

Materials

1. Plastics and Polymers

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

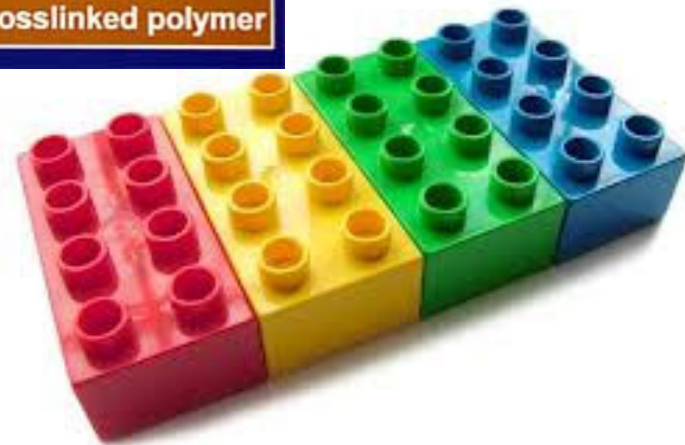
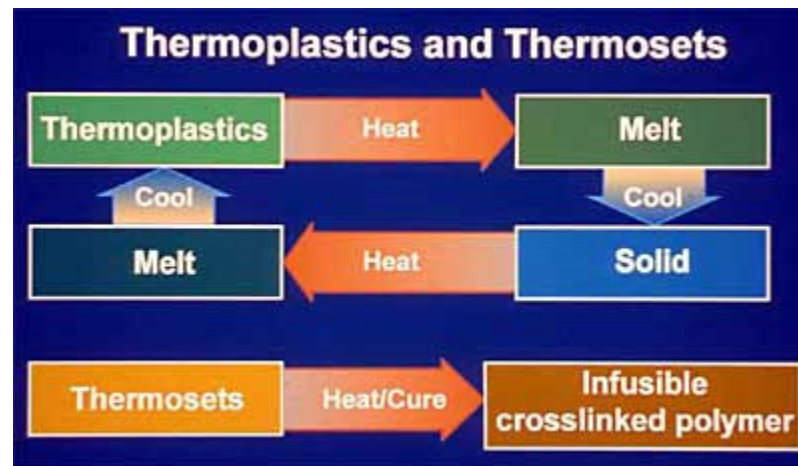
Polymer: *macromolecule* = material of high molecular weight, formed from many repeating units

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



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*

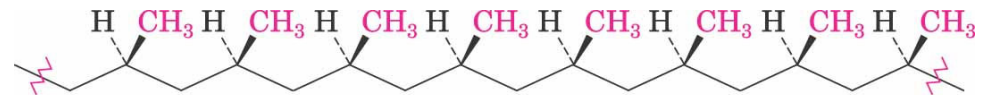


Properties of Polymers depend on their molecular structure

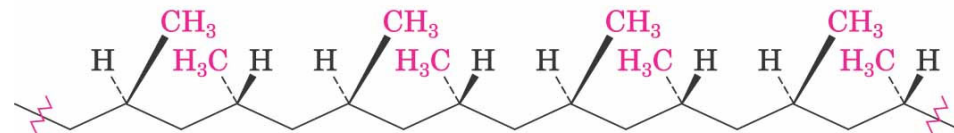
Order in which the monomers are arranged:

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

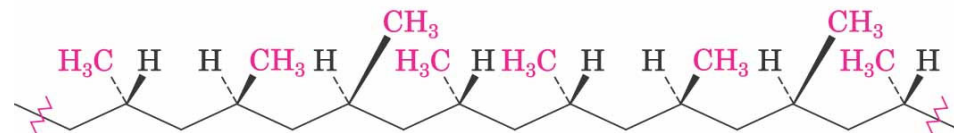
Copolymers: **A-B-A-B-A-B** or **A-A-A-A-B-B-B-B-A-A-A-A**



Isotactic (same side)



Syndiotactic (alternating sides)

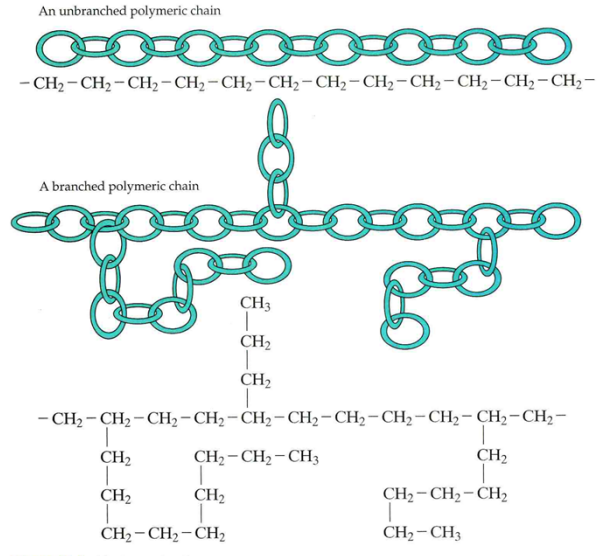


Atactic (random)

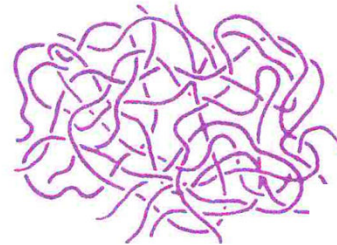
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**Three-dimensional
arrangement within
the chain:**

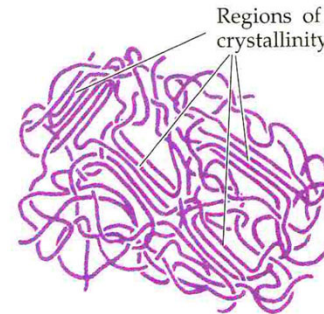
Linear vs. branched



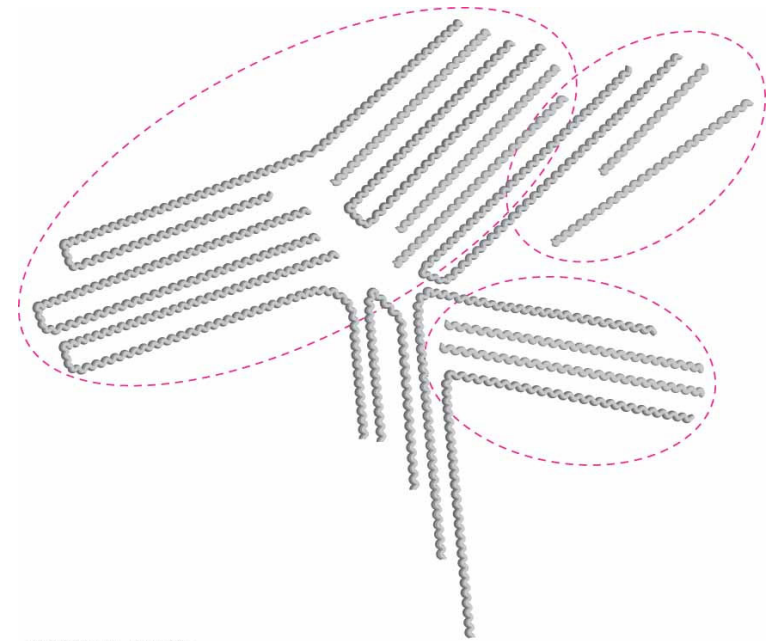
Low density polymer
low melting flexible plastic



High density polymer
denser and more rigid plastic

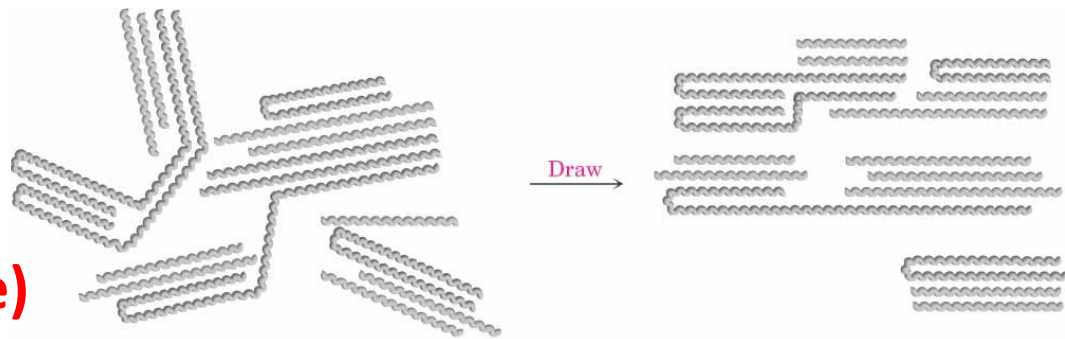


Rigidity is provided by crystalline region



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



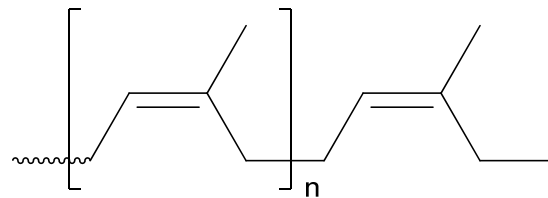
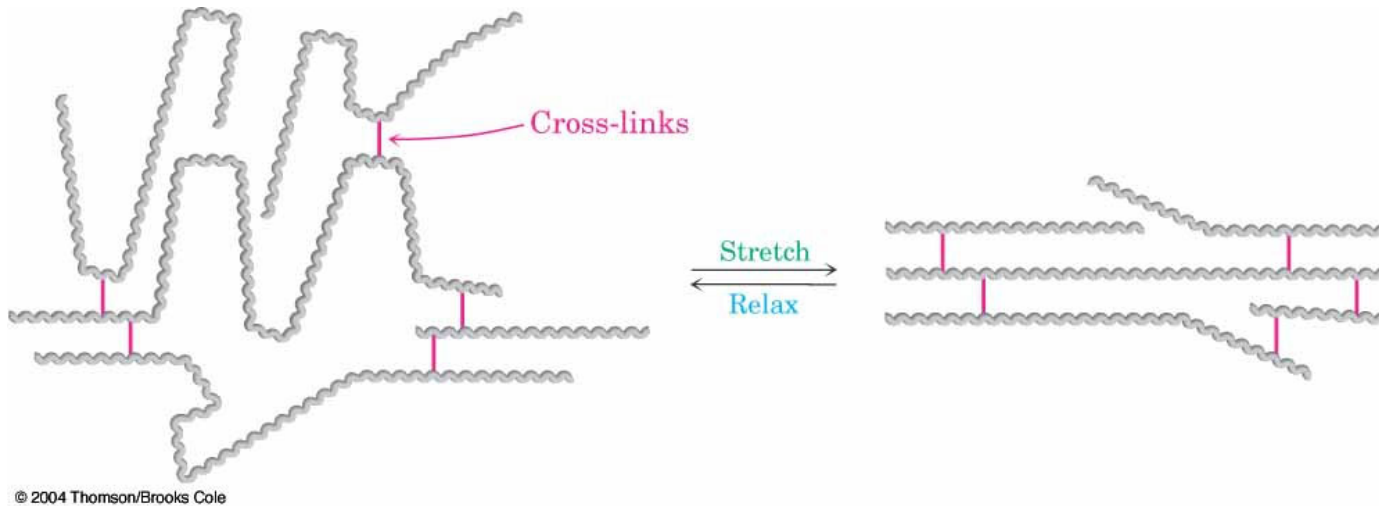
Unoriented crystallites in a thermoplastic

Oriented crystallites in a fiber

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

E.g. rubber

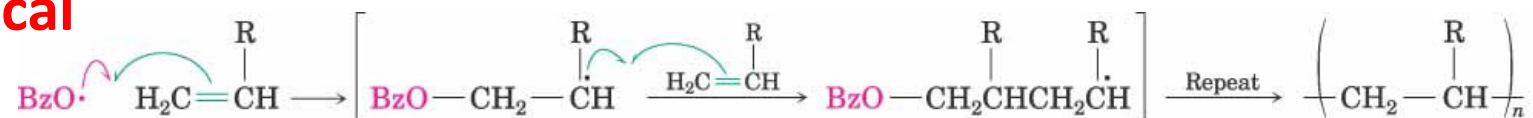


cis-polyisoprene (natural rubber)

Types of synthesis to bring monomers together

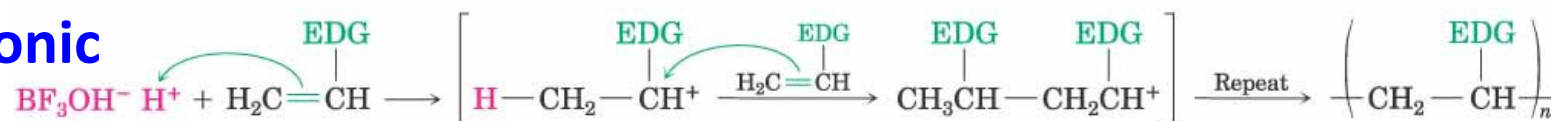
Addition reaction: $A\bullet + A \rightarrow A-A\bullet + A \rightarrow A-A-A\bullet$

radical

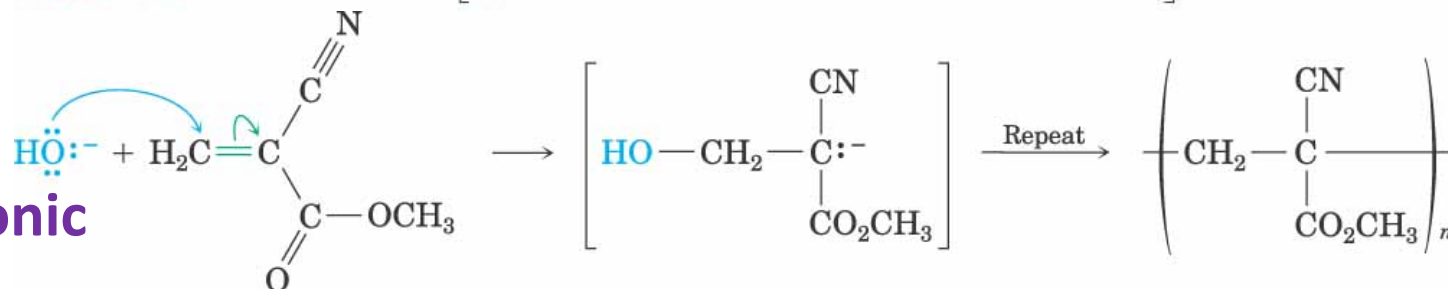


where $\text{BzO}\cdot = \text{Benzoyloxy}, \text{PhCO}_2\cdot$

cationic



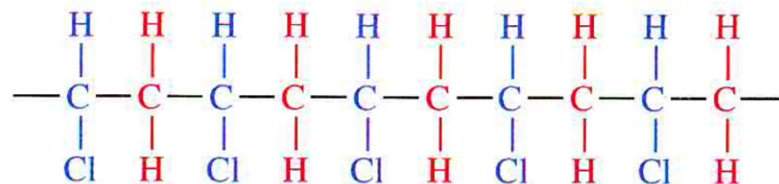
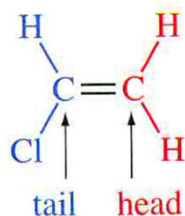
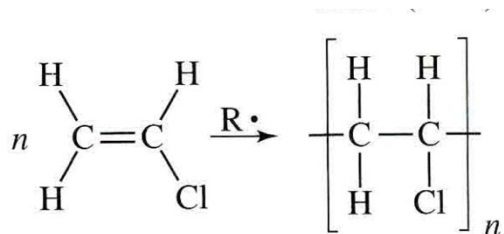
anionic



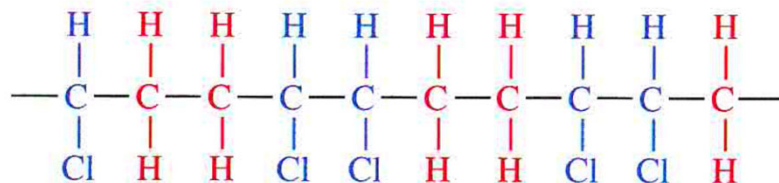
**Methyl α -cyanoacrylate
(Super glue)**

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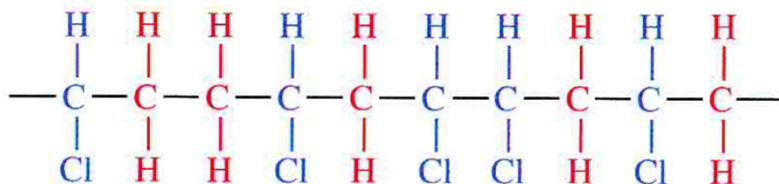
Addition reactions: different products if monomer is non-symmetrical



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



Head-to-head, tail-to-tail



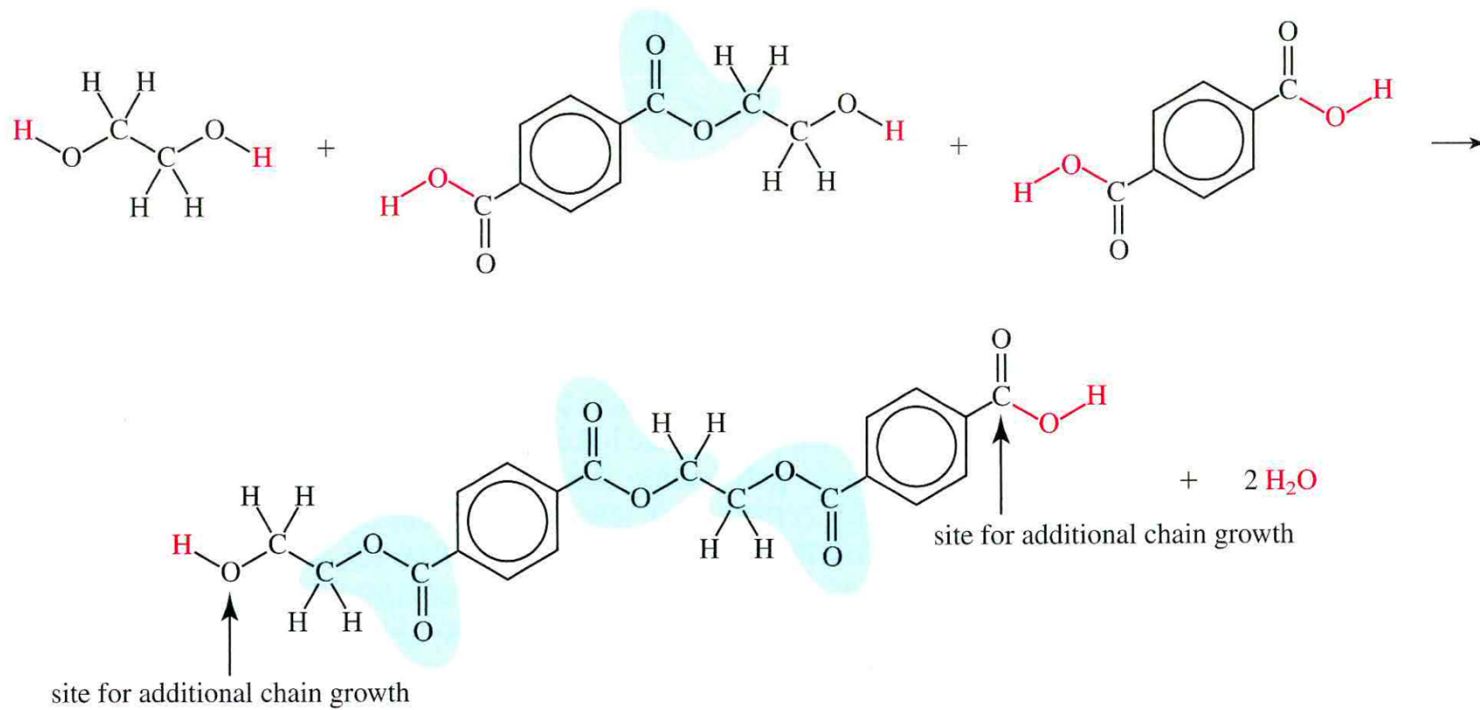
Random

Polyvinyl chloride (PVC)

- tough
- insulating
- heat sensitive

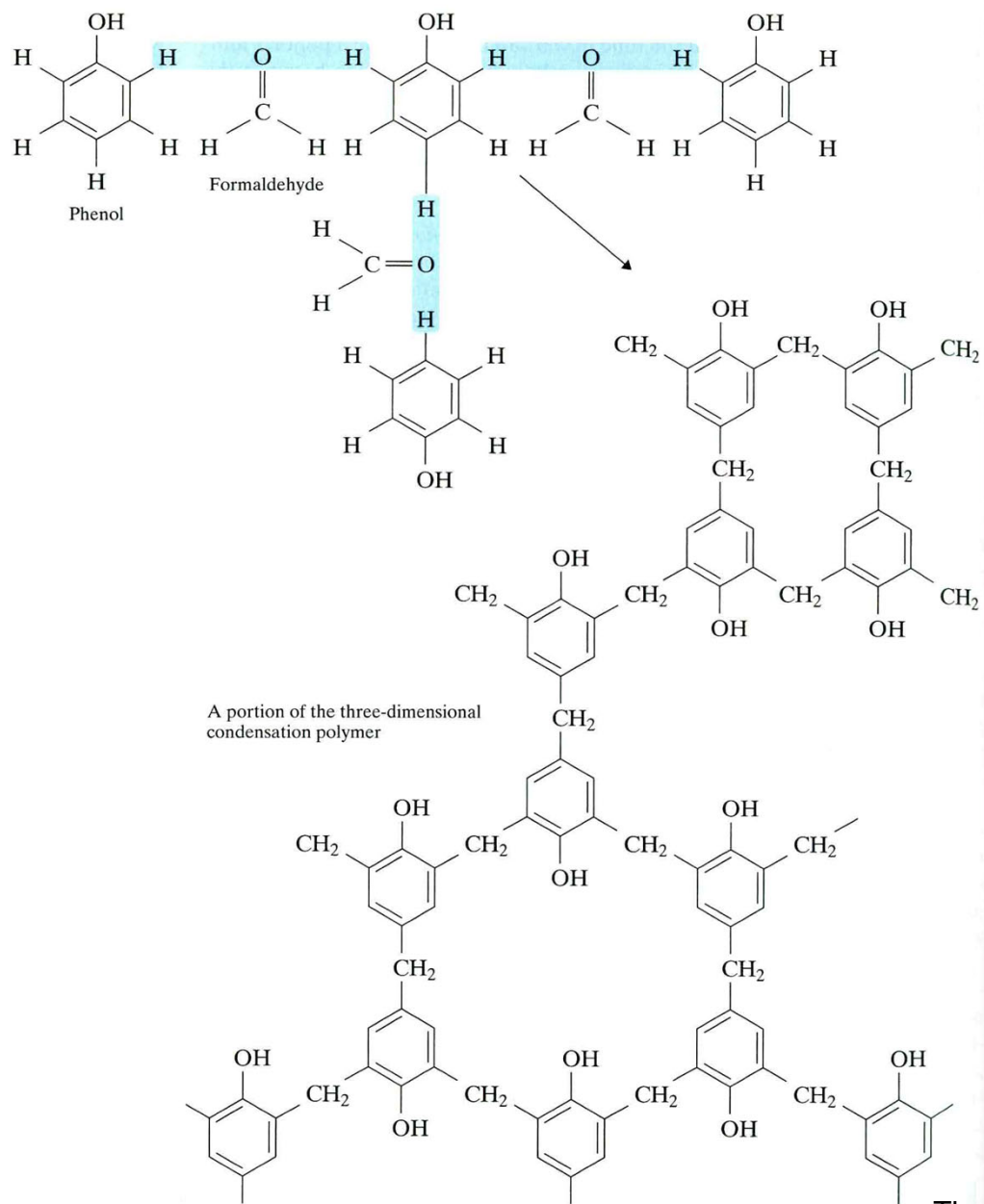
Chemistry in Context 6th Edition, ACS, McGraw-Hill

Condensation reactions: $X-A-X + Y-B-Y \rightarrow X-A-B-Y + XY$



PET = Polyester = polyethylene terephthalate

Similar for polyamides like Kevlar: $\text{N}_2\text{N-Aryl-NH}_2 + \text{HO}_2\text{C-Aryl-CO}_2\text{H}$

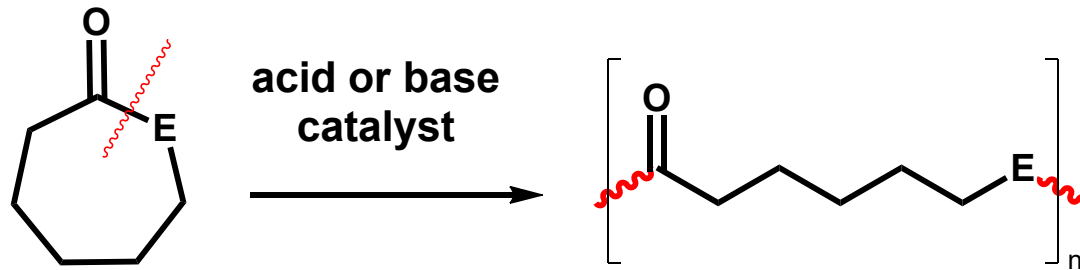


Bakelite (1909):
Phenol-formaldehyde resin
with wood 'flour' also used
to bind plywood layers



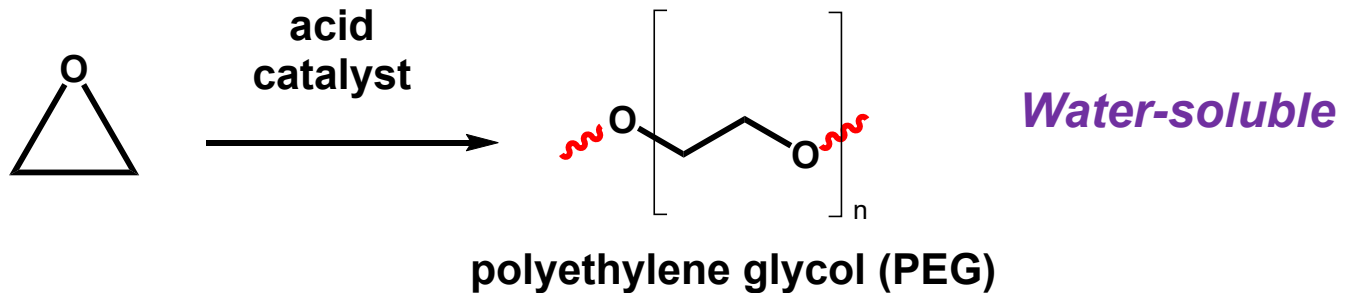
The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Ring opening polymerizations



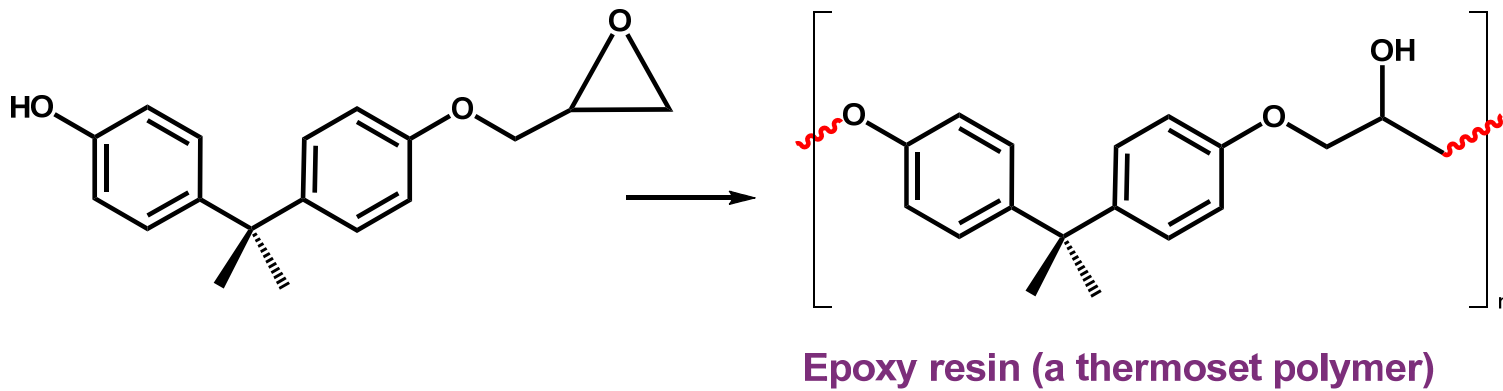
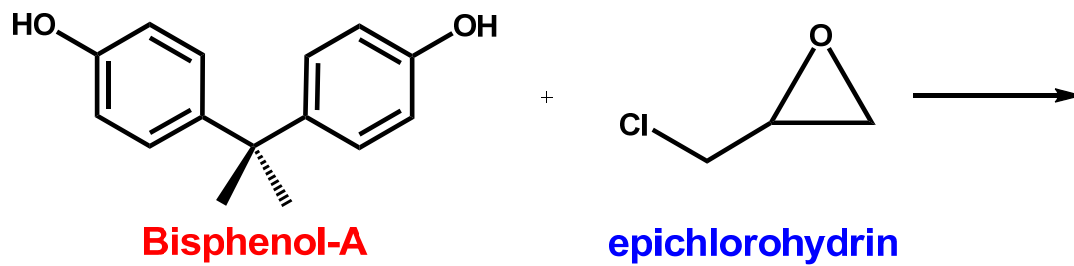
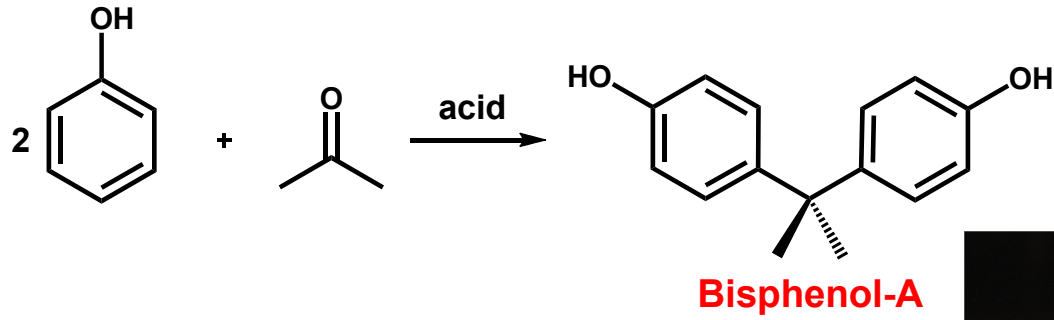
E = O = caprolactone
E = NH = caprolactam

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



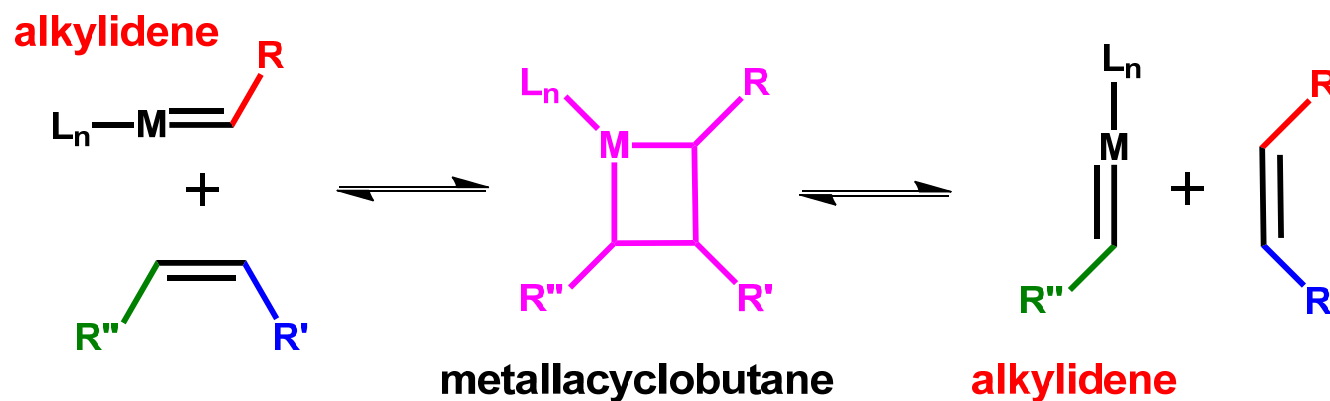
PEG used in surgical applications and can be ingested
Pegylation is attaching PEG polymers to drugs to improve pharmacokinetics

Ring opening polymerizations: Epoxy Resins

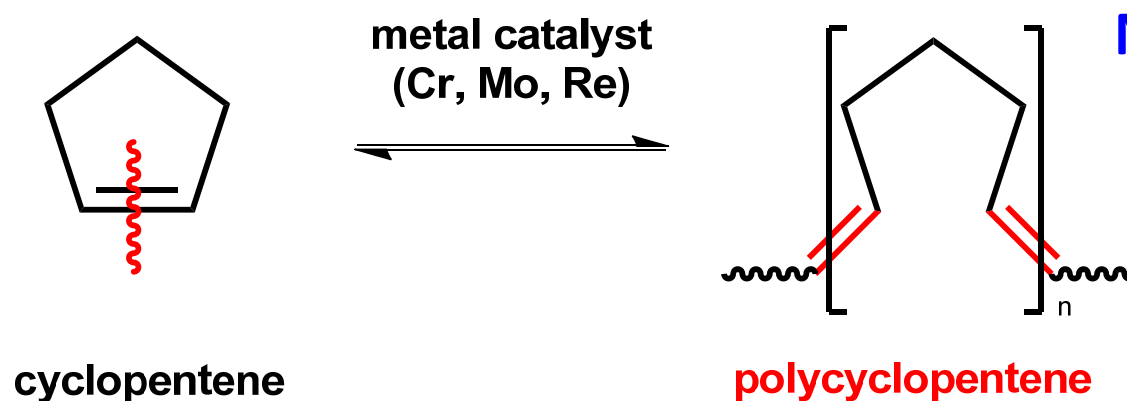


Ring opening polymerizations: **Metathesis (ROMP)**

Metal-alkylidenes are capable of *exchanging* $=CR_2$ ends of alkenes:



If we use cyclic alkenes we get polymerization:



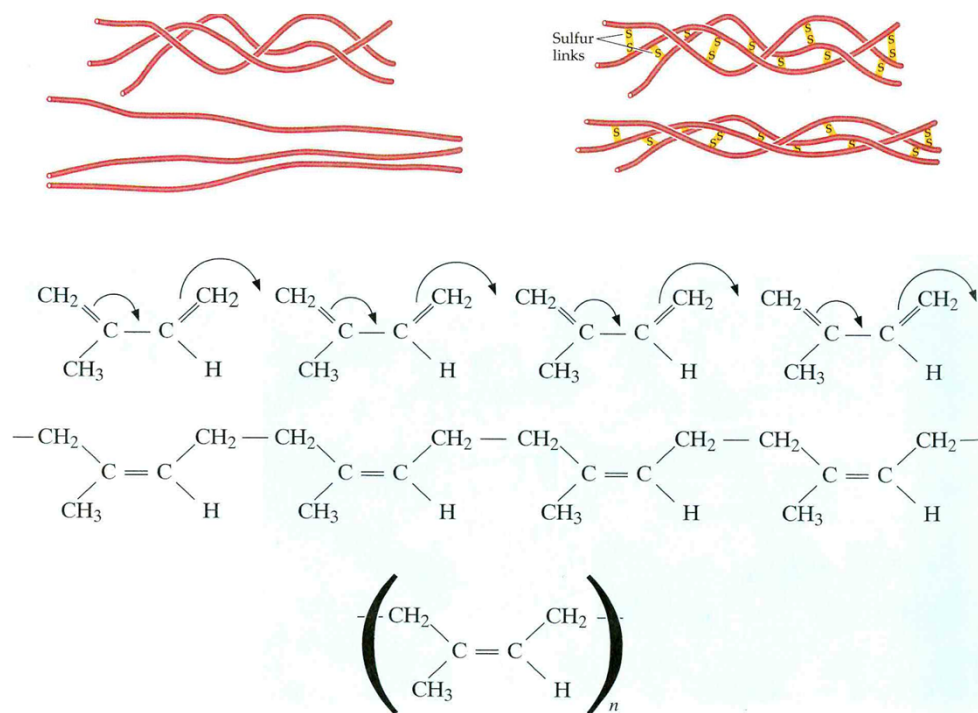
CD blanks

Non-fog plastics

Synthetic Polymers

Synthetic rubber, 1839: Charles Goodyear

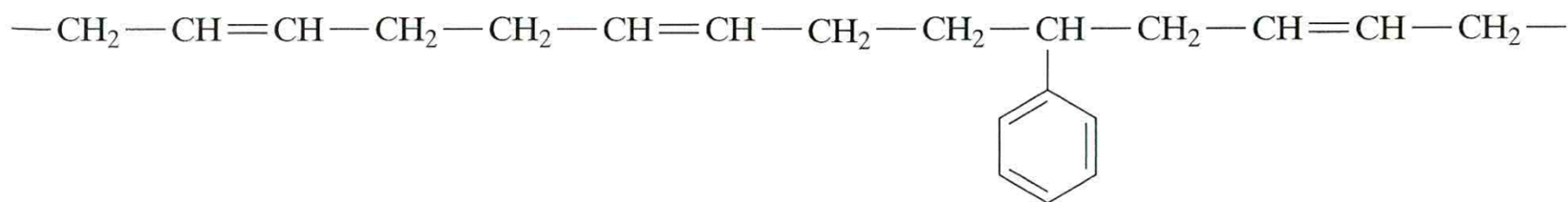
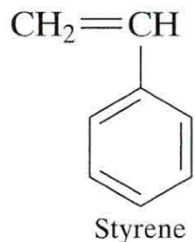
**accidentally dropped a mixture of rubber and sulfur on a hot stove:
mixture was nicely elastic – vulcanized rubber**



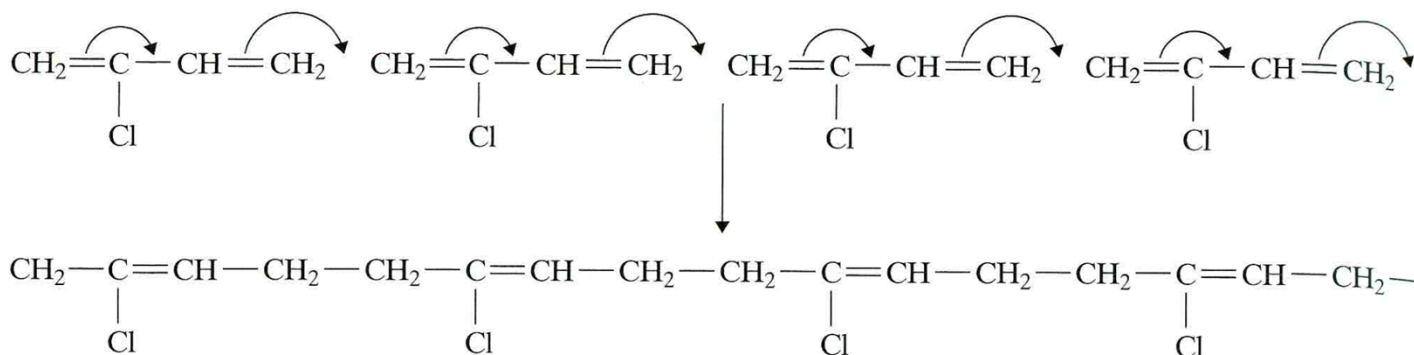
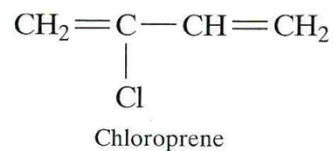
wikipedia

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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)  LDPE	Ethylene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	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)  HDPE	Ethylene $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Similar to LDPE. More rigid, tougher, slightly more dense. 	Opaque milk, juice, detergent, and shampoo bottles. Buckets, crates, and fencing.
Polyvinyl chloride  PVC, or V	Vinyl chloride $\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{Cl} \end{array}$	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.



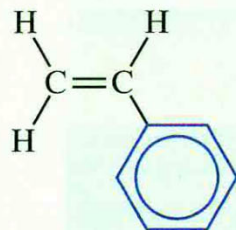
Chemistry in Context 6th Edition, ACS, McGraw-Hill

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

Polystyrene



Styrene



Variable. "Crystal" form transparent, sparkling, somewhat brittle. "Expandable" form lightweight foam. Both forms rigid and dissolve in many organic solvents.

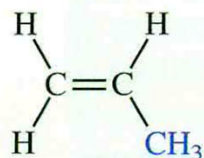
"Crystal" form: Food wrap, CD cases, transparent cups. "Expandable" form: Foam cups, insulated containers, food packaging trays, egg cartons, packaging peanuts.



Polypropylene



Propylene



Opaque, very tough, good weatherability. High melting point. Resistant to oils.

Bottle caps. Yogurt, cream, and margarine containers. Carpeting, casual furniture, luggage.



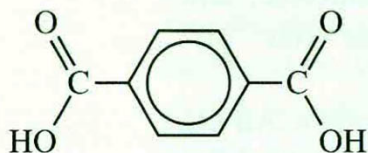
Polyethylene terephthalate



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.



Plastic recycling codes in summary



PETE

polyethylene terephthalate

soft drink bottles, mineral water, fruit juice container, cooking oil



HDPE

high-density polyethylene

milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps



PVC

polyvinyl chloride

trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff



LDPE

low-density polyethylene

crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings



PP

polypropylene

furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars



PS

polystyrene

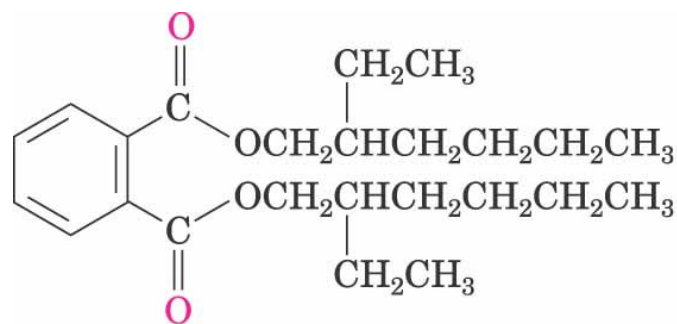
toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, CD cases, vending cups



OTHER

other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass

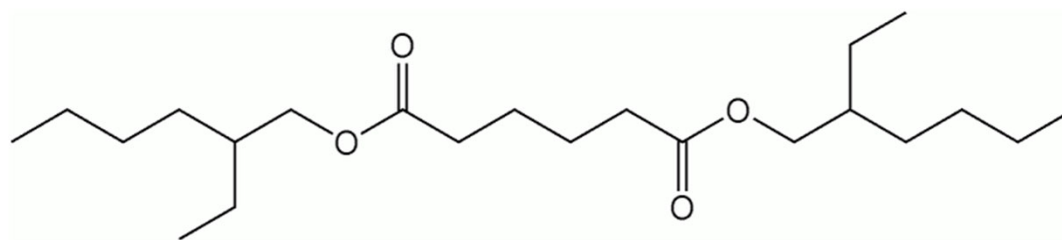
Plasticizers: *lubricants between the chains* to soften polymers: PVC



Di(2-ethylhexyl) phthalate,
a plasticizer

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PVC food wraps contain other plasticizers such as **adipates** and citrates

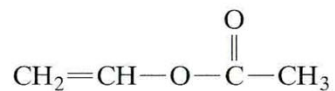


Bis(2-ethylhexyl) adipate – DEHA

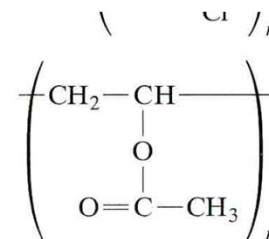
Shown to induce liver cancer in mice but not rats: controversial

Other major polymers

Vinyl acetate



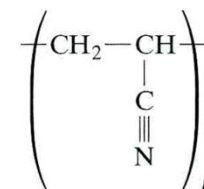
poly(vinyl acetate)
polyvinyl acetate
PVA



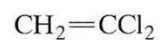
Acrylonitrile



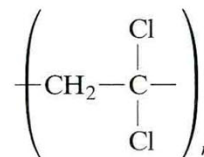
polyacrylonitrile
Orlon
Acrilan
Creslan



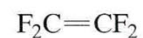
Vinylidene chloride



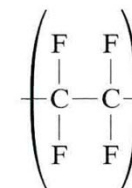
poly(vinylidene chloride)
Saran



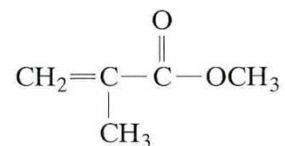
Tetrafluoroethylene



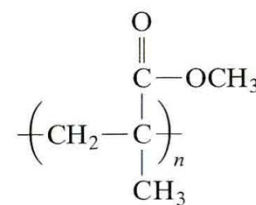
polytetrafluoroethylene
Teflon



Methyl methacrylate

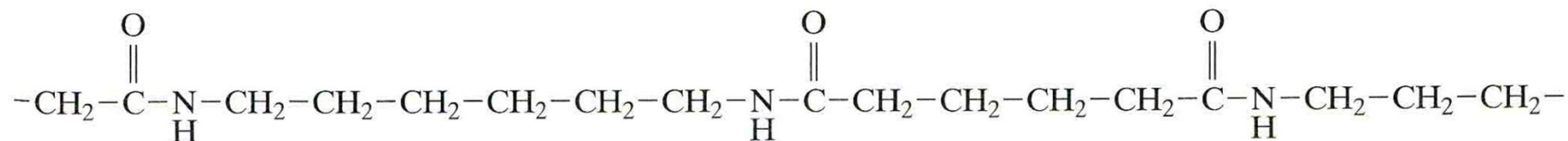
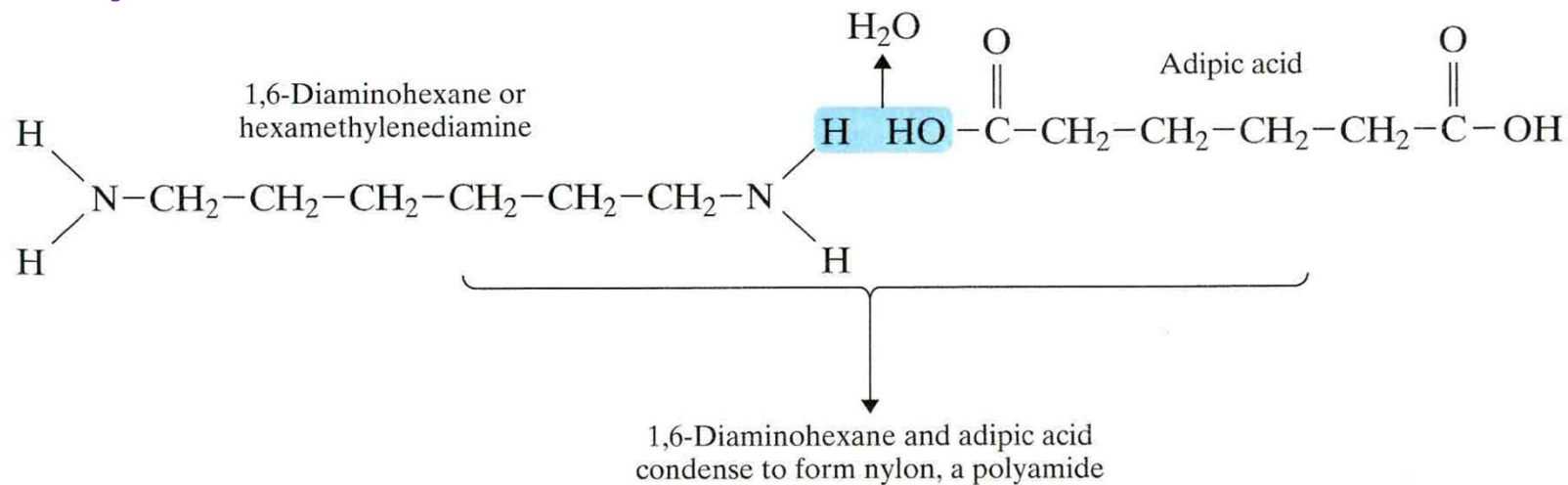


poly(methyl methacrylate)
Lucite
Plexiglas



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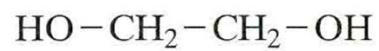
Nylon 6,6



dreamstime.com

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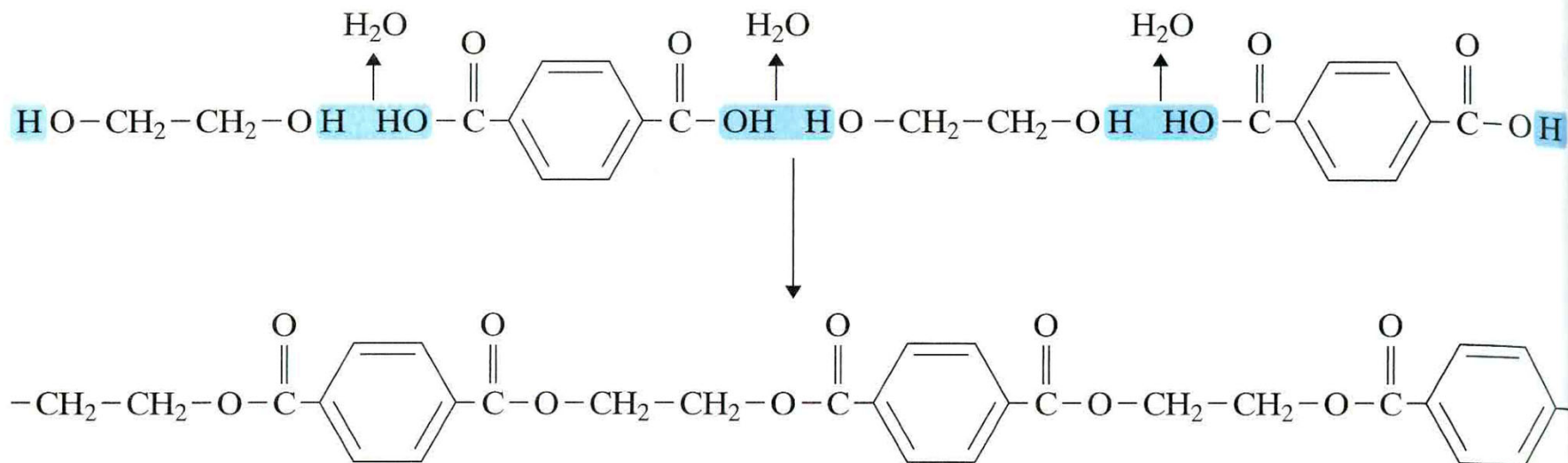
Polyethylene terephthalate: PET



Ethylene glycol



Terephthalic acid



Poly(ethylene terephthalate), a polyester

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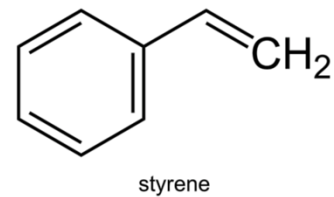
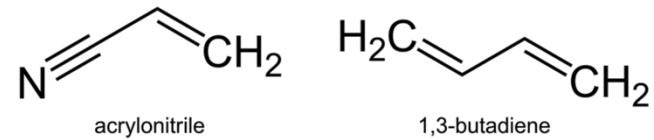
ABS - A_xB_yS_z

15% - 35% - acrylonitrile

5% - 30% - 1,3-butadiene

40% - 60% - styrene

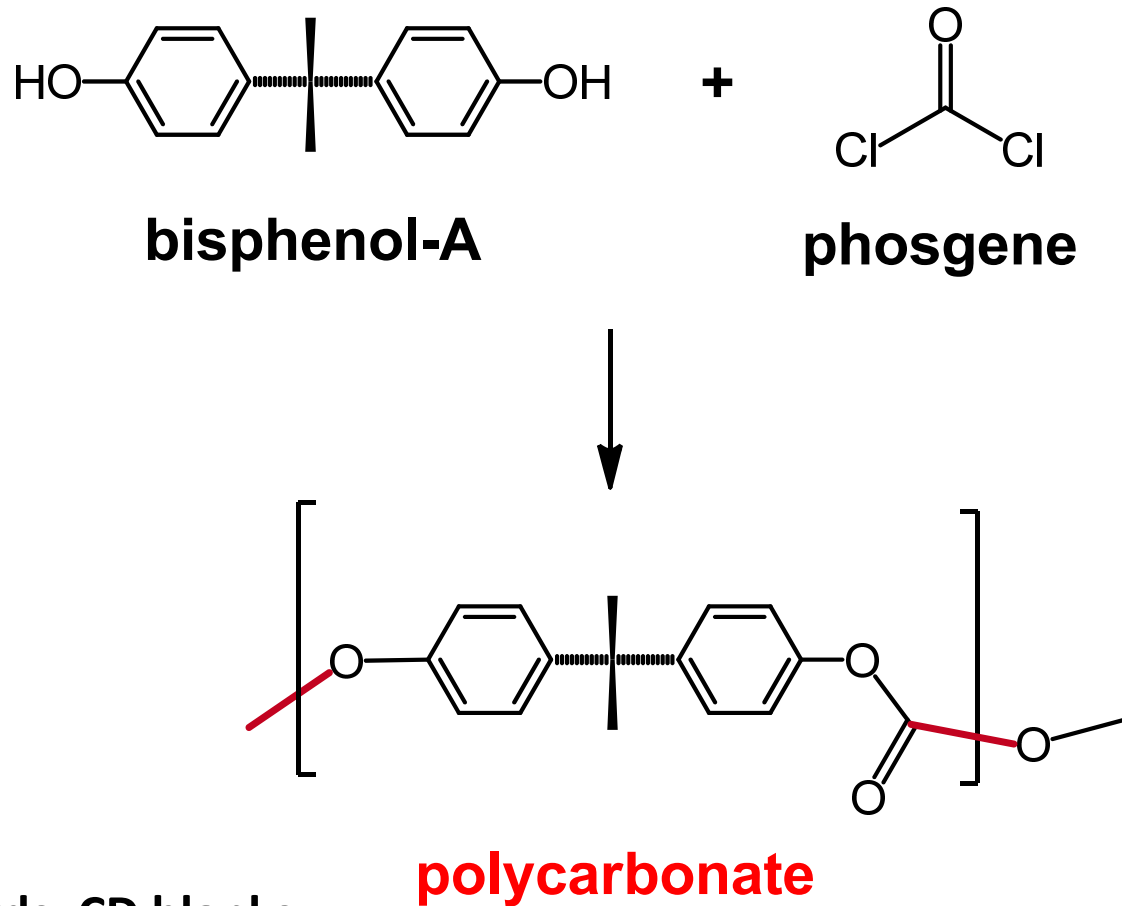
- Tough
- Insulating
- Injection moldable
- Used in: protective equipment, car parts, bottle caps, etc.



Polycarbonates

Usually with
bisphenol-A

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



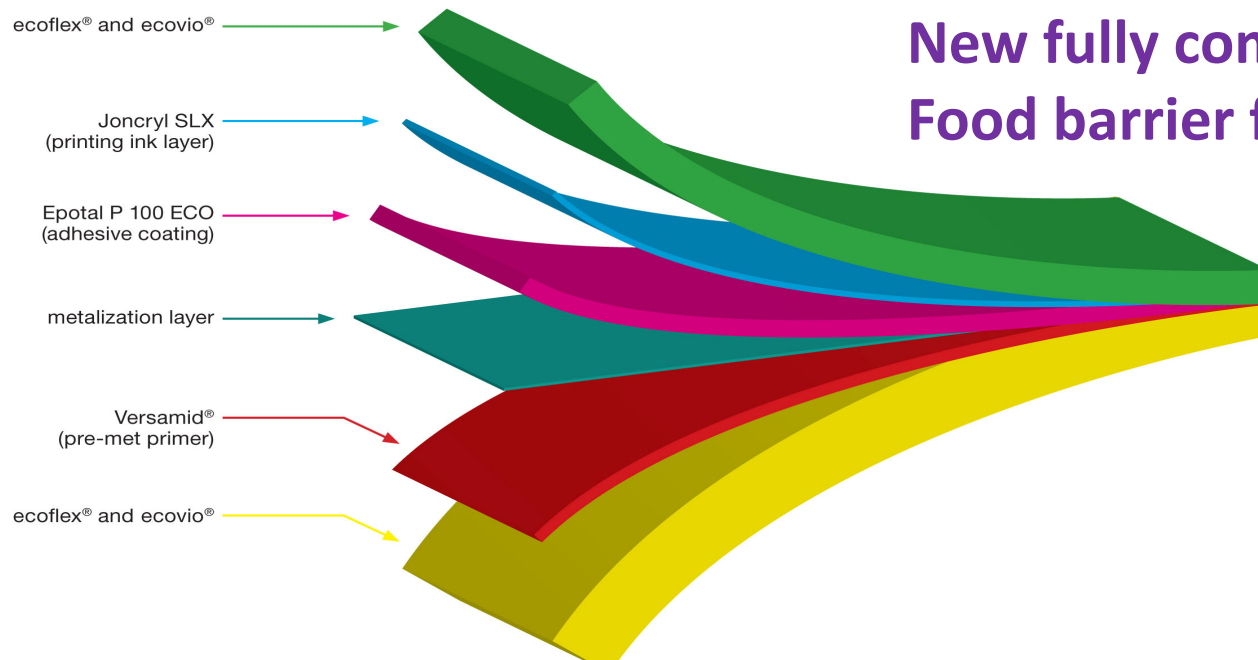
Food packaging: not biodegradable and not recyclable – yet?

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

Each layer has its purpose:

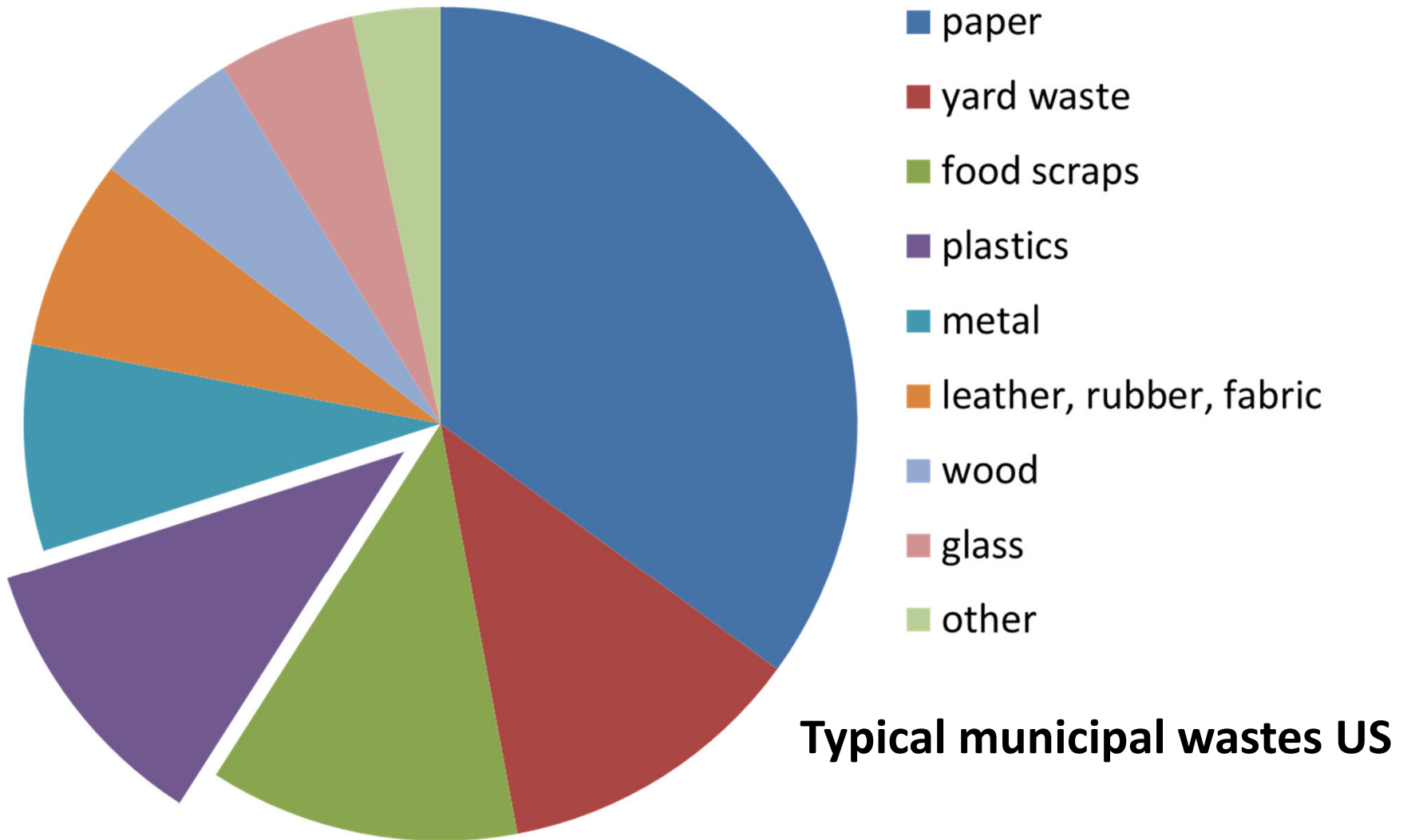
- Low oxygen permeability (nylon)
- Low moisture permeability
- Toughness (polypropylene, HDPE)
- Printable

6 Layers



New fully compostable
Food barrier film from BASF

Recycling



2015 World Recycling Data

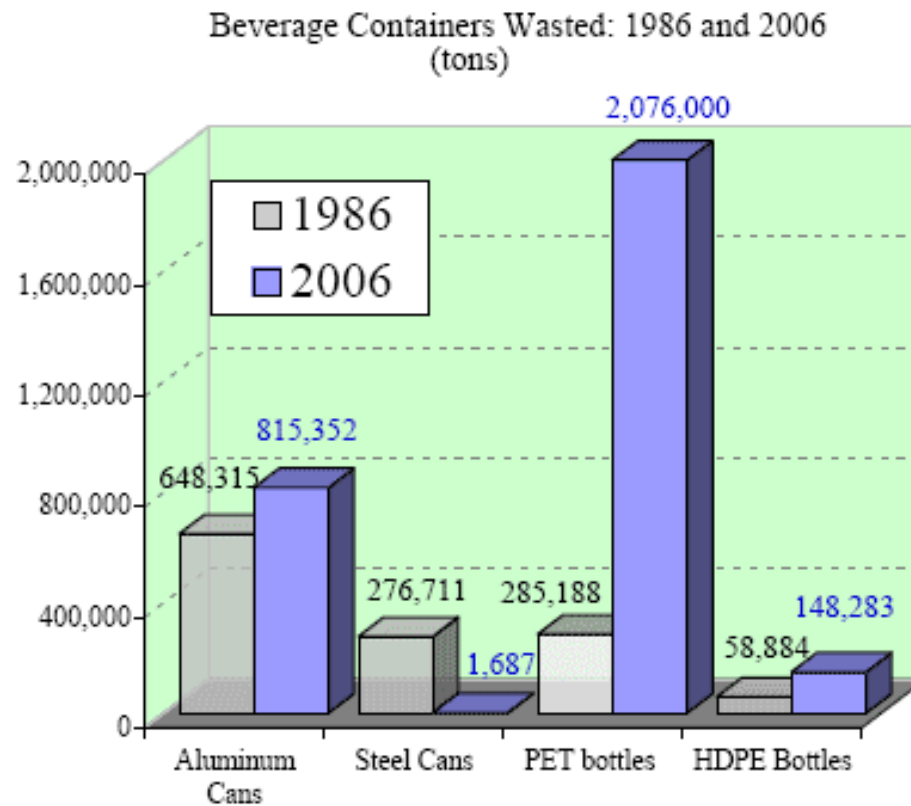
(Source: OECD (2015), "Municipal Waste", OECD Environment Statistics)

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

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 $\text{CO}_2 + \text{H}_2\text{O}$

Incineration

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

Issues:

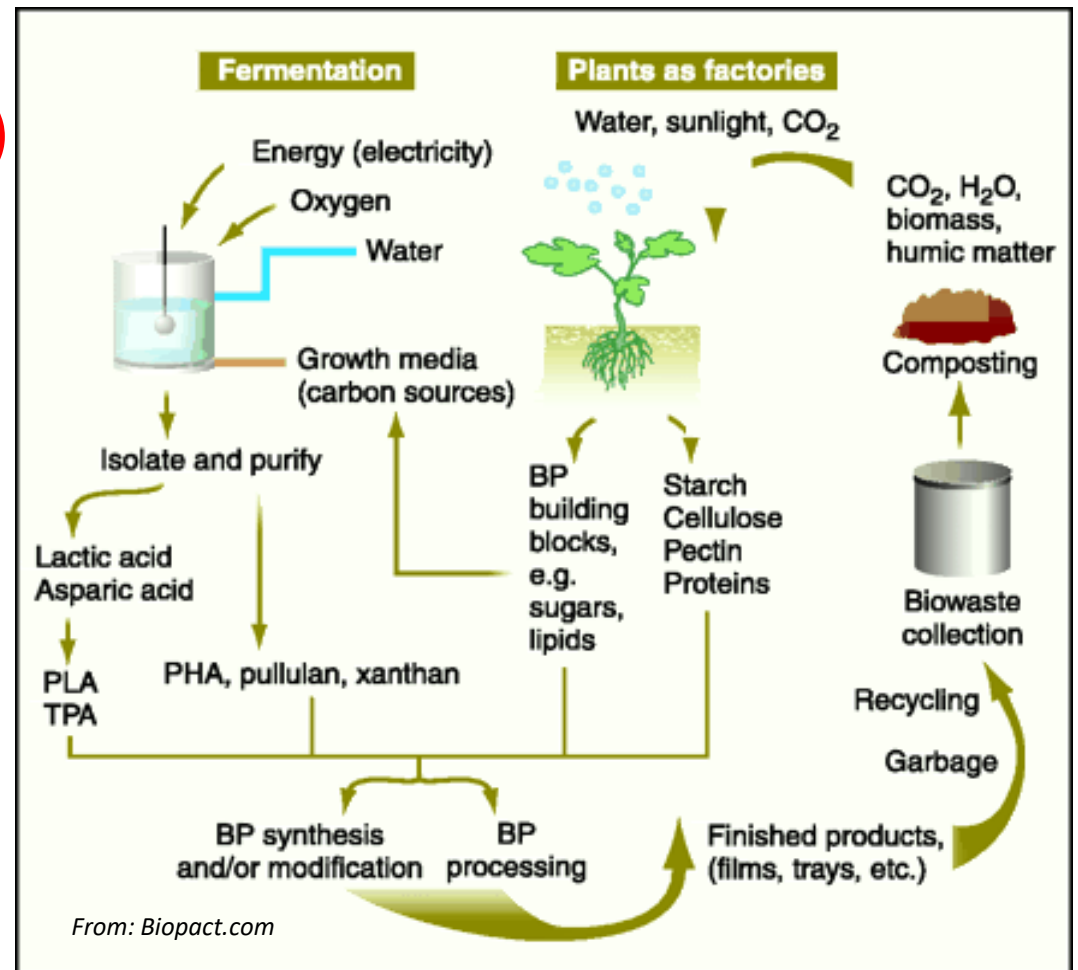
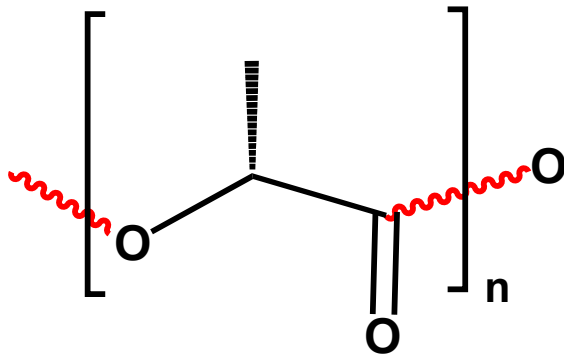
- chlorine based polymers release HCl
- toxic chemicals
- metals in ink in ash (Pb, Cd)

Biodegradable Polymers: *the way forward?*

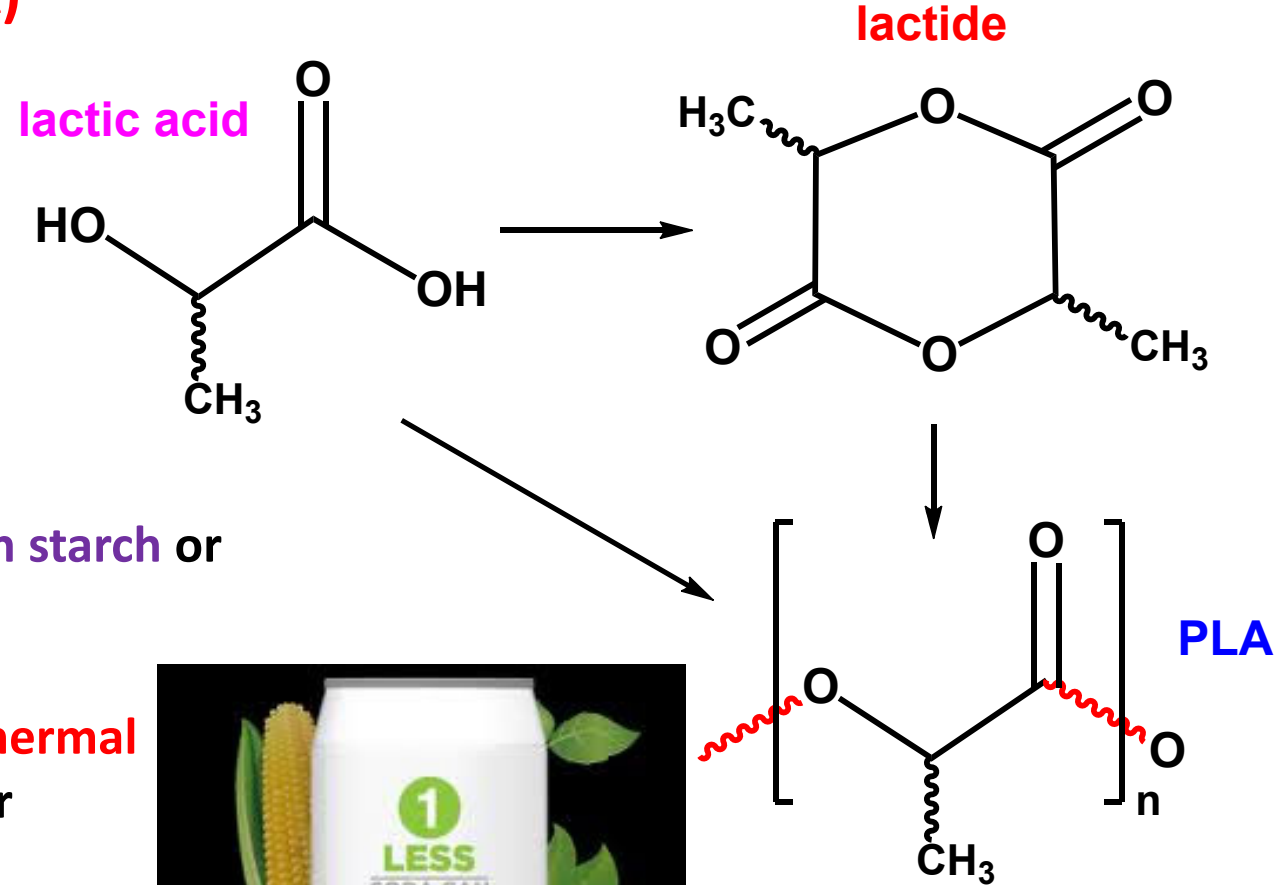
Alkyl esters: much more easily hydrolyzed than PET

Polyhydroxyalkanoates (PHA)

- Monomers from bacterial fermentation of sugars



Polylactic acid (PLA)



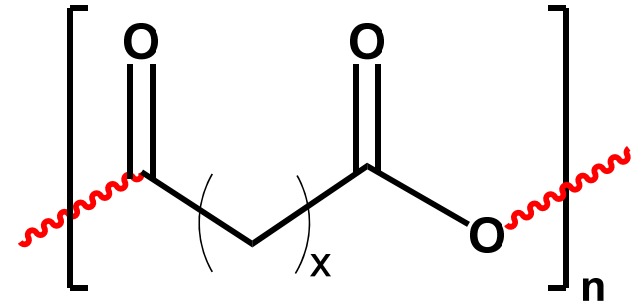
- Monomer from **corn starch** or **sugarcane**
- Degrades quickly
- Easily recycled by **thermal depolymerization** or **hydrolysis**



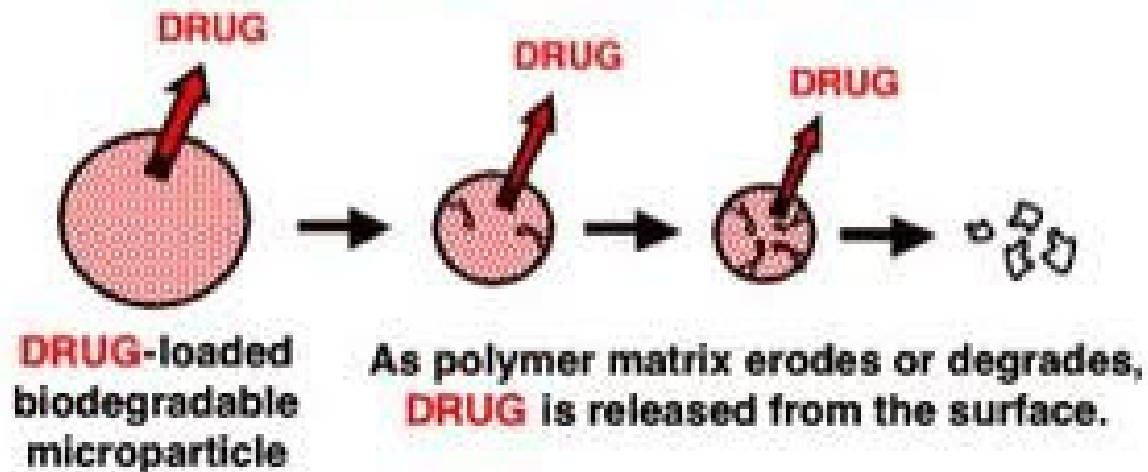
Largest manufacturer
in US:
NatureWorks (Cargill)

Polyanhydrides

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



Biodegradable microparticles

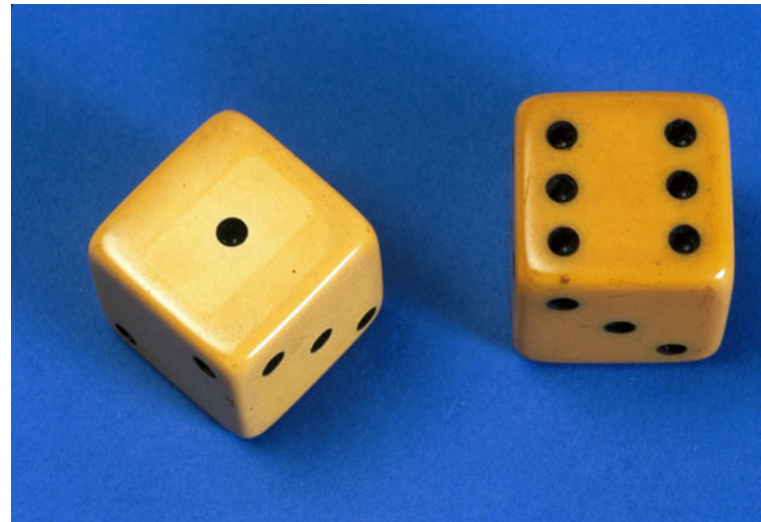
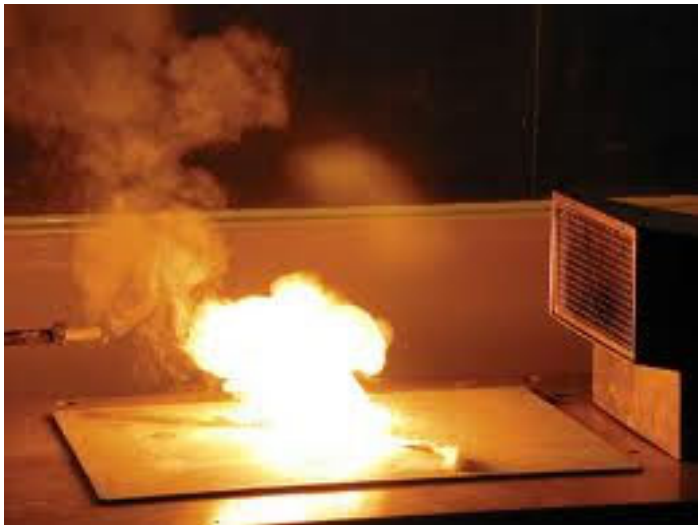
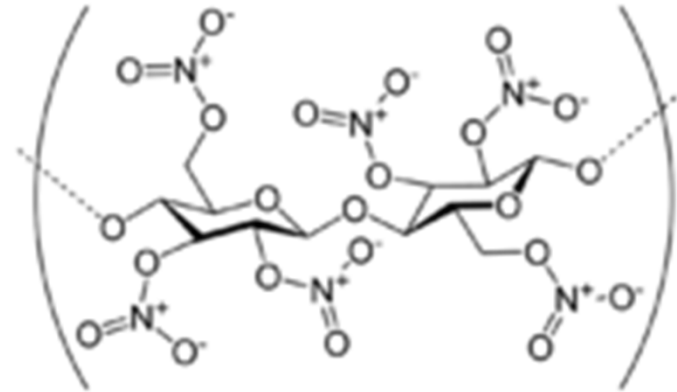


University of Washington Engineering

Cellulose Derivatives

Cellulose nitrate

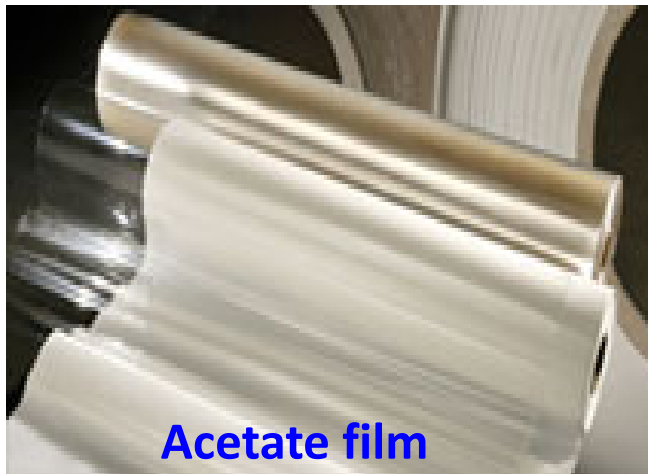
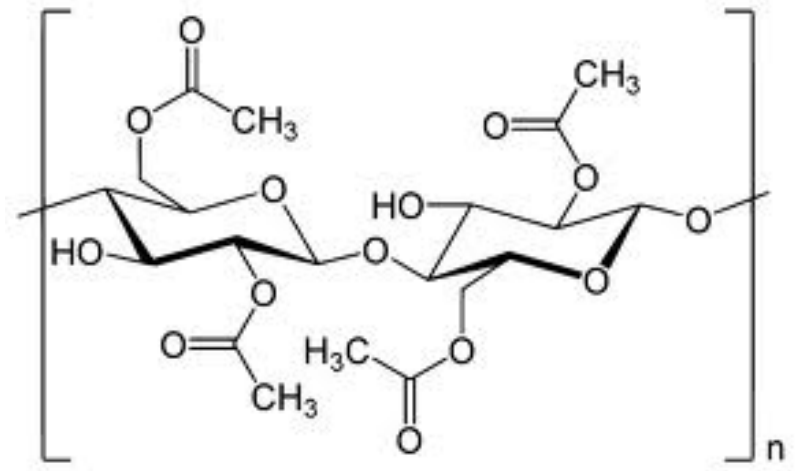
- **Extremely flammable**
- Used for **movie film** until 1948
- Soaking cotton in nitric acid gives the **highly flammable 'guncotton'** (*below*)
- Used for **artificial 'ivory'** in 19th century (*right*)



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



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)

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

From: Canadian Plastics Industry Association website



For an example of a company that specializes in recycling plastics see:

www.postplastics.com

"Recycling for Industry"

POST  PLASTICS

