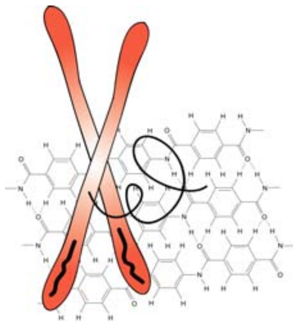
Class 2: Polymer Crystallinity and Synthesis



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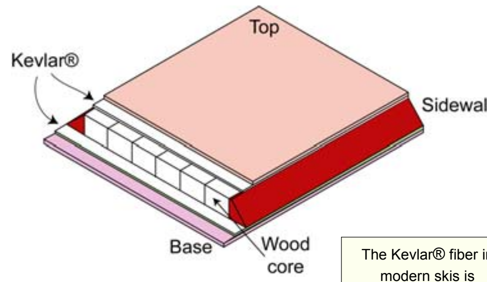
Polymers and polymer composites are the key elements in skis and snowboards.



The Kevlar® fiber in modern skis is sometimes replaced with fiberglass.

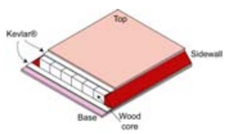
The core of the skis are made up of composites.

Wood, a natural composite, is used as the inner core of a lot of skis and snowboards.

The wood is layered with a polymer based composites (fiberglass, Kevlar® fiber sheets, carbon fiber sheets) that provide extra support.

The composite is strongest in the direction of the fiber so multiple layers of the composite sheets are used.

Epoxy, another polymer, is used to fix the layers all together.



http://www.skibuilders.com/howto/skicon/materials.shtml

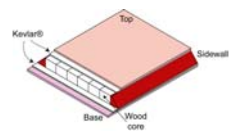
Polymers are used to protect the composite core.

A polymer coating such as polyethylene is put on the, the top-sheet material. It's main purpose is to protect the epoxy from UV radiation.

The bottom base material is a thin sheet of plastic made from UHMWPE (ultra-high molecular weight polyethylene).

Sidewalls and tip spacers are strips to protect the wood core from moisture. A common sidewall and tip spacer is a co-polymer, ABS.

Polymers are also used in rubber strips on the edges of the skis that minimize vibrations and prevent delamination .



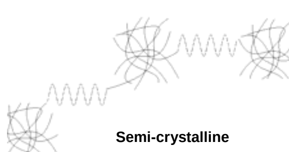
http://www.skibuilders.com/howto/skicon/materials.shtml

Polymers can have a crystal structure (arrangement) to the chains

In polymers, samples can be amorphous, crystalline, or semi crystalline.

Crystalline and semi-crystalline polymers have an arrangement of their chains that comes from packing.

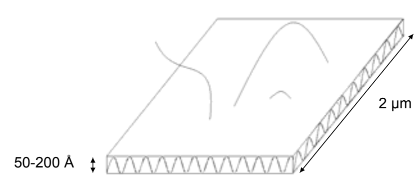
Amorphous



Semi-crystalline

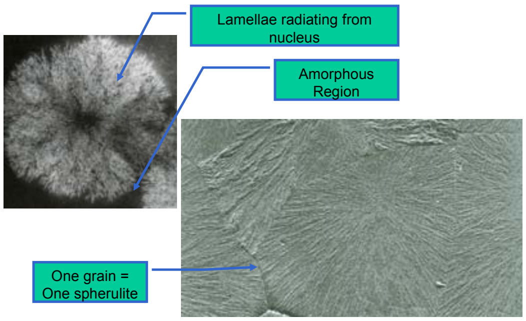
Chains fold back on each other in crystal regions

Lamellar crystals are regions of a polymer where the chains fold back on each other in tight packing



Polymers can crystallize in spheres

Spherulites are crystalline regions of a polymer that form from chain folded lamellae radiating out in 3-D from a nucleus



Left: William D. Callister, Jr - "Materials Science and Engineering an Introduction – 6th Edition"
Right: R.J. Young – "Introduction to Polymers – 2nd Edition"

Degree of crystallinity in a polymer has a very large effect on the mechanical behavior of the material.

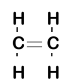
Full crystallinity is never achieved in polymeric materials (i.e., there will always be some regions that are amorphous).

Percentage crystallinity	Density (10^3 kg/m^3)	Tensile Strength (MPa)
65	0.920	13.8
75	0.935	17.2
85	0.950	27.6
87	0.960	31.0
95	0.965	37.9

T.H. Courtney, Mechanical Behavior of Materials, (McGraw Hill, New York, 1990).

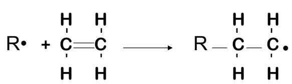
One way a polymer can grow is by breaking the double bonds in a monomer

A common synthesis method is addition polymerization, a process by which monomer units are attached one at a time in chainlike fashion to form a linear macromolecule.



Ethylene

Polyethylene used in the base of skis is made through addition polymerization.



Ethylene

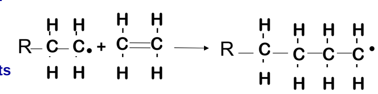
The monomers exist as stable units with a double or triple C bond in them.

During the initiation step, a catalyst (R•) comes along and breaks the double bond.

Propagation involves the growth of the chain as monomers add on.

This leaves a reactive bond that then breaks the double bond of another monomer and adds that to the chain.

Propagation involves the linear growth of the molecule as monomer units become attached to one another in succession to produce the chain molecule.



Chain growth is relatively rapid, the period required to grow a molecule consisting of, say, 1000 mer units is on the order of 10-2 to 10-3 s.

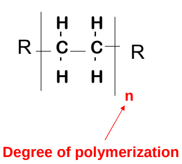
The chains stops growing when a catalyst reacts with the end of the chain

The process stops when a catalyst reacts with the other end

The chain length is determined by the rates of

- initiation: fast initiation would give a lot of chains forming at once
- propagation: fast propagation would give long chains
- termination: fast termination would give short chains

UHMWPE (ultra high molecular weight) polyethylene used in the bases of skis has very long chains.

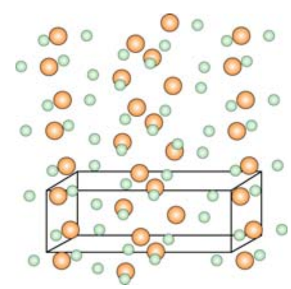


Polyethylene can also form a crystalline structure.

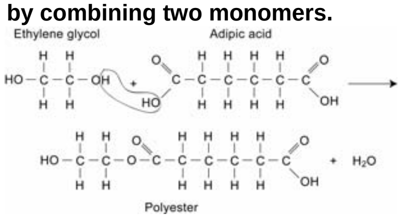
High-density polyethylene (linear chains) has a high-level of crystallinity. This makes it very strong.

It is replacing Kevlar® in many applications (including bullet-proof vests).

In this structure, there are two mers units per unit cell.



In condensation polymerization, a polymer forms by combining two monomers.



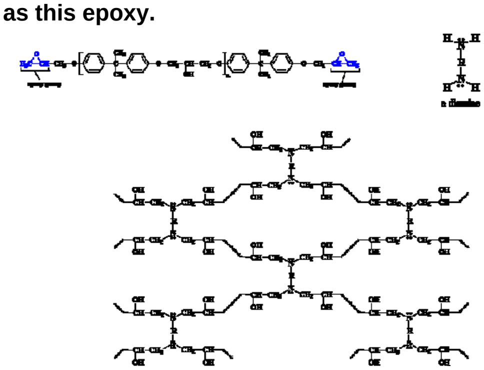
Condensation polymerization is the formation of polymers by chemical reactions that normally involve more than one monomer species.

There is usually a small molecular weight by-product such as water.

No reactant species has the chemical formula of the mer repeat unit.

W.D. Callister, Materials Science and Engineering An Introduction, 5/e, (John Wiley and Sons, New York, 2000).

Condensation polymerization is used for crosslinked and networked polymers such as this epoxy.



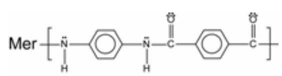
Kevlar® is a polymer with strong interchain bonding.

Fibers of KEVLAR® consist of long molecular chains produced from poly (paraphenylene terephthalamide).

The chains are highly oriented with strong interchain bonding which results in a unique combination of properties.

A single Kevlar® polymer chain could have anywhere from five to a million segments bonded together.

Each monomer contains 14 carbon atoms, 2 nitrogen atoms, 2 oxygen atoms and 10 hydrogen atoms.



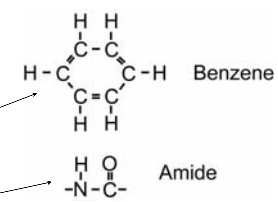
http://www.dupont.com/kevlar/whatiskevlar.html
http://www.lbl.gov/MicroWorlds/Kevlar/

The presence of aromatic amides makes polymers strong.

One of the characteristics that is related to strength in polymers is the presence of aromatic amides.

Aromatic refers to carbon atoms attached in a ring, as shown to the right.

Amides are a group of carbon, nitrogen, oxygen and hydrogen atoms arranged as shown to the right.



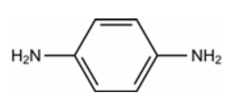
When both of these components are put together you get → KEVLAR®.

Kevlar® is made through a condensation reaction

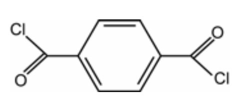
Kevlar® is made from the monomers 1,4-phenylenediamine (also known as *p*-phenylenediamine) and terephthaloyl chloride. They react through condensation polymerization.

After the polymerization, mechanical drawing, called spinning, causes the polymer chains to orient in the direction of the fiber.

Kevlar® has a high price, in part, due to the difficulties arising from the use of concentrated sulfuric acid in its manufacture. These harsh conditions are needed to keep the highly insoluble polymer in solution during synthesis and spinning.



1,4-Phenylenediamine

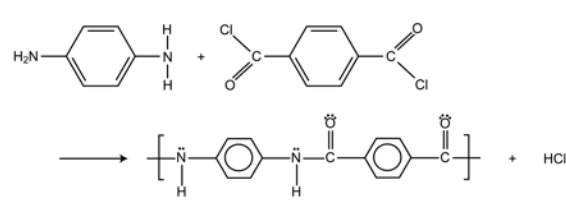


Terephthaloyl chloride

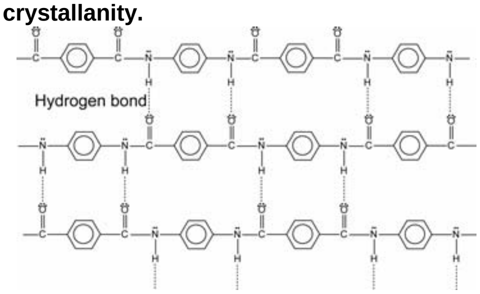
http://www.answers.com/topic/Kevlar

The condensation reaction of Kevlar® gives off HCl.

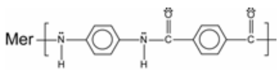
The preparation of Kevlar® involves the condensation polymerization of the two precursors, with HCl as the by-product. As mentioned earlier, the synthesis is done in a solution of concentrated sulfuric acid.



Kevlar®'s structure leads to very high crystallanity.



In Kevlar®, the rings of adjacent chains stack on top of each other very easily, which results in a polymer of very high crystallinity and strength.

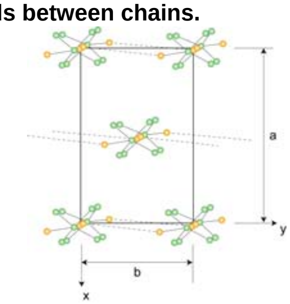


Kevlar® forms a crystal structure with strong hydrogen bonds between chains.

In this figure, the z axis is coming out of the paper.

The dashed lines along the y axis represent strong hydrogen bonds that are connecting the individual chains.

There exist only weak van der Waals forces along the x axis.



Lattice Parameters:

a = 7.80 Å, b = 5.19 Å, c = 12.9 Å, and γ = 90°

In summary, a polymer can form crystalline regions that affect the mechanical properties. Polymers can form by addition or condensation reactions.

Polymers can be amorphous, crystalline, or semi-crystalline

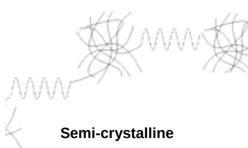
Crystal regions strengthen a polymer.

Crystal regions are formed through packing when chains folded back over each other

Polymers such as polyethylene can be formed by addition polymerization where monomers add by breaking double carbon bonds.

Polymers such as epoxies and Kevlar form from condensation reactions where two monomers chemically combine, giving off a by product such as water.

Amorphous



Semi-crystalline