Free Radical Reactions
3 - Applications of Free Radical Reactions

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Applications of Radical Reactions

Free radical reactions are hard to control hence they have few practical applications – synthetically. This does not mean these reactions don't occur by themselves – where there is enough energy and a bond weak enough to break – these reactions will happen.

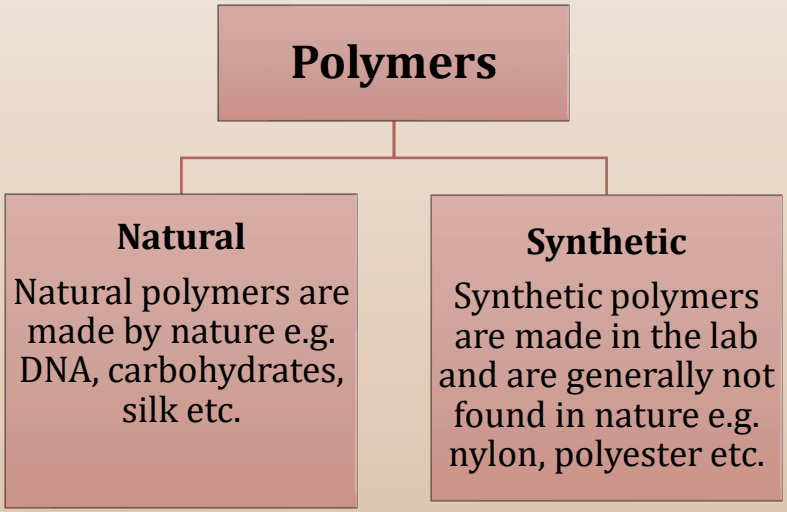
The three reactions that I will cover here are:

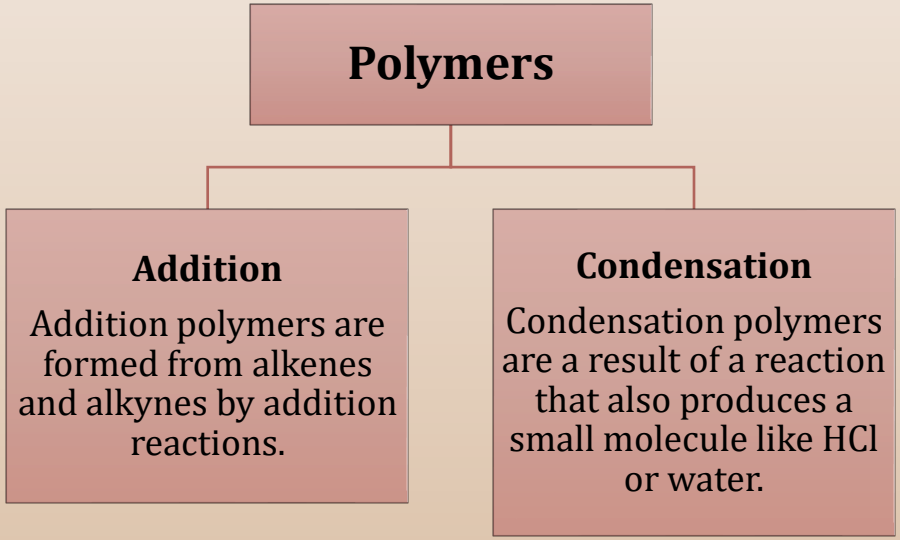
- Polymer synthesis (addition polymers)
- Ozone layer chemistry
- Lipid oxidation

Polymers

Polymers are long chains of small molecules (monomers) joined together in a specific pattern.

- They can be classified in two different ways as shown below.

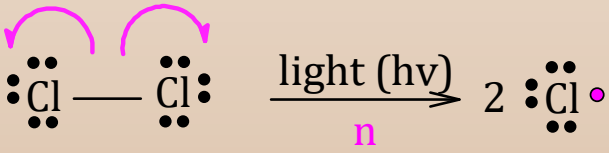


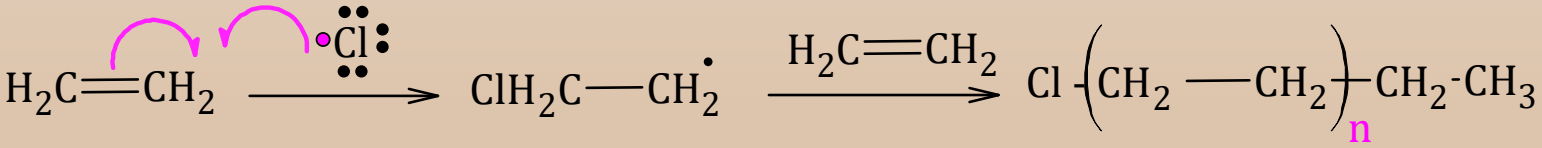


Addition Polymers

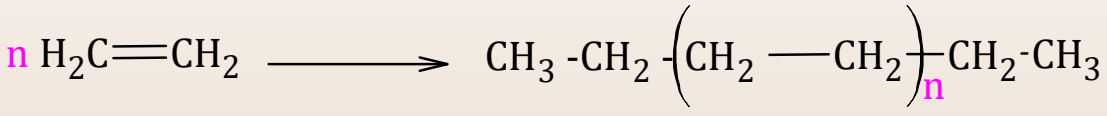
Addition polymers are usually formed in alkenes and alkynes since they have unsaturated bonds.

- Reaction is carried out by free radical because long chains are to be synthesized hence not much control is necessary.
- Once the correct molecular weight is achieved a quencher is added to stop the reaction.
- The next slide shows some common synthetic addition polymers made this way.

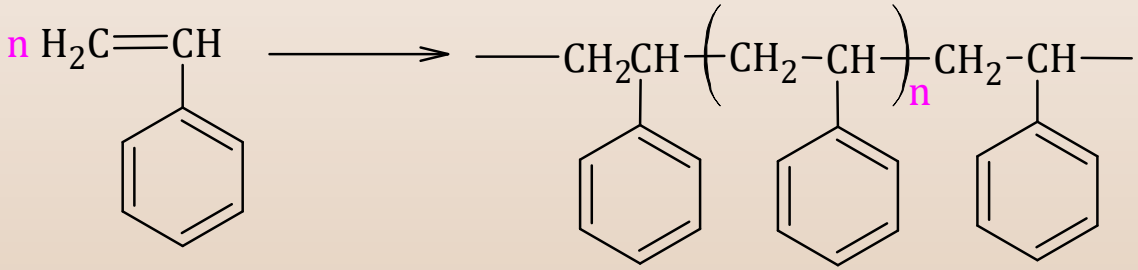




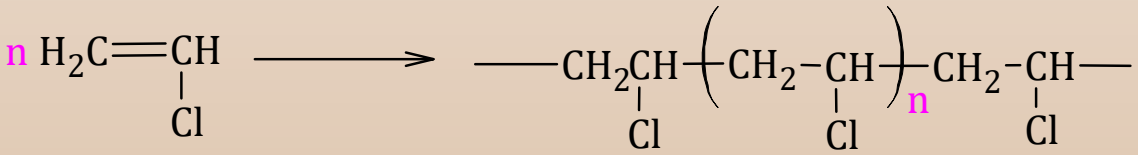
Examples of Addition Polymers



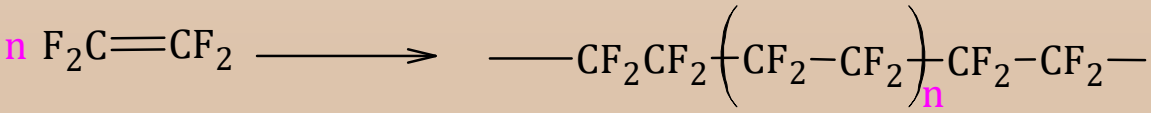
polyethene



polystyrene



polyvinylchloride



teflon

- One major problem that remains of synthetic polymers is their degradation.
- Most of these synthetic polymers don't break down easily when discarded and thus pose a pollution problem.
- Although many of them can be recycled but getting people to recycle is a challenge.
- Some companies are now investing in biodegradable polymers.

Ozone Chemistry

Ozone, O_3, exists in the stratosphere and protects the earth from the harmful UV radiation. It undergoes an equilibrium reaction between O_3 and O_2 using the energy from UV radiation.

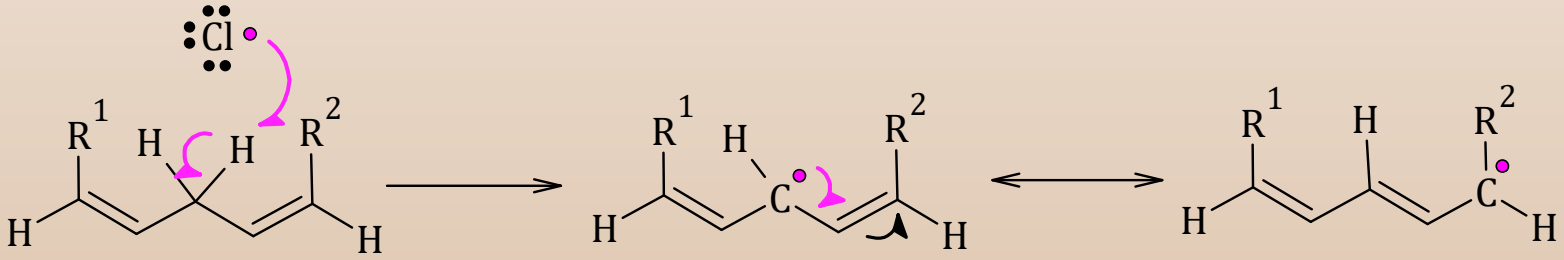
$$O_3 \rightleftharpoons O_2 + O$$

- The ozone layer started getting damaged from the use of chlorofluorocarbons (CFCs) which were used primarily as cooling agents in refrigeration and air conditioning.
- CFCs drifted up to the ozone layer and damaged the layer by behaving as catalysts to promote formation of O_2. (Think about bond energy and how easy it is to break the C-Cl bond).
- The whole chemistry of ozone layer and its depletion is based on radical chemistry and was discovered by two chemists, Sherwood Rowland and Mario Molina, who ultimately got the Nobel Prize in Chemistry.
- Now CFCs are banned in the countries who signed the treaty (Montreal Protocol), however its still prevalent in several developing nations.

Fatty Acid Oxidation

Autoxidation: This is oxidation that requires oxygen, O_2, energy and no other oxidizing agent.

- Occurs by a radical chain mechanism similar to that for allylic halogenation.
- This is common in hydrocarbon chains of polyunsaturated triglycerides because of the presence of 1,4-dienes.



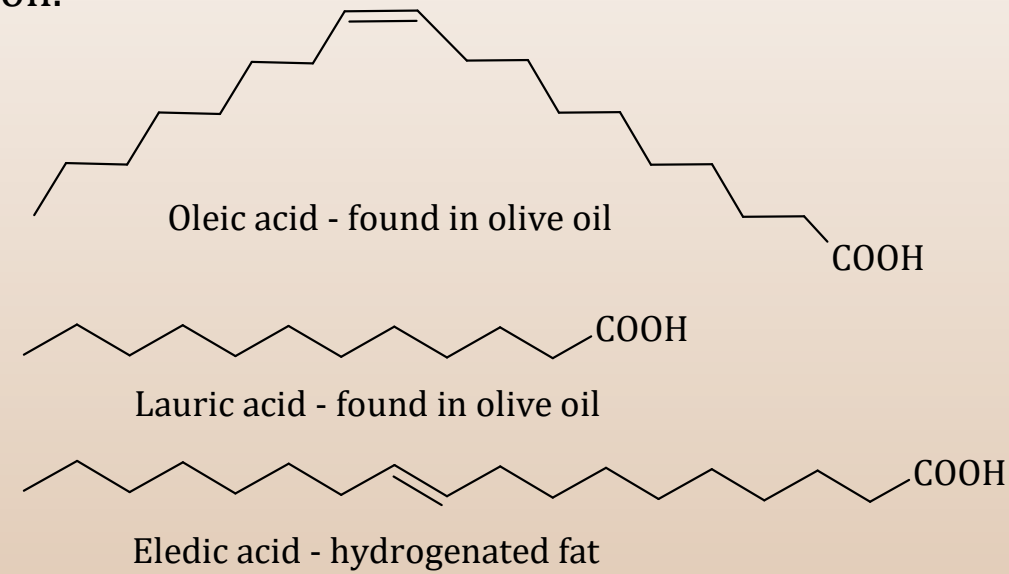
Fatty Acid Oxidation

In our bodies

- This oxidation occurs under conditions of high energy or in the presence of certain molecules that cause the formation of oxygen radicals.
- The radicals produced start reacting with alkenes (fatty acids that are found in the bilipid layer) or other bonds (DNA etc.).
- All this oxidation causes cell breakage (wrinkle formation in skins) and mutations (in DNA) in some cases.
- These oxygen radicals can be removed from our bodies by anti oxidants. Some natural anti oxidants are vitamin E and C (ascorbic acid).
- A good way to prevent radical formation in the body is to eat a wholesome balanced diet with the least amount of processed food as possible.

Hydrogenation of Fatty Acids/Lipids

Fatty acids come in various lengths of carbon chains (C-12 to C-18) and in various degrees of saturation.



- All fats are plant based except for lard.
- Almost all vegetable oils are unsaturated, except coconut oil. The unsaturated oils have lower boiling points than saturated ones (think liquid vs solid Crisco).
- Alkenes are also capable of having cis/trans isomers. Cis isomers will generally have a lower boiling point than trans because trans (just like saturated oils) will have a more dispersion forces.

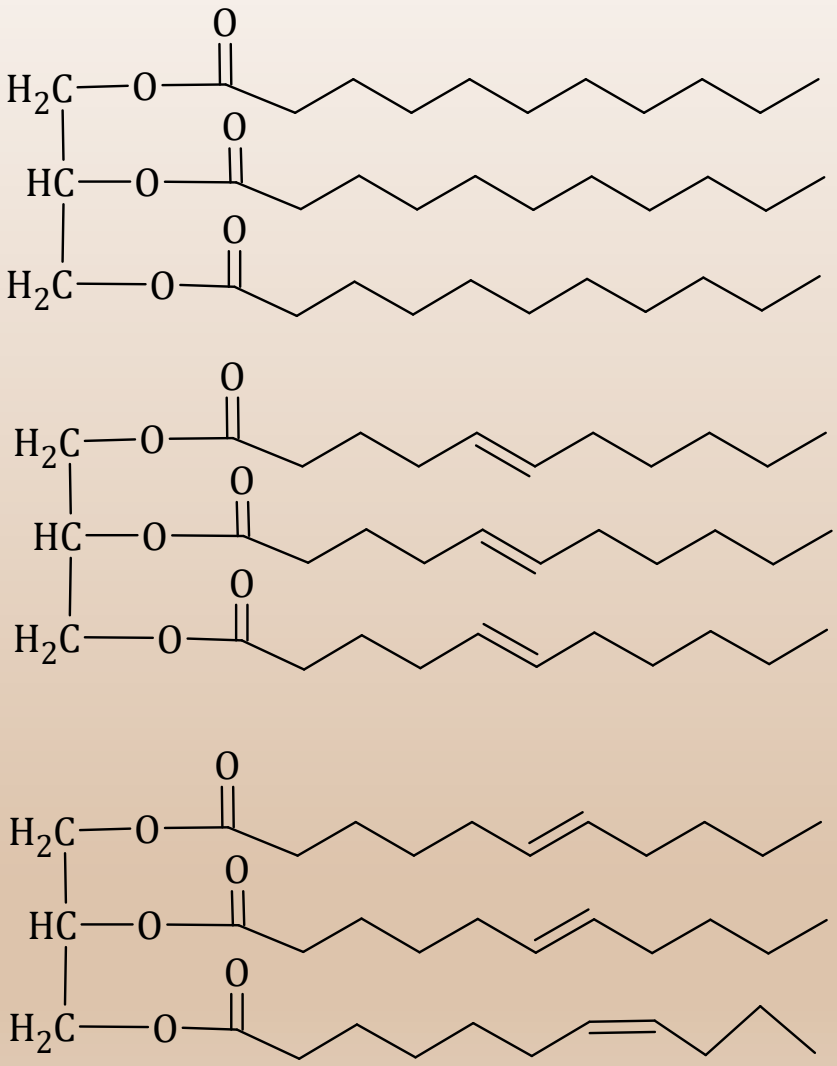
Edible Fats and Oils

Naturally occurring unsaturated fatty acids degrade faster than saturated oils because of the reactive nature of alkenes. Commercial fats are hydrogenated to improve shelf life. During the hydrogenation process some cis bonds start to isomerize into the trans.

- Trans bonds pack differently in our bodies (for the same reason they have high boiling points) and sometimes can lead to heart diseases.
- The smell of rancidity (bad smell) occurs when oils are degraded (fragmented) into smaller fatty acids which have those rancid smells (e.g. butyric acid).
- One can also observe the degradation of fats and oils during deep frying – the more one uses the oil the thicker and more rancid it gets. This all due to the oxidations with water and oxygen at higher temperature. At this point, the fats and oils should be discarded.

Fatty Acids and Triglycerides

- Fats get stored in our bodies as triglycerides and get used as the body needs them (to make membranes, or for energy etc.)
- If we eat saturated fats the triglycerides will be more compact in structure due to the 3D structure of alkane. The body does not have enzymes to process these fats and so they are stored (plaque) and other compact fats.
- Cis isomers of unsaturated fats however will not cause the triglyceride to be so compact and can be more free flowing and therefore will not get stored easily.



Lessons Learned

- Use less CFC's- protect the ozone layer and protect ourselves from UV radiation.
- Use natural polymers or biodegradable ones.
- Eat antioxidants (Vitamins E and C)
- Eat healthy and natural foods – not processed foods.
- Protect your skin from radiation (radical reactions) which causes bilipid layer damage.
- Discard oils when they smell rancid or when they start thickening (increasing in density)
- Eat unsaturated fatty acids as much as possible.
- Live a good healthy, happy life!!