Synthetic Polymers in Modern Life

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We Have Lived in a Polymer Age





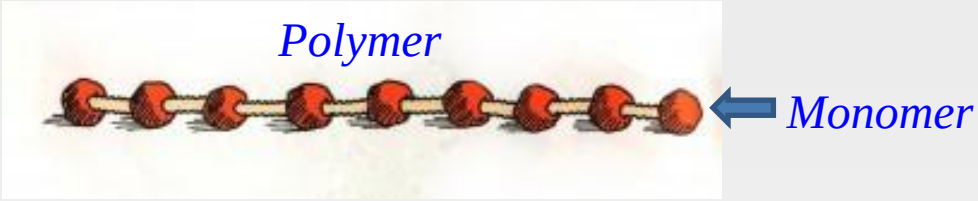







Polymers, Long, Long Chains

- Polymers are large molecules made up of long chains of atoms covalently bonded together.



- Polymer materials were here long before chemists were, and chemists are also made up of many polymers.

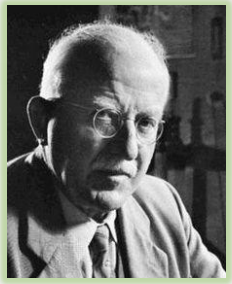
The Basics of Polymers

Natural Polymer	Synthetic Polymer
Proteins, DNA, RNA	Polystyrene, polyethylene
Polysaccharides (cellulose: plants & animals)	Poly(vinyl chloride) Polyesters, Polyurethane, ...

- Many synthetic polymers were originally created as substitutes for expensive or rare naturally occurring materials, or to improve on natural polymer.

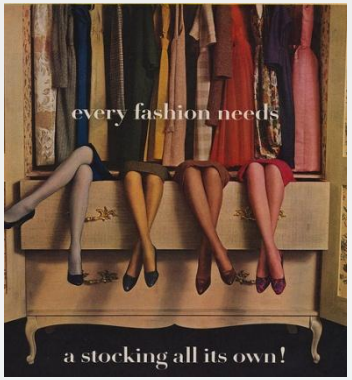
History of Polymers

- Hermann Staudinger (1920) –
  Father of Modern Polymer Chemistry:
  Polymers are long chains of short repeating molecular units linked by covalent bonds.



Staudinger received the 1953 Nobel Prize in Chemistry

- Wallace Hume Carothers (In the 1930s)
  Father of Synthetic Polymer Science:
  Carothers began synthesizing polymers using well-established reactions of organic chemistry such as esterification and amidation.



Commercialization of Selected Polymers

Polymer	Year	Company
Polystyrene	1929/1930	I. G. Farben/Dow
Nylon 66	1939	Dupont
Polyethylene (PE)	1939	ICI
Poly(dimethyl siloxane)	1943	Dow Corning
Poly(ethylene terephthalate) (PET)	1953	Dupont

Polymer – Today's Marketplace

- Over 100 billions pounds of synthetic polymers are produced annually in the United State (~300 lb for every man, woman, and child in the United Stated).
- Polymers show the greatest value increase of exports minus imports with about US$20 billion net favoring exports in the United Stated.
- The number of professional chemists directly employed with polymer as part of their interest and assignment is estimated to be ~60% of all the chemists.
- All of the industrially advanced countries of the world have major chemical producers which are involved directly/indirectly with some form of synthetic polymers.

Classification of Polymers

- Adopt the approach of using their response to thermal treatment:

Thermoplastics: Polymers which melt when heat and resolidify when cool.

Thermoset: Polymers do not melt when heat, but at sufficiently high temperatures, decompose irreversibly.

Classification of Polymers

- Base on the nature of the chemical reactions employed in the polymerization:

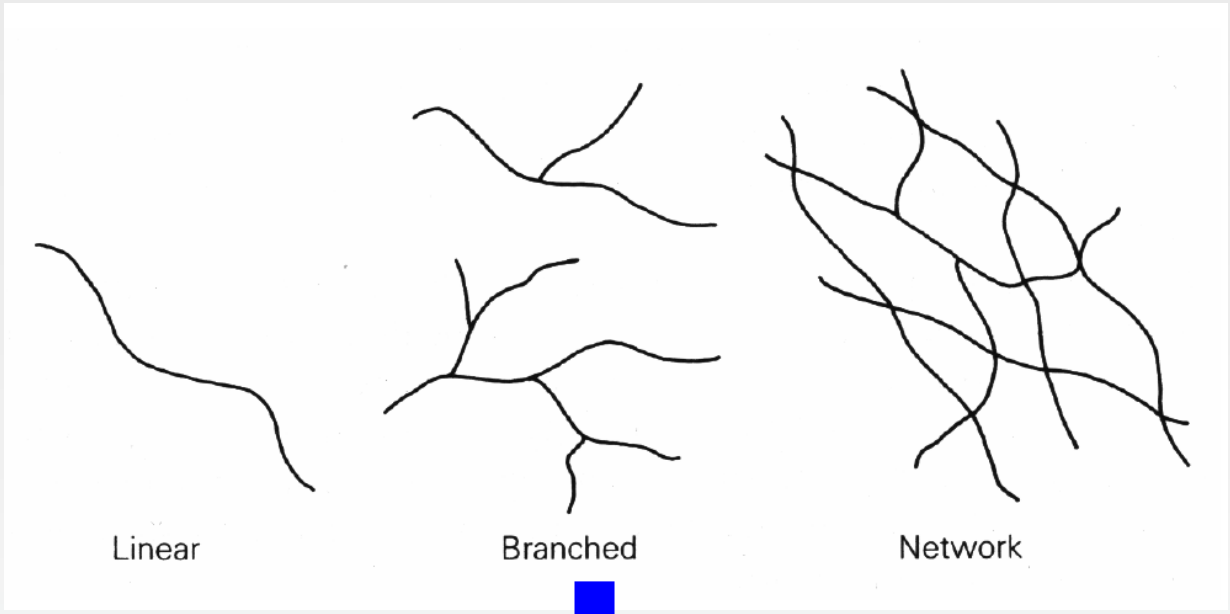
Addition Polymers: Formed by the addition reaction of an unsaturated monomer.

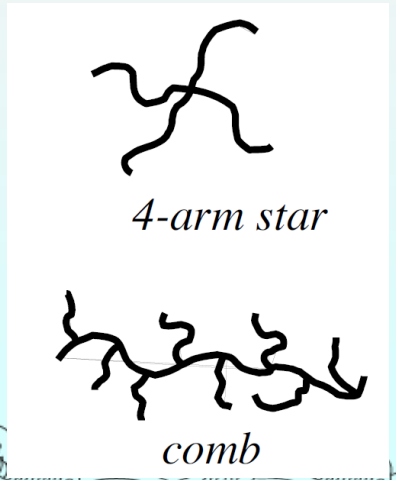
http://www.tvo.org/iqm/plastic/addition.html

Condensation Polymers: Prepared from monomers where reaction is accompanied by the lose of a small molecule.

http://www.tvo.org/iqm/plastic/polycondensation.html

Polymer Architectures





Polymer Properties

The cup is white, opaque, light, soft, and easily deform and torn, but it is an excellent heat insulator.

The CD-case is hard, brittle, glasslike transparent, but it can be scratched easily.

A plastic milk bottle is opaque or translucent; it can be deformed, but not as soft and flexible as many plastics

The properties of polymer must be a consequence of:

- the elements that makes up the materials – *Chemical Composition*
- How the elements are linked together – *Molecular Structure*

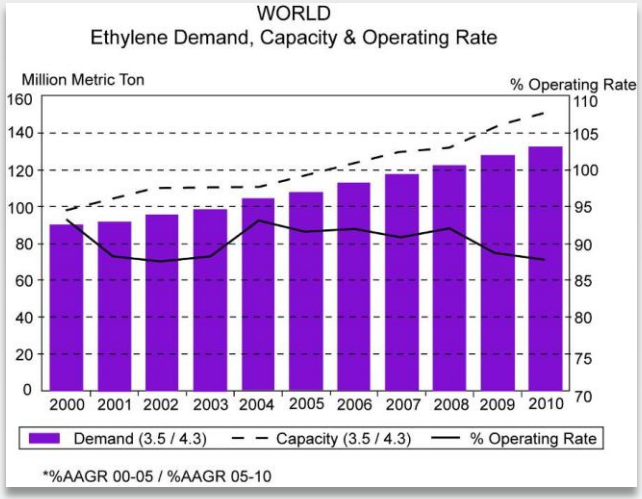
The "Big Six" Plastics

- Polyethylene (PE)
- Polypropylene (PP)
- Polystyrene (PS)
- Teflon
- Poly(ethylene terephthalate) (PET)
- Kevlar

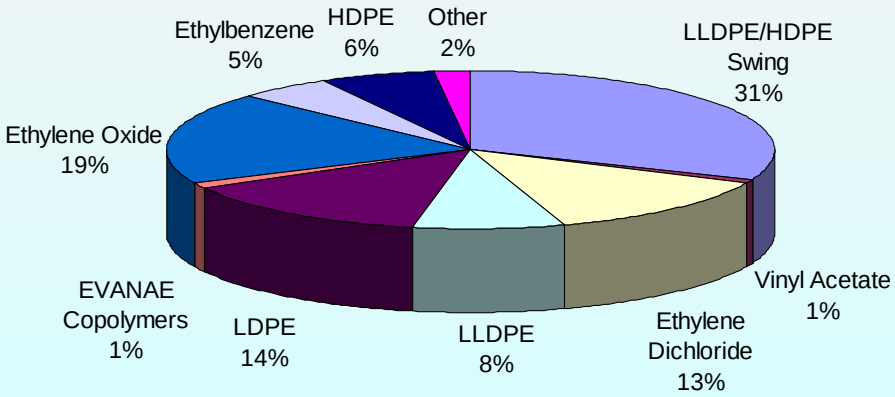
Polyethylene (Polythene), PE

Ethylene, more correctly called Ethene, $CH_2 = CH_2$

- Ethylene is a measure of a country's economic strength.



- Ethylene has rarely been a profitable commodity for the primary producers.

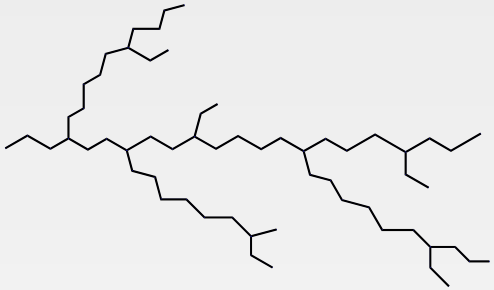


Polyethylene, PE

- PE was discovered in 1933 by Reginal Gibson and Eric Fawcett at the chemical company, ICI, at Winnington in the UK.

Low Density Polyethylene, LDPE

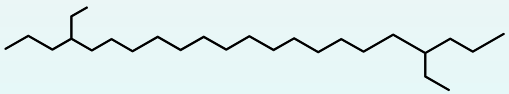
$$CH_2 = CH_2 \xrightarrow[130 - 350\ ^\circ C,\ 1200 - 3000\ atm]{O_2 \text{ or Peroxide Initiator}}$$



LDPE is stretchy, transparent, and not very strong. They are mainly as film and packing.

High Density of Polyethylene, HDPE

$$CH_2 = CH_2 \xrightarrow[\text{or Metal Oxide Catalyst}]{\text{Metal Complex (Ziegler)}}$$



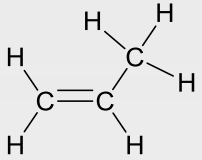
Low Pressure, 100 °C, ~1000 carbon atom

Low Pressure, 20 °C, ~50 000 carbon atom

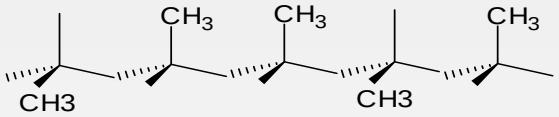
HDPE is opaque and has greater density, rigidity, strength, and a higher melting point than LDPE. They are used to make containers and pipes.

Polypropylene, PP

- Propylene is very similar to ethylene.

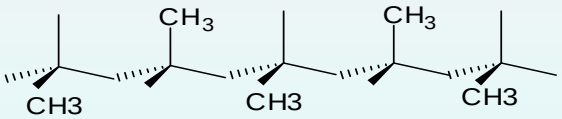


- Propylene polymerizes in the same way as ethylene, but all depends on Ziegler-Natta catalysts.
- The methyl groups give the PP polymer an extra dimension.



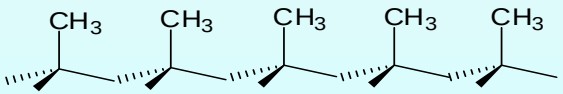
atactic

atactic



syndiotactic

syndiotactic



isotactic

isotactic

Polypropylene, PP

- The Nobel Prize to K. Ziegler and G. Natta (1963)

1953

Karl Ziegler discovers that $TiCl_4$ in the presence of AlR_3 produces high molecular weight linear polyethylene

1954

Giulio Natta by the $TiCl_4/AlEt_3$ catalyst, first polymerized propylene .

Polypropylene, PP

Cheap and cheerful Polypropylene brightens our lives:

Kitchen kettles

Shatterproof glasses

Colourful chair

Wrappers for chocolate

Garden Chairs

Rugged suitcases

CD cases

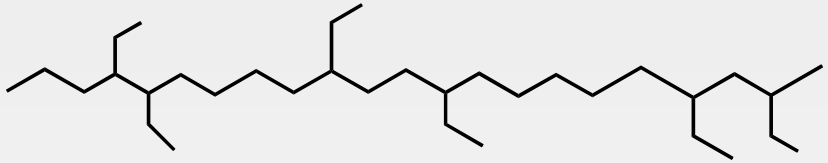
Car bumpers

PP, despite its own benefits, has always been in the shade of its more famous sister, polyethylene. Polymers, like movie stars, need a good name if they are to become a big success. Unfortunately PP never rated a star name, like polythene, nylon, Teflon and rayon.

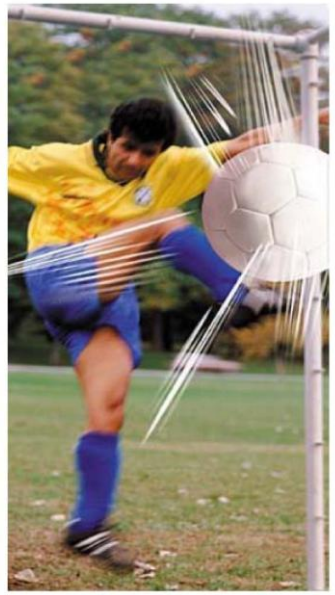
Final Notes about Polyethylene

Linear Low Density Polyethylene (LLDPE)

$$CH_2{=}\,CH_2 + \text{Comonomer} \xrightarrow[\text{or Metallocenes}]{\text{Metal Complex (Ziegler)}} \text{LLDPE}$$



- LLDPE products are copolymers: made by polymerizing two monomers at the same time so that the products have feature of both.
- Comonomers: α-olefin (1-butene, 1-hexene or 1-octene).
- Most of LLDPE are made with Ziegler-type catalysts.
- LLDPE forms a more highly crystalline structure.



Impact resistance is a key feature of SSC-based film, this one made with Dow's Elite polyethylene.

Final Notes about Polypropylene

Adding a little ethylene: increase the range of polymers

Ethylene-Propylene
Random Copolymer

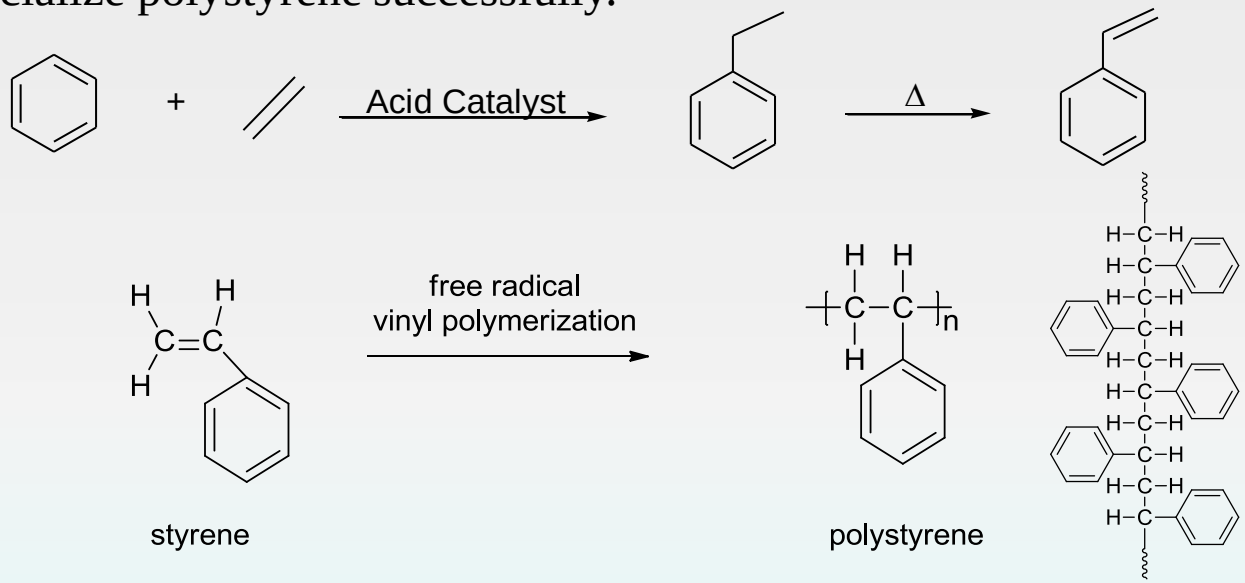
The random copolymer makes the final material less crystalline, softer, more flexible and greater clarity.

Ethylene-Propylene
Block Copolymer

The block copolymer is a superb rubber which is tough and flexible, and remains so down to temperatures as low as – 40 °C.

Polystyrene, PS

- In 1930, the Dow Chemical Company entered the styrene field with the cracking of ethylbenzene and, in 1938, became the first company in the United States to commercialize polystyrene successfully.



- Benzene rings on one chain tend to attract those on another, making the plastic less flexible and more brittle than other polymers.

- The benzene rings on the chain also ensures a tighter packing of the polymer chains, and this results in a transparent material with a high refractive index, giving it the attractive sparkle of glass.

Polystyrene, PS

Three guises in which PS polymer reaches the customer:
as PS; as expanded PS (foam); as high impact PS (HIP)

- The commercial success of polystyrene is largely due to transparency, lack of color, ease of fabrication, thermal stability, low specific gravity, relatively high modulus, excellent electrical properties and low cost. PS is used for a wide range of consumer products such as:

Disposable drinking glasses

Eye-shadow compacts

Audio cassette

Windows of business envelopes

Polystyrene, PS

As expanded PS (Styrofoam)

- How is PS foam made? – PS foam is produced from a mixture of about 90-95% polystyrene and 5-10% gaseous blowing agent, most commonly pentane or CO_2.

http://www.youtube.com/watch?v=q6OVD_2xliM

http://commons.wikimedia.org/wiki/File:Expanded_polystyrene_foam_dunnage.jpg

- Expanded PS foam offers a package of benefits that makes it unique. Because it is so light, PS foam packaging also reduces transport costs.

- Civil engineers use PS foam as a insulating material.

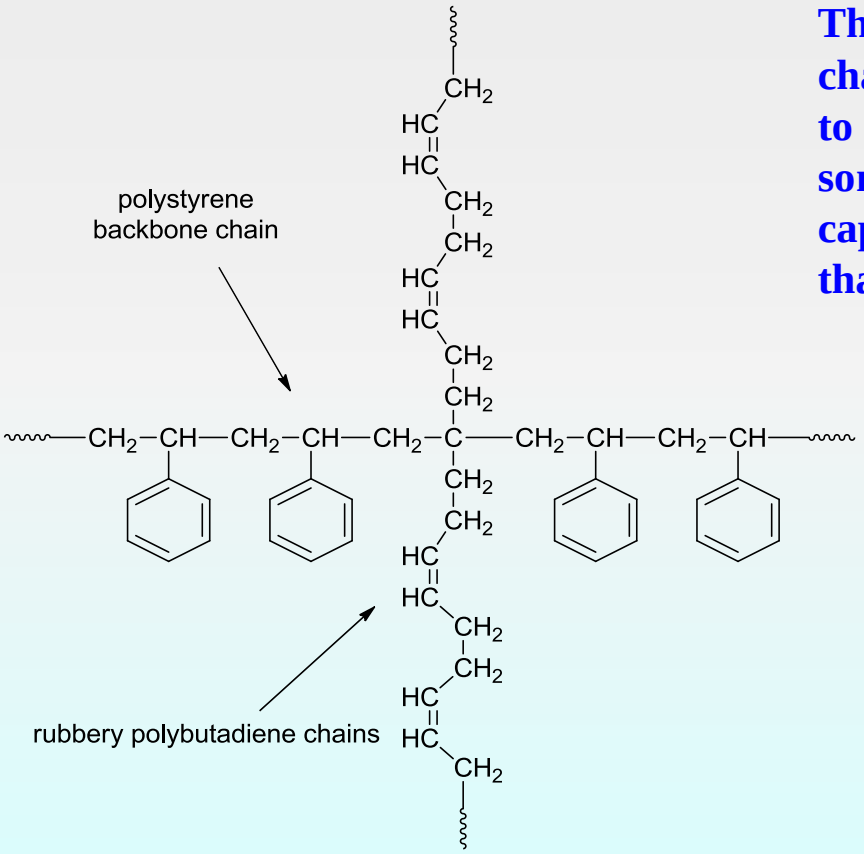
- Set designers choose PS foam for dramatic and violent scenes.

- Thin-walled cups and food containers designed to hold hot drinks and hamburgers became the target of environmental campaigns in the 1980s.

Polystyrene, PS

As high impact PS (HIP)

Polymerization of styrene in the presence of 10% polybutadiene



These rubbery chains hanging off of the backbone chain do some good things for polystyrene. They act to absorb energy when the polymer gets hit with something. This makes it stronger, not as brittle, and capable of taking harder impacts without breaking than regular polystyrene.

Fridge interiors

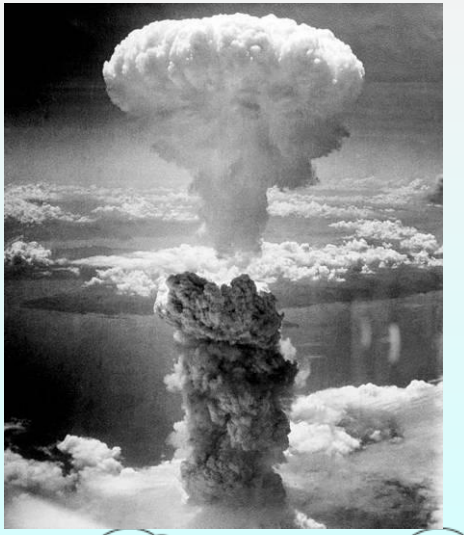
Yogurt pots

Toys

Teflon

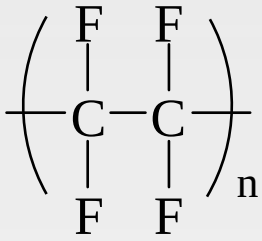
- The Moon-landing (20 July 1969) would have been impossible without the coating of non-stick frying pans?

- What is important of Teflon in the production of of the atomic bombs?



Teflon

- Teflon is one of the trade names for the polymer poly(tetrafluoroethylene), which is abbreviated to PTFE in the trade.



- The PTFE plastic had some remarkable properties: it was not attached by hot corrosive acids; it did not dissolve in solvents; it could be taken down to -240 °C without becoming stiff and up to 250 °C without affecting its performance; it could also be heated to over 500 °C without burning, and it had a peculiarly slippery feel.

- In 1950s, Louis Hartmann sought to bond PTFE to aluminium.

Tetra Ethylene
Fluorine
Aluminium
(Tefal)

Teflon

Atomic bomb

- Shortly after Teflon discovery, it was in demand for the Manhattan Project.
- Container for the most reactive gas, fluorine: fluorine gas was needed to make uranium hexafluoride, from which the fissionable isotope uranium-235 can be separated.

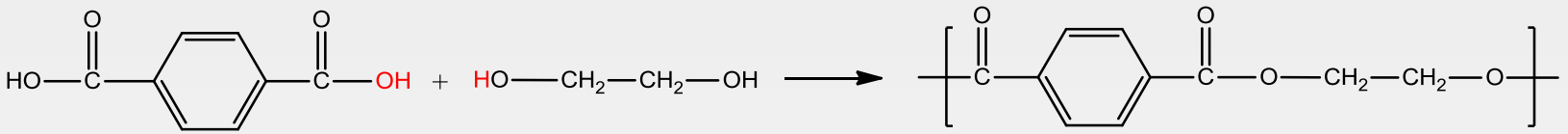
The race into space

- The year that saw the walk on the Moon also saw the launch of remarkable fabric made of PTFE – Gore-tex (Dr. Bob Gore, 1969).
- The environments of extreme cold, low pressures, and the corroding effects of activated oxygen in the upper atmosphere requires a material with unearthly properties, and PTFE was the only one suitable.

Gore-tex

Poly(ethylene terephthalate) (PET)

- PET, known by trade name Dacron™, is prepared by a reaction of purified terephthalic acid (TA) with ethylene glycol (EG).



Terephthalic acid | Ethylene glycol | Terephthalic acid - ethylene glycol ester

- A major application of PET is in manufacture of bottles that are used for fizzy drinks (50% ends up in this way), mineral waters (20%), edible oils (5%), fruit juices (5%) and others (10%).

Poly(ethylene terephthalate) (PET)

- PET resembles glass, not only in its crystal clarity but also in its ability to provide an air-tight container over a long period.

- PET has almost supplanted glass as the preferred container, because it is lighter to carry, easier to handle, cheaper to transport, and safer to stack and use.

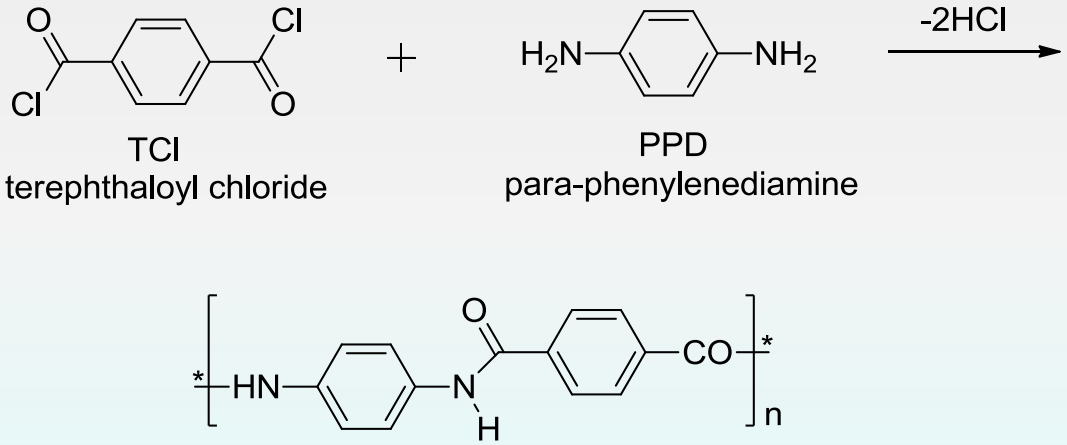
- The beer market has been the toughest nut for plastic containers to crack, but bear is sensitive to oxidation and PET by itself cannot prevent some oxygen getting through.

Will beer drinkers can be persuaded to buy ales in plastic bottle?

Kevlar

- Kevlar: lightweight, high-strength, manmade organic fiber, and five times stronger than steel.

- Kevlar was discovered in 1965 by Stephanie Kwolek, working for the US chemical giant, Du Point. She won "National Medal of Technology" in 1996.

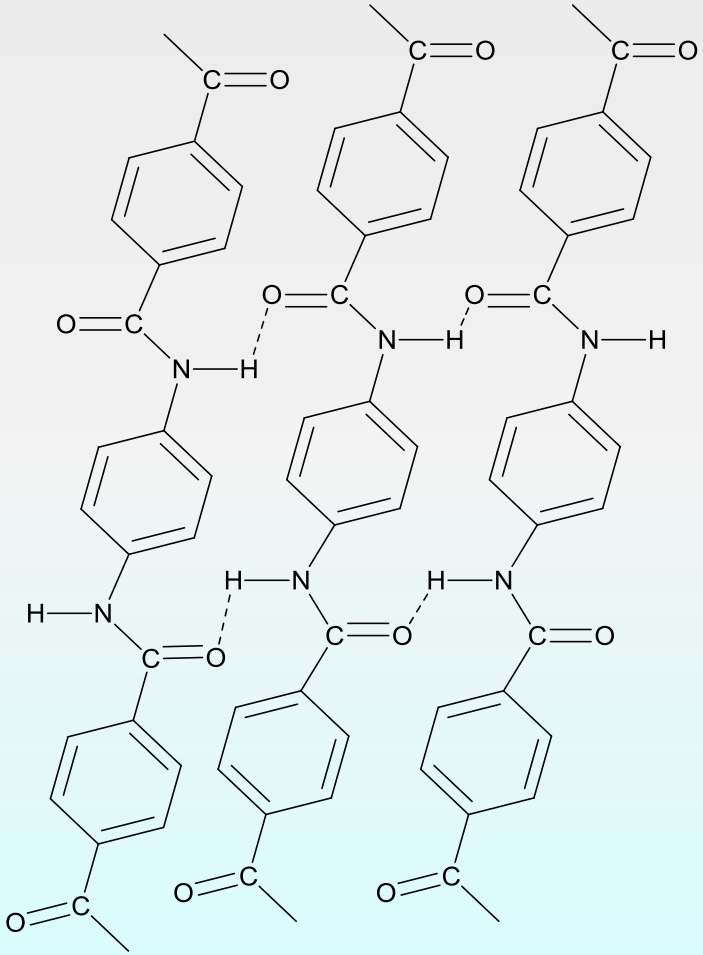


Solvent: Dimethyl acetamide, *N*-methyl pyrrolidone and hexamethylphosphoramide (HMPA)

- The polymerization solvent (HMPA) is carcinogen. This delayed its launch until 1982, by which time it had cost $500 million to develop.

Kevlar

- What gives the polymer its remarkable strength is its regularity of structure.



Kevlar was hailed as "a miracle in search of a market" – it is still searching for the elusive mass market.

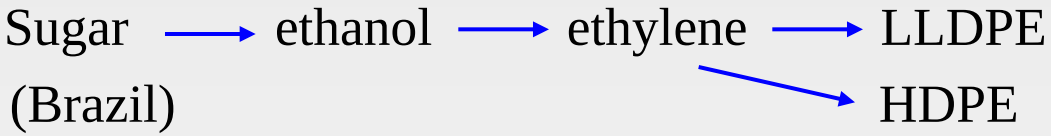
- It does not become brittle even as low as -70 °C – coating optical fibres which are exposed to the severity of mountain conditions.
- It is flame resistant – for conveyor belts, especially in mines, and for hose in the chemical industry and engines.
- It is light and can be tailored – for body armour, flak jackets and head gear.
- It has good rigidity-to-weight ratio – Formula One racing car.

Polymers: Where from and Where to?

- Petroleum is the main source of the monomers used to make most synthetic polymers.
- Planet's supply of petroleum is limited and non-renewable.
- There seems to be a more concern about where polymer go than where they come from.
- Only a very small percentage of plastics are recycled today. The most successful case is PET. About 1% of HDPE is recovered.
- Much of the plastics we use eventually ends up in a landfill, along with lots of other types of municipal and domestic solid wastes.

Green Polymer

Polyethylene (PE) from Renewable Resources (Sugar)



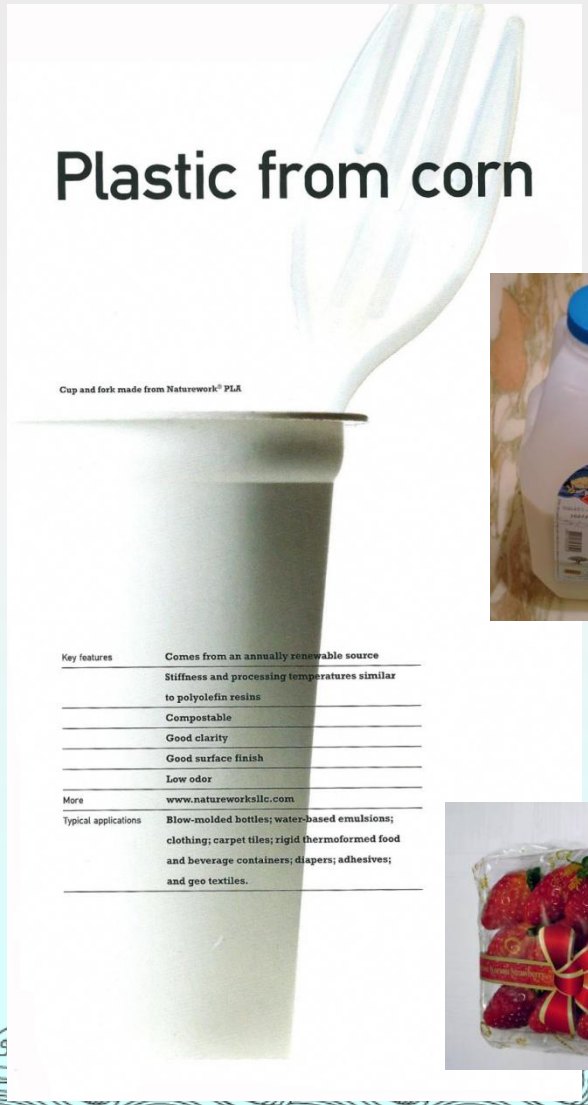
- Brazilian petrochemical maker Braskem plans to produce 200,000 metric tons of HDPE from sugar in a plant it expects to start up in 2009.

- Dow Chemical and Brazilian sugar and ethanol maker Crystalsev plan to build a commercial-scale facility in Brazil to make "cost-competitive", bio-mass-based, LLDPE for local markets. The joint venture plans to build a facility by 2011 to produce 350,000 tons of LLDPE.

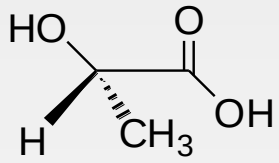
Chemical & Engineering News (C&EN) July 23, 2007, p17.

Biodegradable Polymer

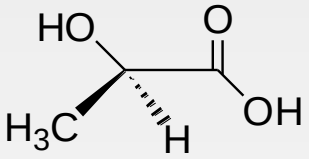
Polylactic Acid (PLA): An Exciting New Packaging Materials



- Polylactic acid (PLA) is a biodegradable polymer derived from lactic acid.



L-Lactic acid

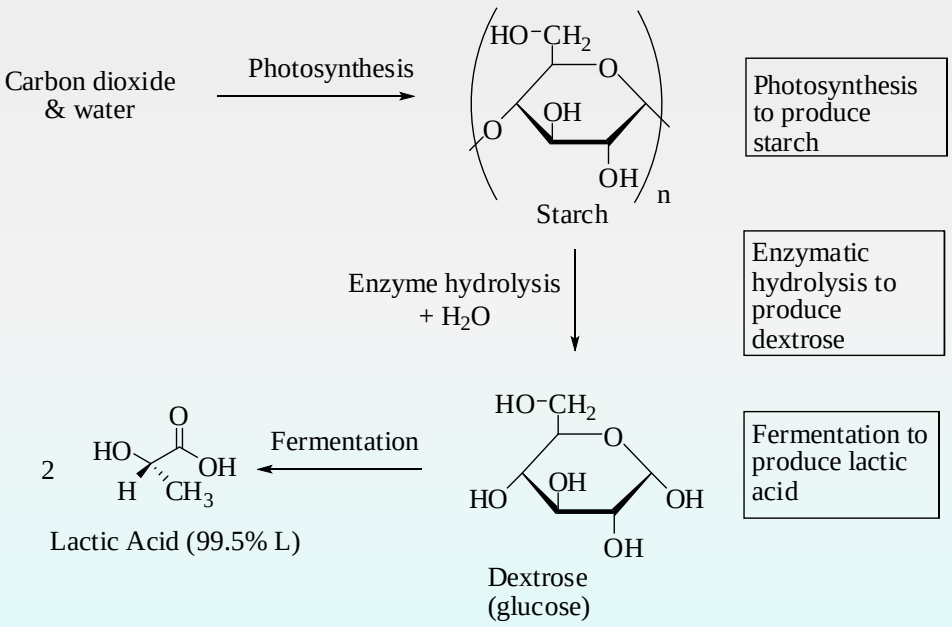


D-Lactic acid

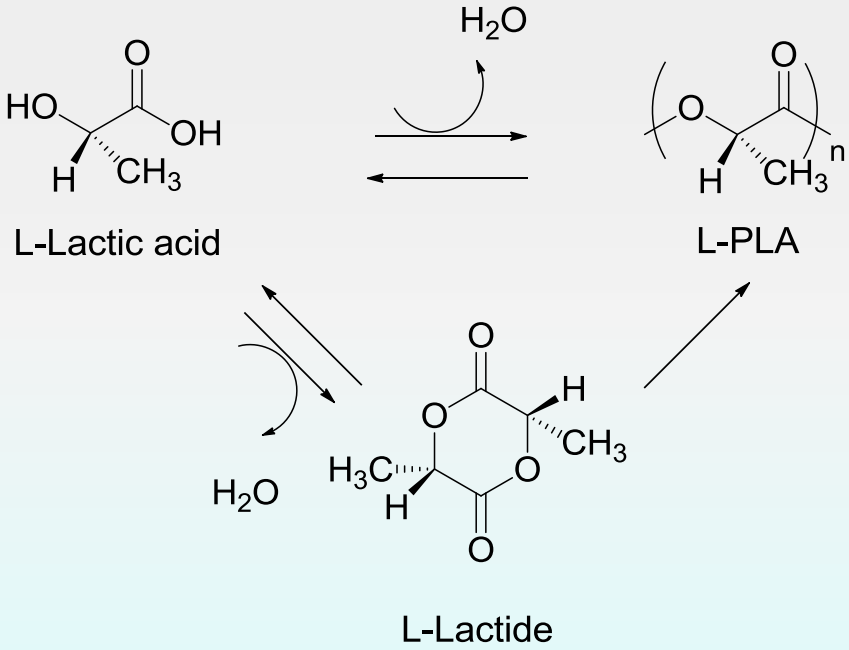
- It is made from 100% renewable resources like corn, sugar beets, wheat and other starch-rich products.

Polylactic Acid (PLA): How Is It Made?

Lactic acid formation



Polymerization routes to PLA



Messages Taken to Home:

- Synthetic polymers are at the very center of modern living.

- Over the past 70 years, chemists have created an amazing array of polymers and plastics – new materials that have made our lives more comfortable and more convenient.

- The chemical industry has given consumers what they want, but there now appears that we would like them to deal with responsibly – mountains of soft drink bottles and miles of plastic bag.

- To create a new world of plastics and polymer will require the intelligence and efforts of policy planners, legislator, economists, manufacturers, consumers, and of course, ***chemist.***

Reference and notes:

1. Emsley, J. *Molecules at An Exhibition: Portraits of Intriguing Materials in Everyday Life*, Oxford University Press, Oxford, UK, 1998, pp116-145.

2. Eubanks, L. P.; Middlecamp, C. H.; Heltzel, C. E.; Keller, S. W. *Chemisty in Context: Applying Chemistry to Society*, 6th Ed.; McGraw-Hill, New York, 2009, Chapter 9, pp368-403.