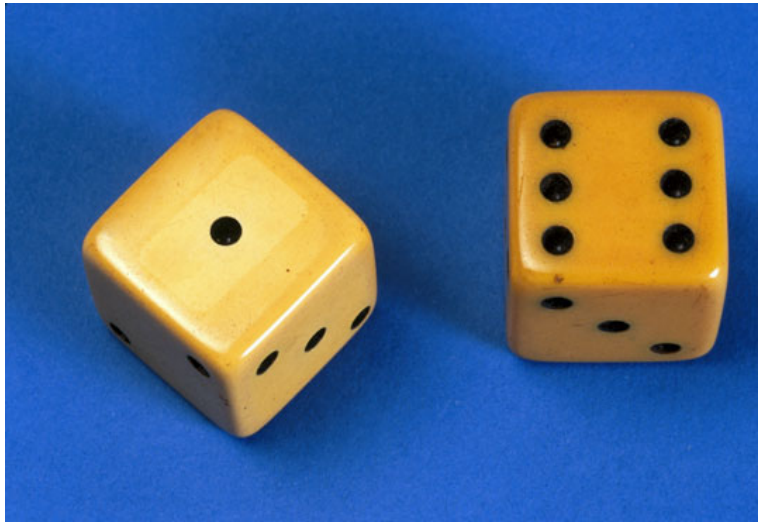
Cellulose Derivatives

Cellulose nitrate



- **Extremely flammable**
- **Used for movie film until 1948**
- **Soaking cotton in nitric acid gives the highly flammable 'guncotton' *(below)***
- **Used for artificial 'ivory' in 19th century *(right)***





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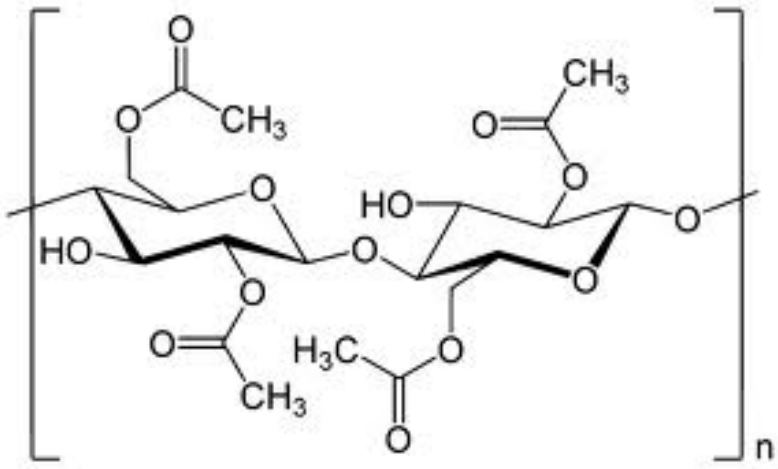
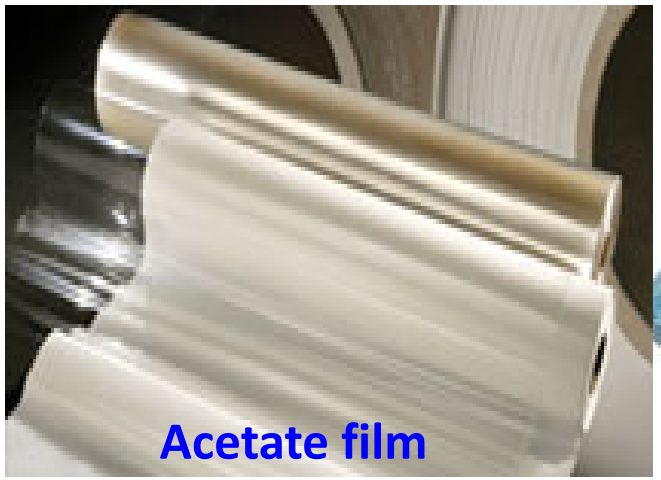
Cellulose Derivatives



Cellulose acetate

- Replaced cellulose nitrate film
- Used in computer tape
- Breaks down with heat, compostable
- Fibres highly desirable for clothing: breathable, dries quickly, no static cling, soft, easily dyed and retains bright colours well



Acetate film

Carpet fibre and backing

Rayon fibres

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Recycling:

- **Collection**
- **Transportation**
- **Sorting**
- **Melting – used directly or pelletized for future use**

Recycled-content product: **materials would have been waste**

Post-consumer content: **material previously used and recycled**

Pre-consumer content: **material that was waste (scraps, clippings)**

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Sorting by density

Consider This 9.28 Sink or Float?

When placed in a liquid, a plastic will float if its density is less than that of the liquid and sink if it is greater. Here is the density for PET and three other plastics that are likely to be found with it in a recycling bin.

Plastic	Density (g/cm^3)
PET	1.38–1.39
HDPE	0.95–0.97
PP	0.90–0.91
PVC	1.18–1.65

The densities of six liquids at the same temperature are:

Liquid	Density (g/mL)
methanol	0.79
an ethanol/water mixture	0.92
a different ethanol/water mixture	0.94
water	1.00
saturated solution of $MgCl_2$	1.34
saturated solution of $ZnCl_2$	2.01

Chemistry in Context 6th Edition, ACS, McGraw-Hill

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From: Canadian Plastics Industry Association website

For an example of a company that specializes in recycling plastics see:
www.postplastics.com

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