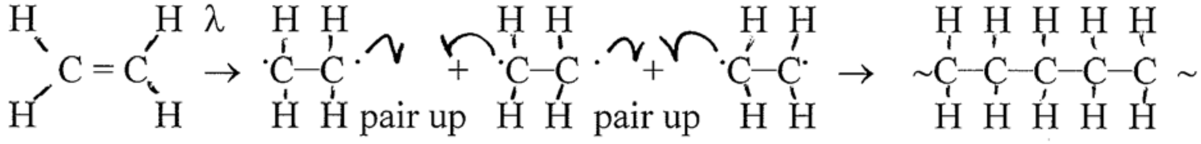
3.10 POLYMERIZATION

Polymerization is the formation of extremely long molecules from small molecules called **monomers**. The plastics and rubber are examples of the most common polymers which are commonly used in both everyday life and in medical applications. The exact properties of polymers depends on a variety of chemical details and this unit will give you a brief introduction into some of the common polymers and how their properties depend on their specific chemical details.

Polymers can be formed by a variety of reaction pathways. In this unit we will look at those formed by the process of free radical polymerization. Suppose we have a container full of ethene (ethylene) monomers and we unpair the pi electrons by a suitable method, either by appropriate radiation, or a **free radical initiator** such as a peroxide molecule (the most common way of producing them industrially).

By one means or another, we produce free radical ethylene molecules which can pair up with each other to form a long chain:



Our example just shows one molecule of monomer as a reactant, although in fact there are large numbers of them that will react with each other to form the polymer:

The one sided arrows indicate that one electron goes to each C atom. This is in contrast to the previous reaction pathways where both electrons went to the same atom and we showed a double sided arrow. The ~ indicates that the chain can extend for many thousands (or even millions) of C atoms.

What sort of functional group have we produced in the product? It's an alkane. However, it is named on the basis of the fact that it is formed from polymerization of ethylene: polyethylene.

We can diagrammatically represent this polymerization reaction with a monomer, A, being polymerized into a long chain of A:

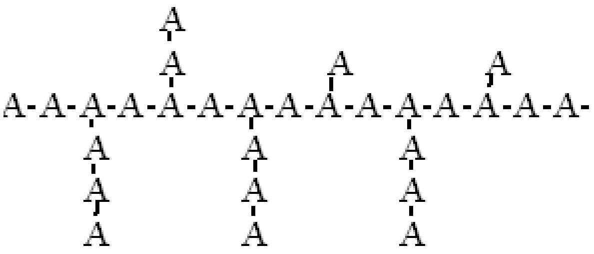
Many A monomers ——>   ~A-A-A-A-A-A-A~

Polyethylene

The long chains of A can line up to each other somewhat like adjacent strands of spaghetti in a very fairly compact mass and be extruded in thin sheets to make plastic. This form of polyethylene is called **high density polyethylene**, abbreviated **HDPE** and is labeled on the plastic recycling system as #2.

It is used for laundry detergent jugs, plastic milk bottles, fuel tanks, Tupperware and wood plastic composites which are resistant to rot.

Branches in this long polyethylene chain can be introduced so the chains look more like:

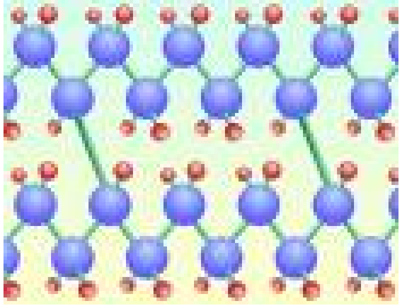


In this case the chains of somewhat branched polyethylene cannot snuggle as closely together and we have **low density polyethylene**, abbreviated **LDPE,** # 4 on the plastics recycling numbering system.

The attractions between the strands are not as strong since the chains are held somewhat apart by the branches, but the plastic is less opaque than HDPE. It is used in polyethylene bags, 6-pack plastic rings, and the inside coating of soda cans where it protects the aluminum can from corrosion by the acid of the soda.

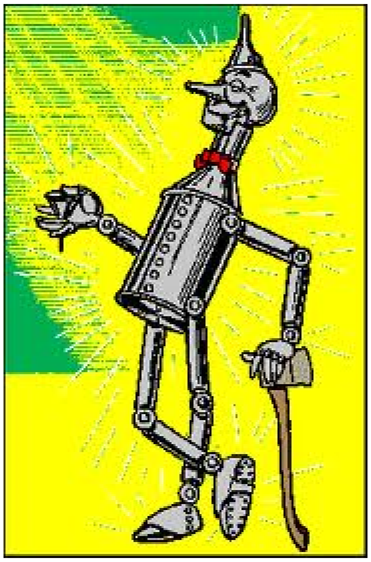
A third form of polyethylene has **extensive cross-linking** between the long chains of polyethylene and is called **PEX (polyethylene crosslinked)**

Schematically it looks like

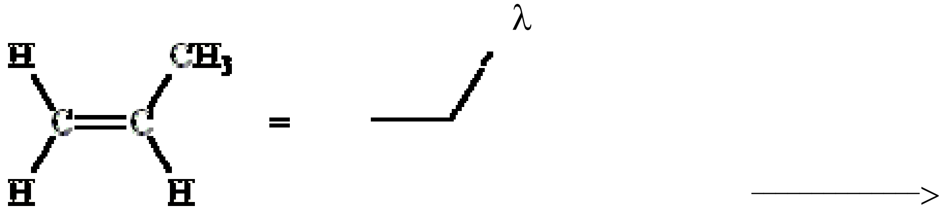


PEX is much stronger than HDPE or LDPE due to the cross-links and PEX is seeing increased use in water pipe systems. It is very strong (due to the cross-linking) but still has enough flexibility to expand if the water freezes inside it, so that PEX does not typically crack if the PEX pipes are frozen during cold weather. This is a distinct advantage over steel, copper, and PVC pipes which often crack if water freezes inside them.

In medical applications PEX is being used as a low-friction liner between the acetabulum and femoral head in total hip replacements. The PEX provides a very durable, low friction surface between the metal head (typically made of titanium or high grade stainless steel) and the acetabulum.(Can’t just squirt some oil in like the Tin Woodman!)

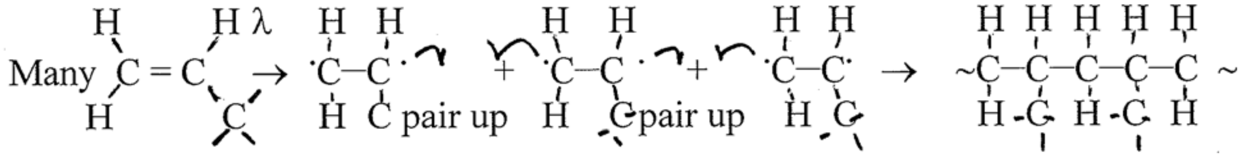


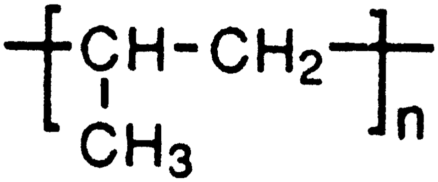
Polypropylene



Propene

Propylene(common name)



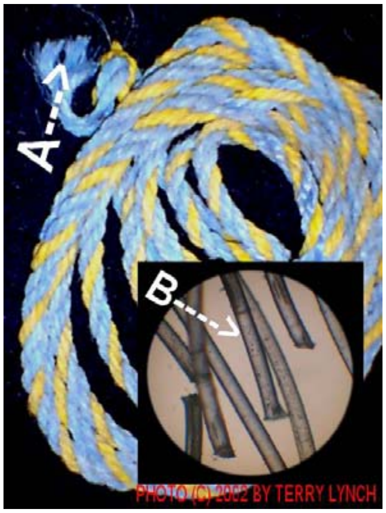


$$-\!\!\left[\mathrm{CH(CH_3)-CH_2}\right]_n\!\!-$$

=

Polypropylene

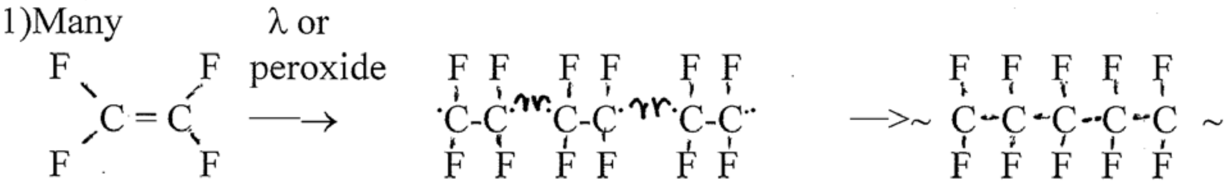
Polypropylene is commonly used to make plastic rope This rope is commonly used in marine applications because it floats. (Can you suggest why?). It is also used for medical instruments that will be autoclaved at temperatures at 120°C. It is also seeing increased used in plastic containers such as yogurt containers. Polypropylene can withstand this temperature where polyethylene cannot. It is also used for making medical suture thread, although nylon is more common.



It does have the recycle designated number of 5, although polypropylene is not currently recycled very much.

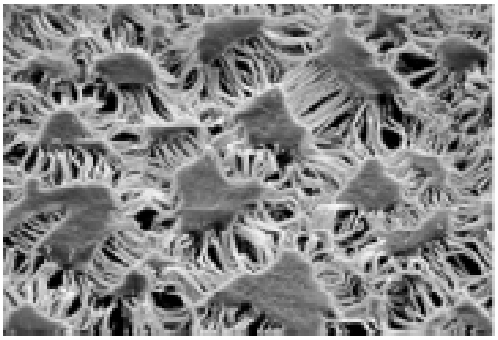
Thought question: What effect will adding a small amount of 1- propene to a polymerization mixture of ethene have? What sort of polyethylene will result?

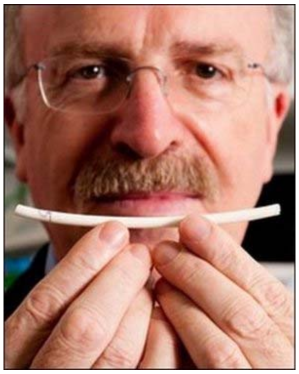
Teflon



1,1,2,2-tetrafluorethene polytetrafluoroethylene (PTFE orTeflon)

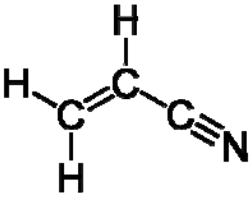
Besides use in coating non-stick cookware, PTFE membrane is the basis for Gore-tex outdoor clothing. The Gore-tex is woven in a microscopic level fabric that allows water vapor molecule to pass out, but is too small to allow water droplets to pass in, thus providing a raincoat that breathes.



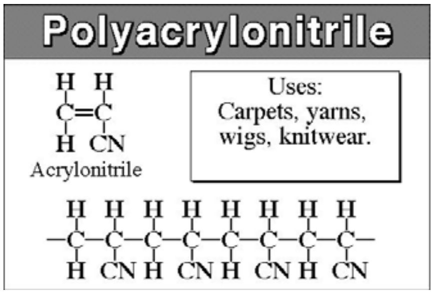


Gore-tex is also used in a variety of medical applications such as replacing portions of blood vessels that are damaged or clogged with atherosclerotic plaque with a piece of Gore-tex tube called a graft. (Normally surgeons prefer to take a piece of similar sized vein from the same patient but this is not always possible if the replacement is on a very large blood vessel such as the aorta or if multiple repairs are needed.)

Polyacrylonitrile



—>



Polyacrylonitrile

Acrylonitrile

Uses:
Carpets, yarns,
wigs, knitwear.

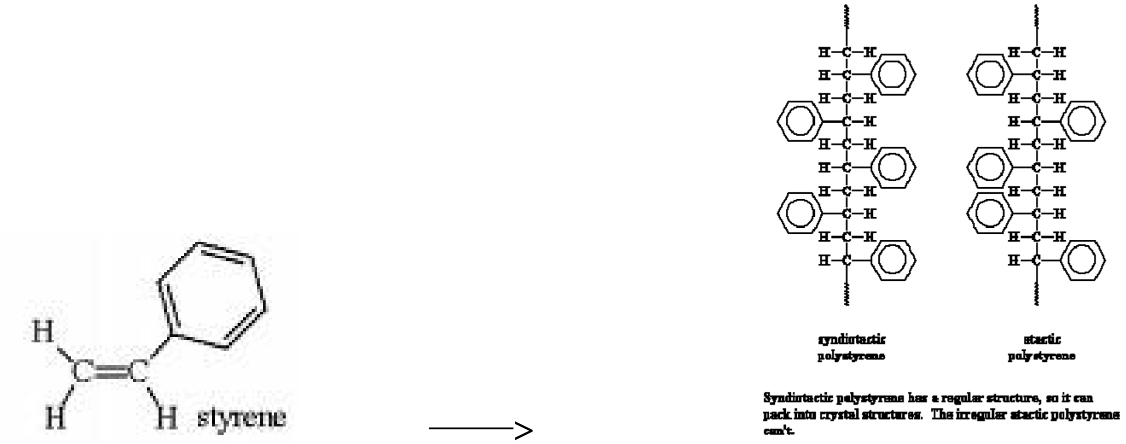
acrylonitrile

polyacrylonitrile (PAN)

(Orlon)

Polyacrylonitrile is being used to make rubber gloves that substitute for latex gloves.

Polystyrene



syndiotactic polystyrene

atactic polystyrene

Syndiotactic polystyrene has a regular structure, so it can pack into crystal structures. The irregular atactic polystyrene can't.

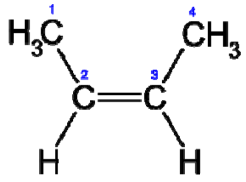
Free radical initiator

polystyrene

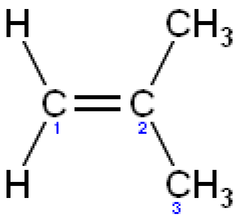
If air or other gases are blown into the polymer when it is synthesized we end up with **Styrofoam,** a very common insulating material used in packaging and in coffee cups, to name just a few uses.

Draw the structure of the polymerization product when the monomers shown below are polymerized:

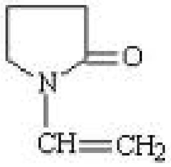
Many:



——————>



——————>



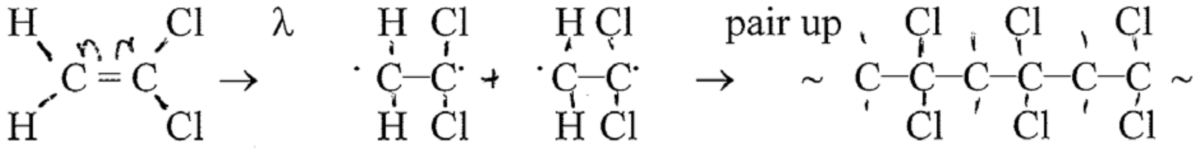
λ

———>

The common name of the last monomer above is vinyl pyrrolidone. The polyvinylpyrrolidone (PVP) polymer has many uses. Medical uses include combination with iodine to make Betadine, which releases iodine slowly into wounds and kills bacteria. It is also mixed with other polymers to make copolymers.

Polyvinylidene chloride (Saran)

Many

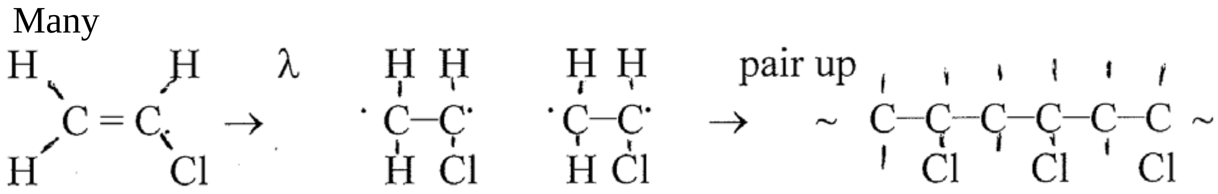


Vinylidene chloride
(1,1 dichloroethene)

polyvinylidene chloride
marketed as SaranR

Sheets of polyvinylidene(Saran) are marketed for wrapping food and keeping it fresh. The Saran polymer is impermeable to oxygen in the air and hence limits oxygen from getting into the food reducing the rate at which it gets stale; also volatile aroma molecules typically don’t get out of the wrapped food and this helps keep it tasting fresh. On the downside, **chlorinated polymer molecules break down only very slowly** and hence make a significant contribution to the buildup of non-biodegradable trash.

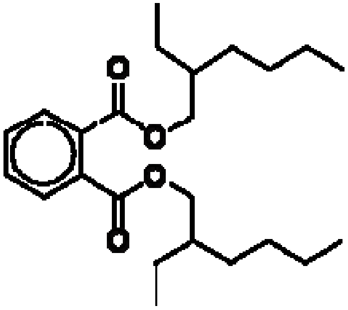
Polyvinylchloride (PVC)



vinyl chloride polyvinylchloride(PVC)

Plasticizers

Pure polyvinyl chloride (and some other plastics) can be quite brittle and non-flexible. In order to make it more flexible, small **plasticizer** molecules are added which slip in between long strands of polymer, lubricating them and making the whole mass more flexible. The most common plasticizer for PVC has been the molecule di (2-ethyl hexyl) phthalate, affectionately abbreviated DEHP.



DEHP

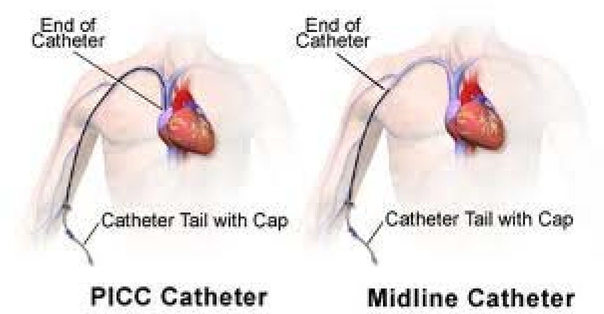
Identify the functional groups found in DEHP. Can you identify the ethyl and hexyl goups in this structure?

DEHP makes PVC more flexible. Very small amounts added to PVC give it slight flexibility while still retaining a pretty rigid form. Addition of larger amounts increases flexibility still further. Concern has been raised by a variety of consumer advocate groups that very small amounts of the DEHP plasticizer may act as an **endocrine disruptor** and may alter biological hormone levels. This is of particular concern for pregnant women.

Concerns have also been raised about the plastics used for food containers especially during heating in microwave ovens. Heating food with plastic containers containing plasticizers can increase the amount of plasticizers that leach out into the food. The amount is fairly small and plastic manufacturers generally claim it is too small to be of concern. Some consumer advocates argue that even though the amounts are small some of these plasticizers can act as carcinogens or endocrine disruptors which can act as hormones and change biological activities in potentially very disruptive ways. There is particular concern about the effect of these chemicals on the fetus.

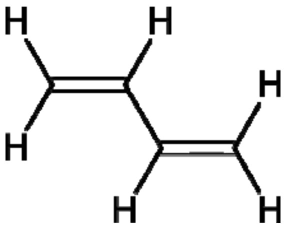
The addition of large amounts of DEHP produce a very flexible plastic which is used in a large variety of plastic applications including medical equipment such as catheters and IV bags.

Very small amounts of DEHP can dissolve into the contents of the catheter, IV bags and other medical devices and be transported directly into the bloodstream. Even though the amounts are very small, it is directly entering the bloodstream! This possibility has led to a lot of controversy and the reformulation of many medical plastic items to remove DEHP. Polyethylene, and polyurethane have been substituted as well as the use of plasticizers other than DEHP.



[Smell of plasticizer in new cars]

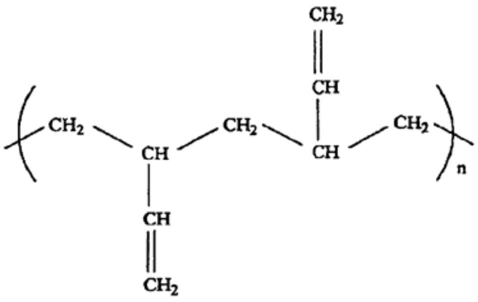
Polybutadiene(skip)



1.3 butadiene

Note that 1.3 butadiene has two double bonds rather than just one. This creates more options during the polymerization process.

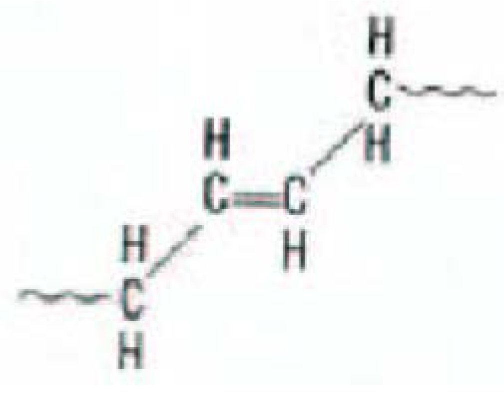
When the first double bond becomes a free radical, the free radical on the # 1 C atom can pair with another free radical on a butadiene. This leaves an unpaired electron on C # 2 which can react with another butadiene as shown below:



butadiene This type of reaction is called a 1,2 addition because the first and second C's on the molecule are the ones which react. It leaves a second double on the other end of the molecule which can react.

Actually this type of reaction only occurs about 20% of the time

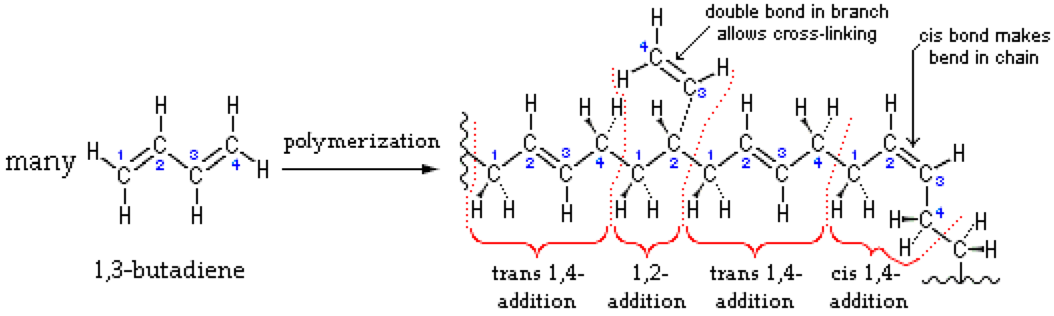
The reaction which occurs about 80% of the time (and one you would not have predicted) is shown below:



Polybutadiene

The second double bond unpairs its electrons and pairs up the unpaired electron on # 3 with the unpaired electron on C # 2. The unpaired electron on C # 4 can then react with an unpaired electron on another butadiene molecule to form a long polymer chain with C=C. Since an unpaired electron on C#1 reacts with an unpaired electron on C #4, it is referred to as a 1,4 addition polymerization.

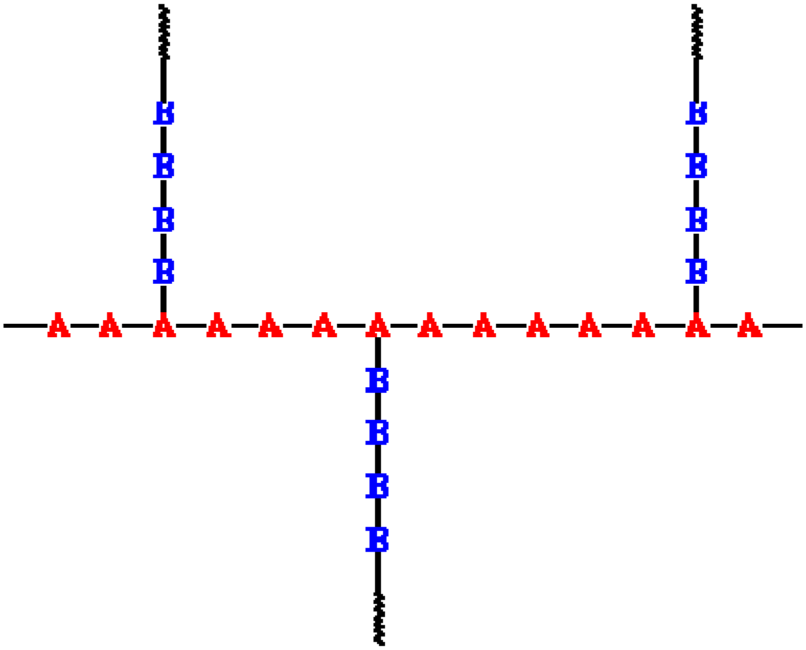
Under most common conditions a polymer is produced that is a mixture of both of the above reactions.



Notice that the presence of a double bond in the resulting polymer provides the opportunity for a polymer with either cis double bonds or trans double bonds (or a mixture. The initial work on this polymerization occurred in the 1930’s when chemists were searching for a substitute for natural rubber. Initial experiments produced random cis and trans isomers, producing polymers which were not very useful. Further research produced specialized catalysts which result in either pure (or nearly pure) cis isomers or trans isomers. The resulting pure cis isomeric polymer is very elastic, but too soft to be useful as a replacement for tires.

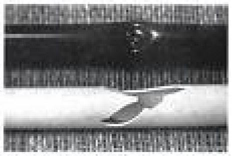
Copolymers

Chemists ended up making polybutadiene and then carrying out a polymerization of styrene mixed with the polybutadiene. In addition to reacting with other styrene molecules, styrene free radicals could react with the remaining double bonds of the polybutadiene, crosslinking the polybutadiene chains producing an SBS **copolymer**. This cross linking reduces the flexibility of the polybutadiene chains and makes the rubber harder and stronger, producing a rubber that can be used to make tires. The general name for this process is **graft copolymer.** It is called a copolymer to indicate that we are mixing two (or more) types of polymer, and graft indicates that we are grafting (or crosslinking) stretches of one polymer onto another type of polymer.

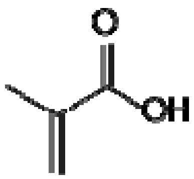


graft copolymer

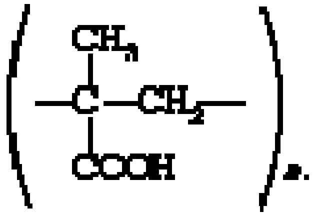
Acrylonitrile is combined with polybutadiene and styrene to make acrylonitrile/butadiene/styrene (ABS) copolymer that consists of long chains of polybutadiene crosslinked with chains of styrene and acrylonitrile. The ABS plastic is commonly used in plastic piping (black ABS piping) as well as protective head gear, toys, autobody parts. Finely ground (~ 1 mcm diameter) colored ABS granules are used in some bright colors used in tattoos.

Polymethacrylate

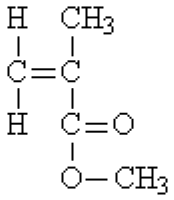


Many ——>

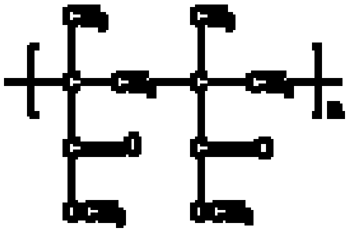


Methacrylic acid polymethacrylate

Polymethylmethacrylate



Many ————>

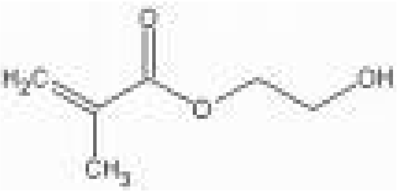


Methyl methacrylate Polymethylmethacrylate(PMMA)

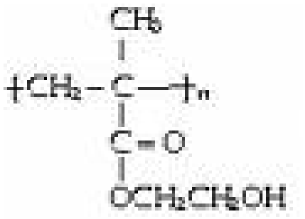
The polymer PMMA has a huge variety of uses in both medical and non-medical applications. In sheet form it is better known by the trade name products Plexiglass and Lucite. Plexiglass is used as a substitute for glass. It is half the density of glass, and it is more resistant to breakage. It is more easily scratched than glass although hard coatings can be applied to its surface. It does not absorb ultraviolet radiation, in contrast to glass, which does. It is commonly used in aquariums and auto headlights. It is also used to make acrylic paints.

Medical uses include the manufacture of **dentures** and its use as **bone cement** when putting in prosthetic implants (i.e. hip replacements). PMMA was used in some of the earliest hard contact lenses.

One of the problems with the original hard contact lenses made of PMMA was that they had very low oxygen permeability thus depriving the cornea of essential O_2. This problem has been addressed by making a more polar polymer from 2-hydroxyethyl methacrylate (HEMA) and producing a polyHEMA. The increased content of polar OH groups increases the water content of the contact lens, making it softer (more comfortable) and more oxygen permeable as well.



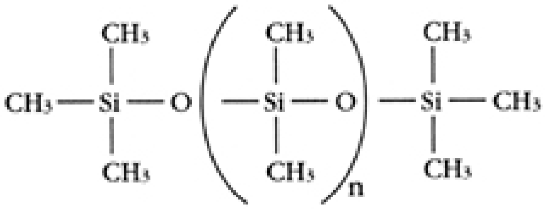
——>



2-hydroxyethyl methacrylate (HEMA) polyHEMA

Silicone polymers

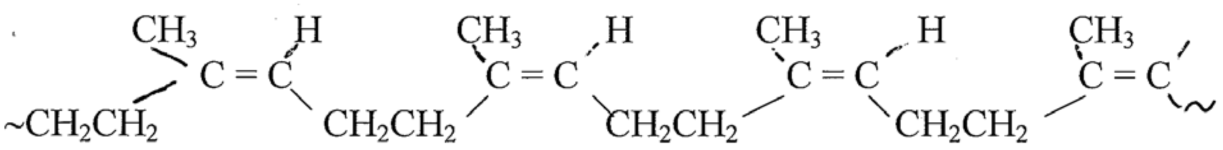
In 1999 silicone contact lenses, which are extremely oxygen permeable, were introduced.



$$CH_3-Si(CH_3)_2-O\left(-Si(CH_3)_2-O\right)_n-Si(CH_3)_2-CH_3$$

Natural polymers:

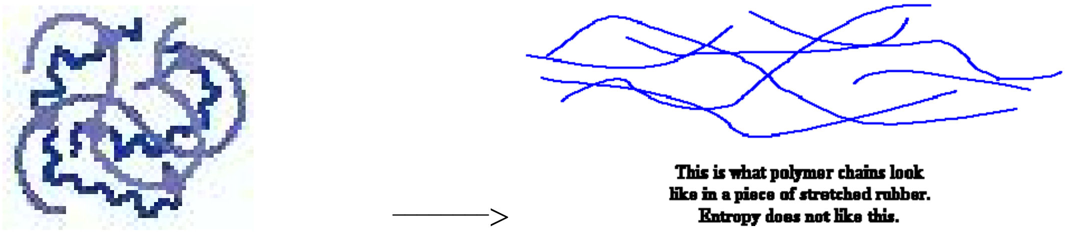
1)Latex Rubber comes from the sap of the tree, Hevea brasiliensis. It is a polymer containing cis geometric bonds



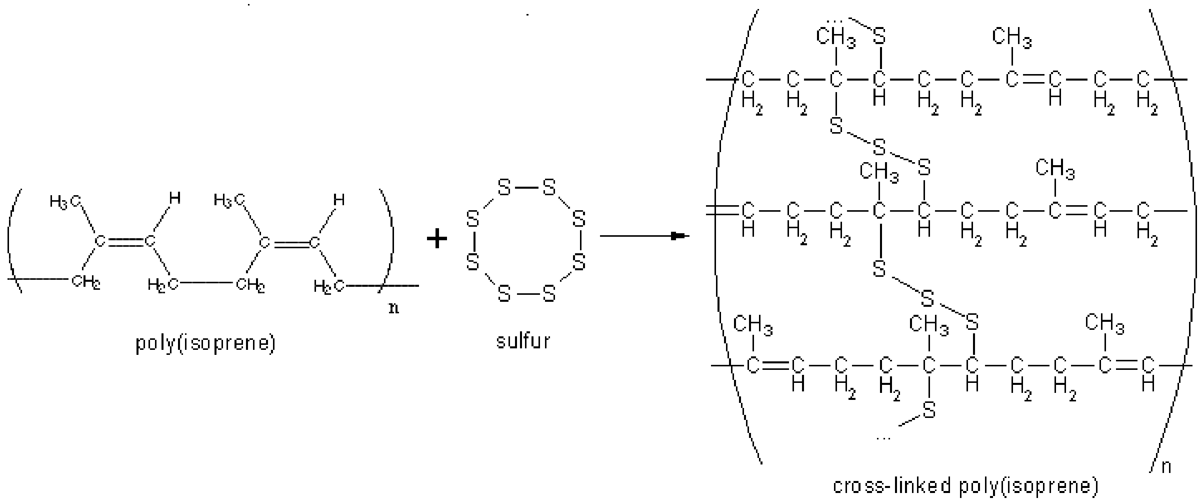
cis geometric isomer (latex rubber)

In the cis isomer the long polymer chain comes in and goes out on the same side of the C-C double bond.

The long chains of rubber are partially coiled up with occasional cross-links. As one puts tension on the rubber, it takes the slack out of the partially coiled polymer chains until they are nearly rigid. If there are very few cross-links, further tension will cause the long chains to slide past each other, similar to what happens with silly putty. Adding increasing cross-linking will limit or entirely stop this sliding of polymers past each other. When the tension is released, the extended chains will tend to reform their coiled forms, giving the rubber its characteristic and valued property of elasticity. (Further elongation after the slack is taken out of the chains will cause rupture and tearing of the material.)

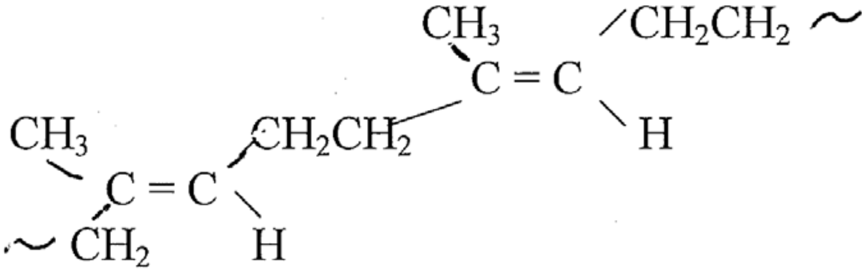


Cross-linking is done in a process called **vulcanization**, which adds disulfide and trisulfide bonds across various chains and reduces the amount of slippage that can occur between polymer chains. In effect, vulcanization turns all the polymers into one huge molecule.



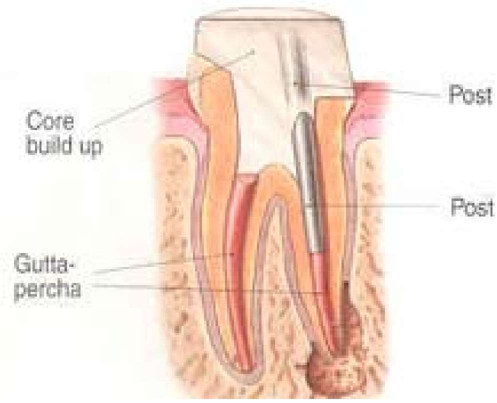
(corrected structure)

2)Gutta percha is a geometric isomer of latex with trans bonds



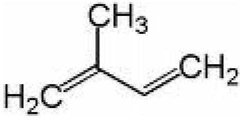
trans geometric isomer (gutta percha)

In gutta percha, the long chain comes in and goes out on opposite sides of the C=C double bond, hence making a trans geometric isomer. It is a polymer that is similar, but less elastic, than latex rubber. In the gutta percha tree one gets all-trans isomer, producing a hard material with less elasticity; it is used in golf balls and in root canal fillings.



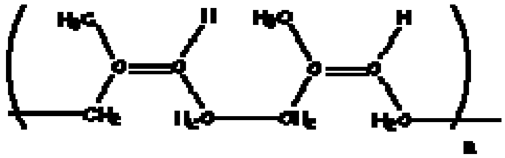
In the rubber tree, pure cis isomers produce elastic rubber   When Japan invaded Indonesia in World War II, it took over the major supplier of natural latex rubber. Organic chemists were asked to make synthetic rubber from petroleum in a factory. Their first efforts produced a polymer with random mixture of cis and trans isomers which did not have the desired elastic properties. Organic chemists eventually came up with a reasonable substitute.

Synthetic latex rubber is now made by the polymerization of **isoprene** (2-methyl-1,3-butadiene) from petroleum.



———>

Isoprene (2-methyl-1,3-butadiene)



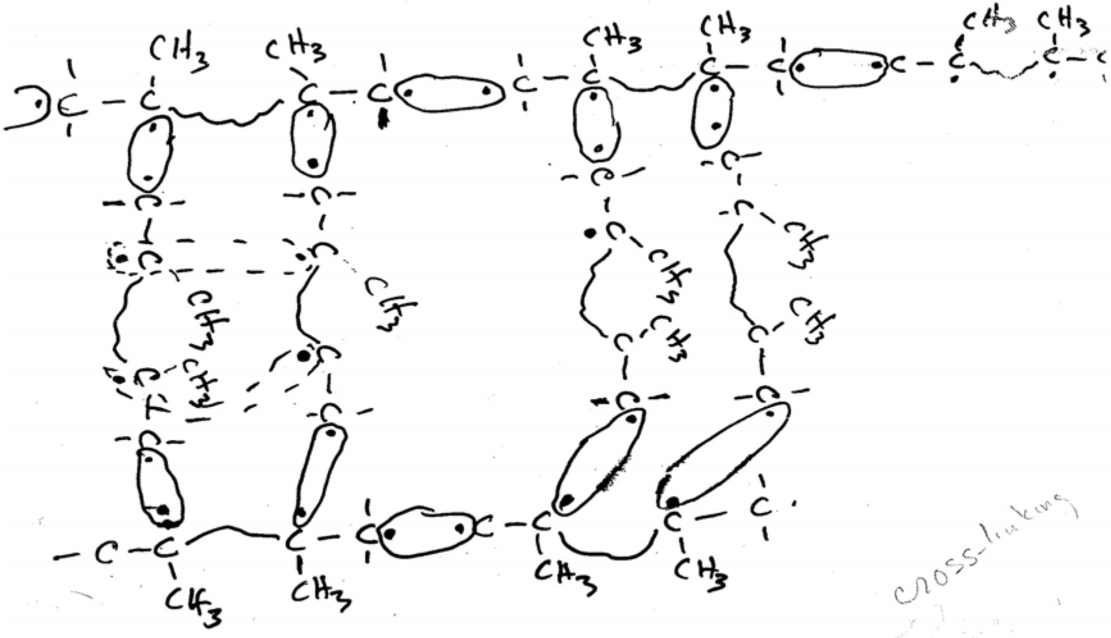
Latex is commonly used in latex gloves that are commonly used by medical and dental personnel. It is also used for the dental dams that dentists used to isolate a tooth from the rest of the mouth during their work..

Increasing publicity about allergic reactions to latex is resulting in increasing use of gloves made from **acrylonitrile** or other chemicals. (Although there are problems reported with nitrile gloves also!) Low grade rash is most common type of allergic reaction, but some individuals may actually go into anaphylactic shock. The more severe reactions are thought to be due to some residual proteins in the latex rubber.

A latex gum called **chicle** from a different tree was the original latex gum used for making chewing gum, but other natural gums and polymers from petroleum sources are cheaper and have replaced chicle in virtually all chewing gum.

Dental sealants and filling materials

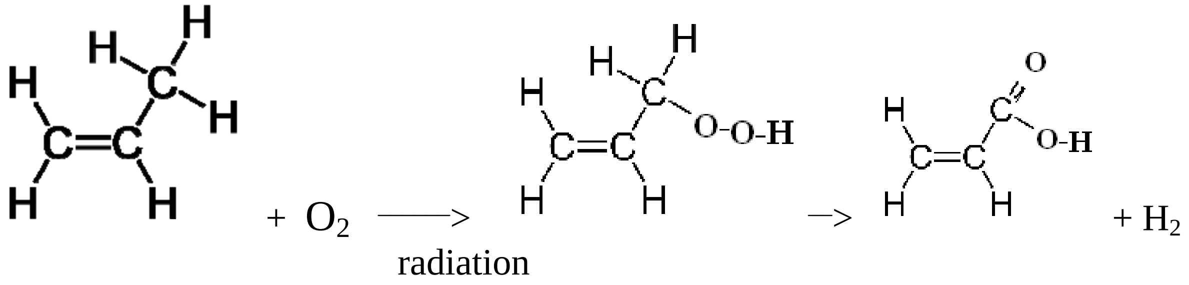
Dental sealants and some filling materials are made from a molecule that is abbreviated **bis-GMA.** Notice that this molecule has 2 double bonds rather than just one as was the case in the previous molecules. Thus when light is shown on the molecule, both double bonds can form free radicals and react as shown:

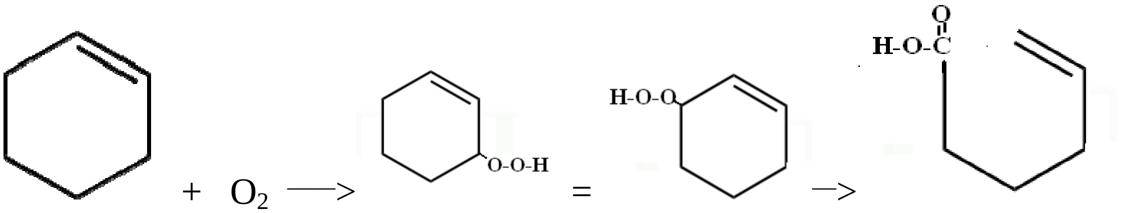


This **crosslinking** allows the formation of a 3 dimensional crosslinked polymeric material rather than a string. Like the situation with PEX (cross-linked polyethylene) and vulcanized rubber, cross-linking increases the hardness of the plastic at the expense of flexibility. This hardness and inflexibility are very desirable in dental sealants and dental filling materials. One can of course vary the flexibility of various plastic polymeric materials by varying the amount of cross-linking to meet particular needs.

3.11 OXIDATION

One last example of reactions of alkenes is oxidation, the addition of oxygen atoms to an alkene molecule. The exact nature of the oxidation products depends on what form of oxidizing agent is used. We will look at just one example, namely the oxidation of alkene molecules with molecular oxygen, O_2. Alkenes react with 0_2 to produce hydroperoxides which themselves are not very stable and can decompose to form two aldehyde or carboxylic acid functional groups. Oxidation of alkenes is speeded up by exposure to radiation which can produce free radicals and the addition of the O_2 molecule actually most commonly occurs at a C adjacent to the double bond (called an allylic C atom) as shown below.





C atoms in between two C=C are even more susceptible to oxidation by O_2.

a)