Polymer Structures

Contents:

A. Synthetic polymers derived from petroleum

Most commercial polymers are synthetic.

polyolefins

The most abundant and cheapest synthetic polymers are polyolefins. Polyolefins are synthesized from olefins (the common name for alkenes). Olefins are obtained from petroleum.

An olefin is a hydrocarbon that contains at least one carbon-carbon double bond.

The simplest olefin is ethylene,

$$CH_2{=}CH_2$$

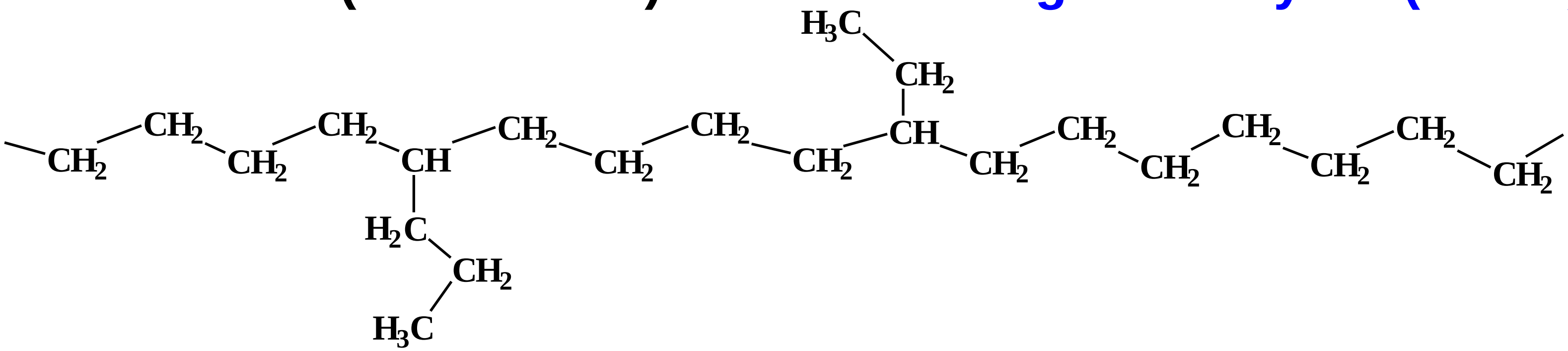
The simplest polyolefin is polyethylene (PE). A simple representation of polyethylene is

$$-\!\!\left[CH_2-CH_2 \right]\!\!-_n$$

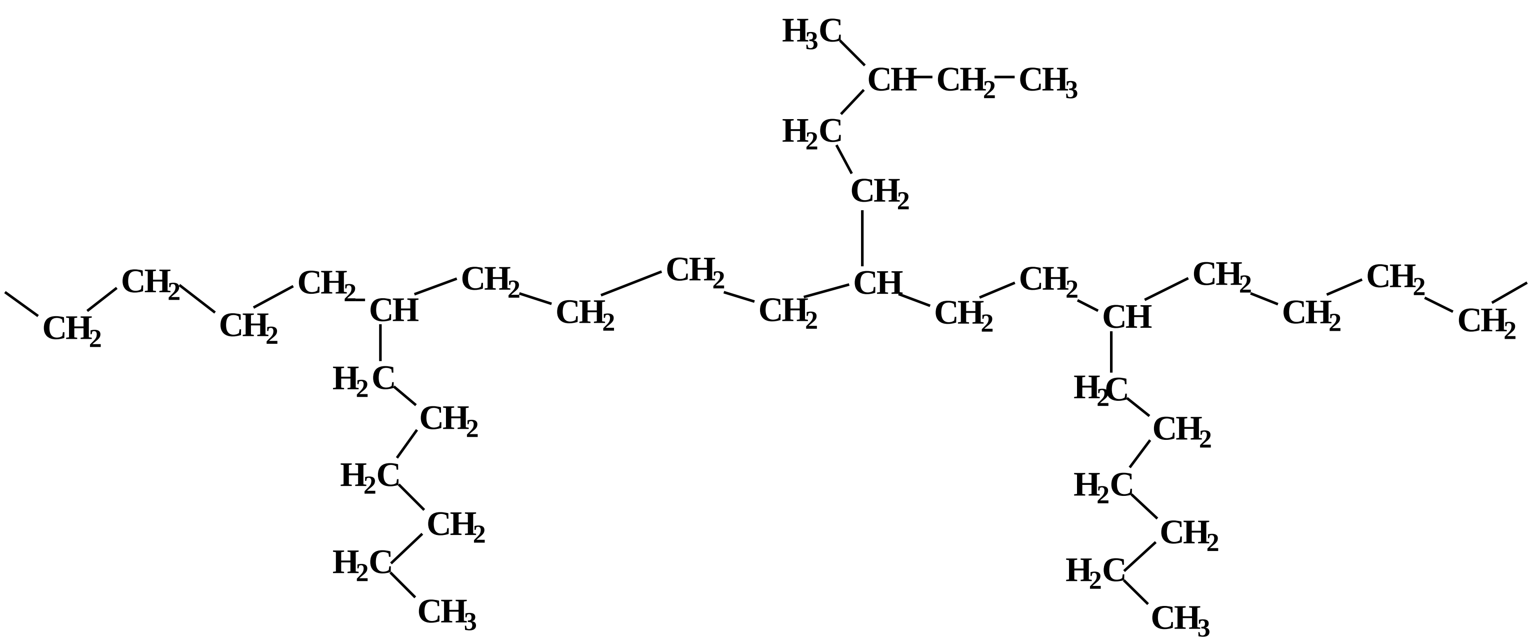
where the n is the number of monomer units.

In the polymerization, the double bond is lost.

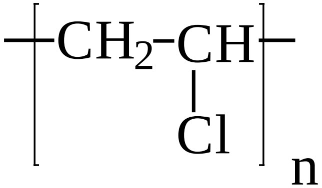
If the polyethylene chain is produced to have few and short branches (side chains) the result is **high-density PE (HDPE)**.



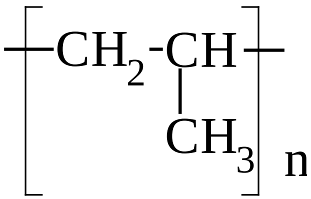
If the chain is produced to have many, longer branches, the result is **low-density PE (LDPE)**.



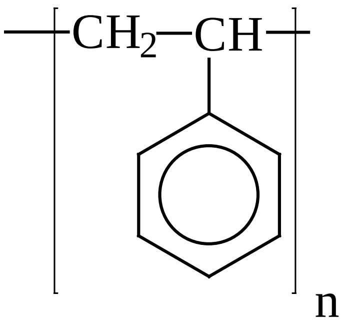
Other polyolefins



poly(vinyl chloride) (PVC) **(from ethylene chloride)**



polypropylene (PP) **(from propylene)**

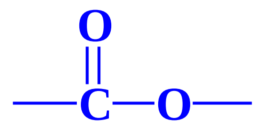


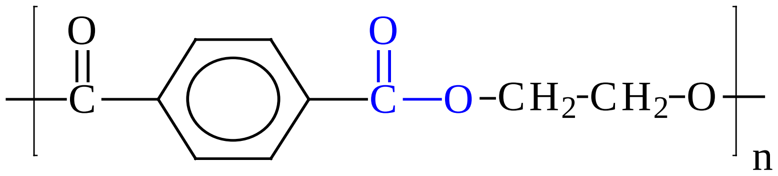
polystyrene (PS) **(from styrene)**

Polyolefins are very stable. Oxidative degradation is extremely slow. If not recycled, they are landfilled or incinerated. They are not biodegradable or compostable.

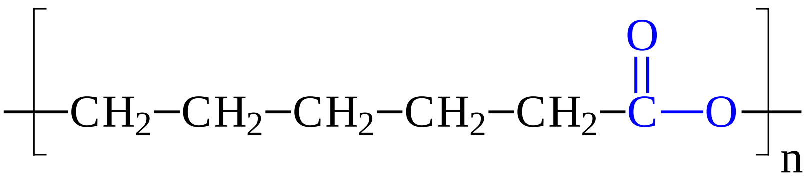
The single most important reason for their stability is that they have carbon-carbon single bonds in their backbone.

polyesters

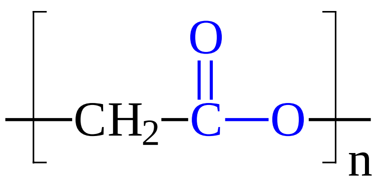
Polyesters contain the ester group, 



poly(ethylene terephthalate) (PET)



poly(ε-caprolactone) (PCL)

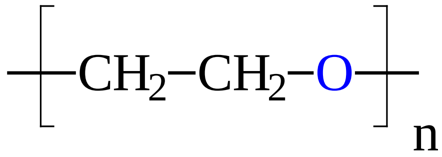


polyglycolic acid (PGA)

PGA and PCL are biodegradable; the heteroatom (an atom other than carbon) in the backbone leads to environmental degradation by hydrolysis.

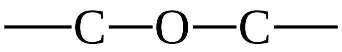
PET is not biodegradable in spite of the oxygen in the backbone, because its high crystallinity impedes access of water molecules. Most recycled plastic is PET.

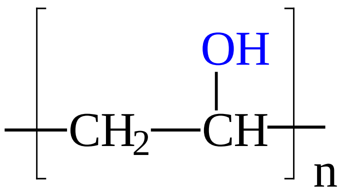
Other polymers synthesized from petroleum:



poly(ethylene glycol) (PEG)

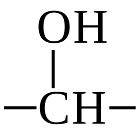
(a polyether)





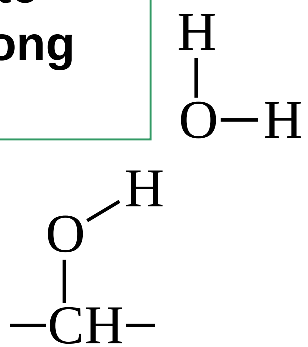
poly(vinyl alcohol) (PVA)

(a polyalcohol)



Both are environmentally degradable. PEG has a heteroatom in its backbone and environmentally degrades by hydrolysis.

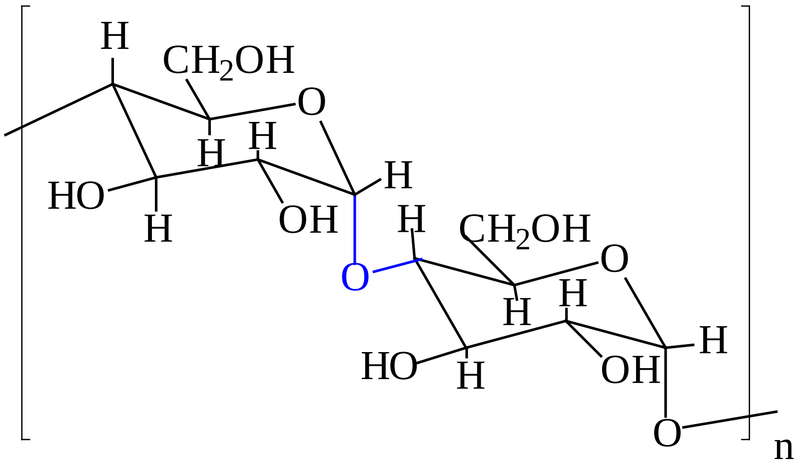
PVA also degrades by hydrolysis, in spite of its –C-C- backbone, because the hydroxyl group on alternate carbon atoms leads to strong interactions with water.



B. Biological (natural) polymers [biopolymers]

starch (amylose and amylopectin)

The major polymer components of starch are amylose and amylopectin.

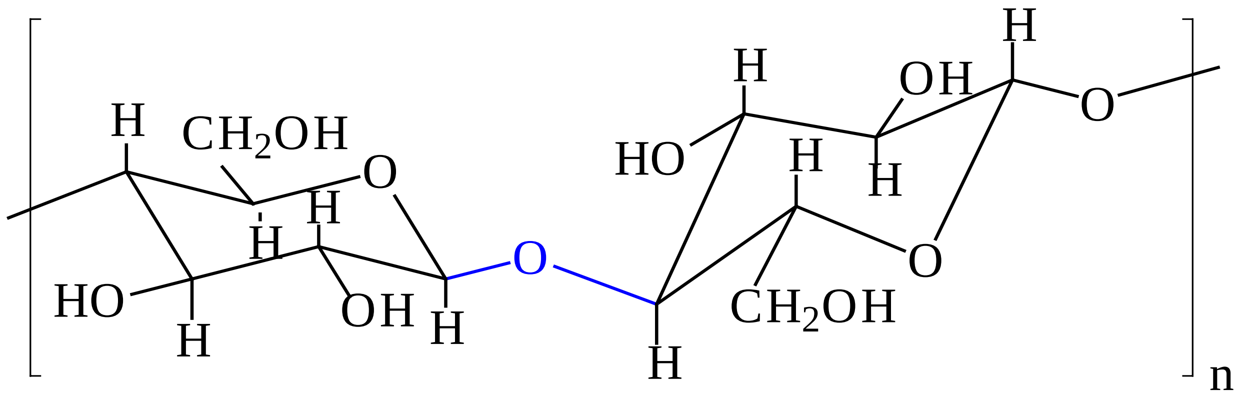


amylose, a major component of starch

Amylose is a linear polymer. It is α[1→4]-linked D-glucose. Its molecular weight ranges from 2 x 10^5 to 2 x 10^6.

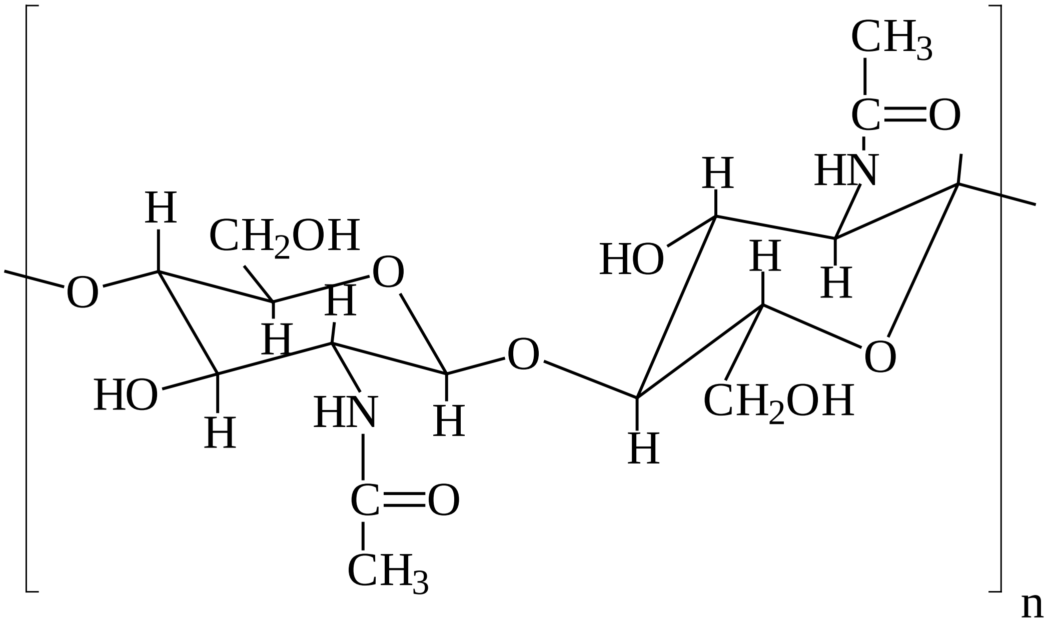
Amylopectin is branched at the hydroxymethyl position; i.e., it has the same backbone as amylose, but with α[1→6]-linked D-glucose at branch points. It has molecular weights up to 4 x 10^8.

cellulose



Cellulose and amylose differ only in the geometric arrangement about the linkage.

chitin and chitosan

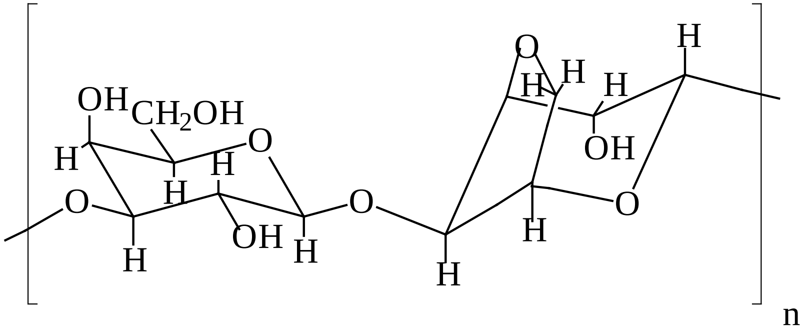


chitin

Chitosan is deacetylated chitin.

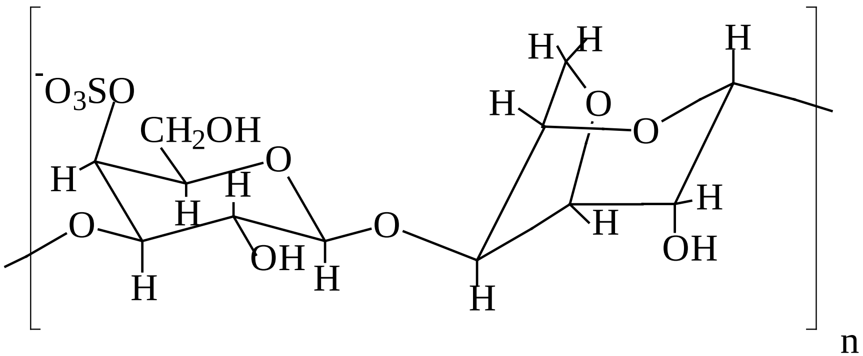
Chitin is another abundant polysaccharide; it is found in shellfish and insects and some fungi.

agar



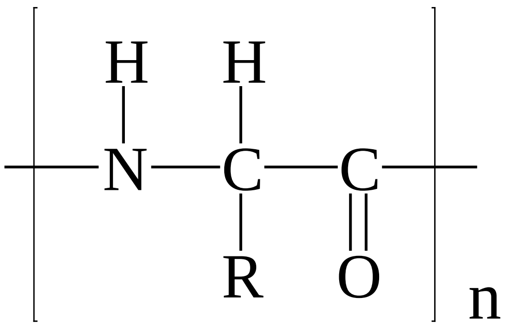
Agarose, the main component of agar.

carrageenan



Agarose, carrageenan, and alginate are seaweed polysaccharides. They are gelling polysaccharides, and form good cast films. They have been used to form encapsulating gel beads for drug delivery systems.

Proteins



Structural formula
for a generic protein

R represents the side chain of an amino acid. Each specific protein is made up of a characteristic sequence of amino acids.

Proteins are polymers formed by the condensation polymerization of amino acids.

The carboxyl group of one amino acid joins with the amino group of another amino acid, eliminating a water molecule and forming an amide linkage, called in the case of proteins a peptide bond.

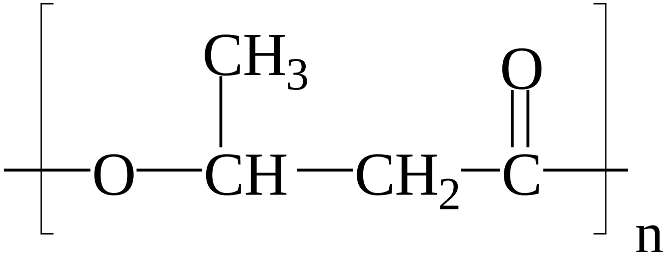
Abundant and commercially important proteins include both animal and plant proteins.

animal proteins:	**gelatin (denatured collagen)**
	casein
	whey protein
	silk
	keratin
plant proteins:	**soy protein**
	zein from corn(maize)
	wheat gluten
	potato proteins
	pea proteins

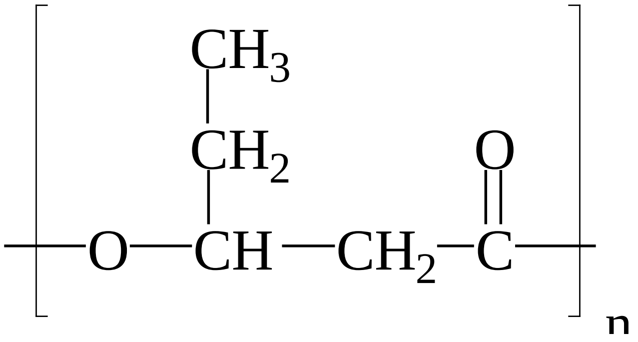
Microbial polyesters:Polyhydroxyalkanoates (PHAs)

Bacteria produce polyesters, including polyhydroxyalkanoates (PHAs). PHAs typically occur as inclusion bodies deposited in granules in the cytoplasm. PHAs serve as energy and carbon storage materials in bacteria. PHAs accumulate when carbon is in excess but some other nutrient limits growth. They are consumed when no external carbon source is available.

The most abundant PHA in nature, and the first to be discovered, is poly-3-hydroxybutyrate (PHB). Other PHAs have since been discovered, including those containing hydroxyvalerate units, as in poly-3-hydroxyvalerate (PHV).



PHB



PHV

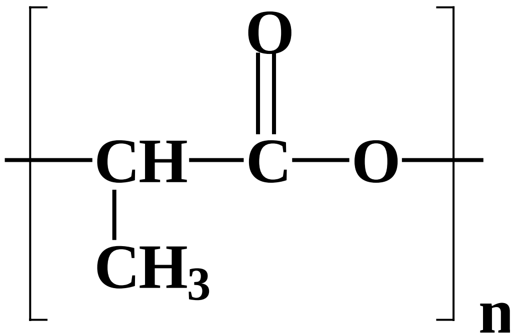
Copolymers, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), have a range of properties depending on composition.

The composition of the copolymer is controlled through the ratio of feedstocks used: glucose or sucrose for butyrate; propionic acid for valerate.

C. Poly(lactic acid) is a synthetic polymer, but derived from a naturally occurring monomer, produced through fermentation.

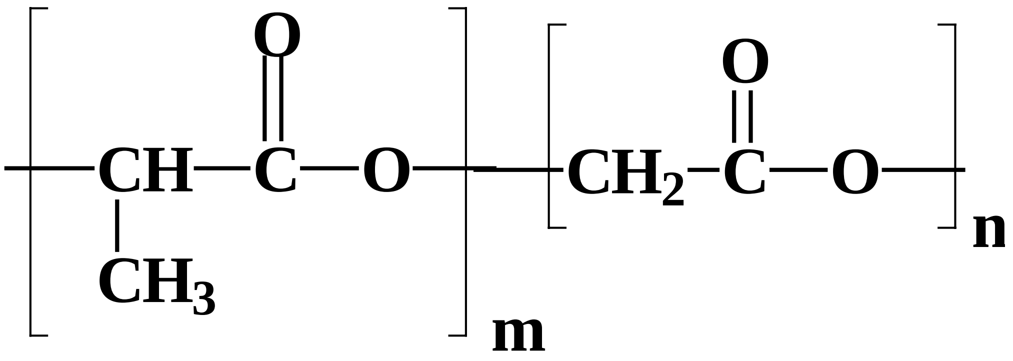
Hydrolyzed starch (or some other sugar feedstock) is fed microorganisms to produce lactic acid, ($CH_3CHOHCOOH$) on large scales.

Poly(L-lactic acid) (PLA) is then chemically synthesized from lactic acid.



PLA is a polyester and is biodegradable.

Poly(lactic acid-*co*-glycolic acid) is a random copolymer that has been used for several types of biomedical application, including microcapsules for drug delivery systems. It has also been used to make orthopedic bone regeneration-repair materials.



Poly (lactic acid-*co*-glycolic acid)