Lecture on Basics of Polymer Science & its Chronological Development

Course Instructor:

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Introduction

Polymer: (poly)+(mer)

$\downarrow$

Monomer (elementary repeat unit)

- Number of small molecules capable of polymerizing

- Mass of one polymer chain (M)=N^{x}M$_{mon}$

  $\downarrow$ (No of elementary repeat unit)

monomer $\quad O$

dimer $\quad O + O \longrightarrow O{-}O$

trimer $\quad O{-}O + O \longrightarrow O{-}O{-}O$

tetramer $\quad$ ------ ------ ------

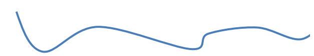
------ ------ ------

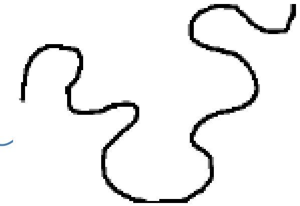
oligomer $\quad \left[-O-O- \right]_m + O \longrightarrow \left[-O-O- \right]_{m+1}$

polymer $\quad \left[-O-O- \right]_n + O \longrightarrow \left[-O-O- \right]_{n+1}$

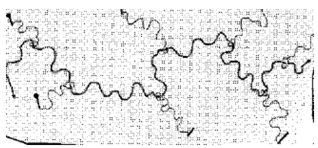
❖ Skeletal Structure

- ❑ Linear skeletal:- Chain with two ends

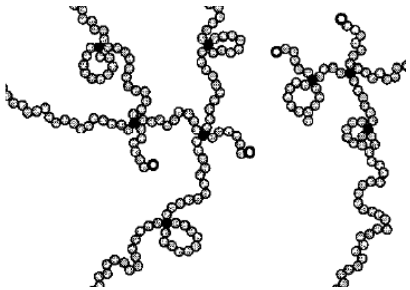




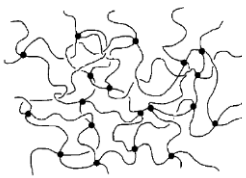
- ❑ non-linear skeletal
  - **Short Branch skeletal**



Large branch skeletal



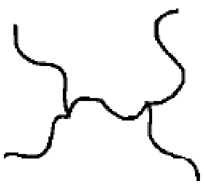
  - **Network skeletal**



  - **Ring**

  - **Star-branched**

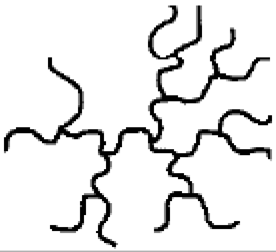
  - **H-branched**



  - **Comb**

  - **Ladder**

  - **Dendrimer**



- **Density:** **Depends on packing of polymer chains**
- **Strength**
  - **Linear PE has higher MP about 20 than that of branched PE**
  - **Unlike linear or branched polymers Network does not melt upon heating and will not dissolve**
  - **It may swell in compatible solvents properties can be change by tailoring crosslink density.**
  - **Crosslinked polymer characterized by their crosslink density or degree of crosslinking related to (no. of junction points per unit volume)**

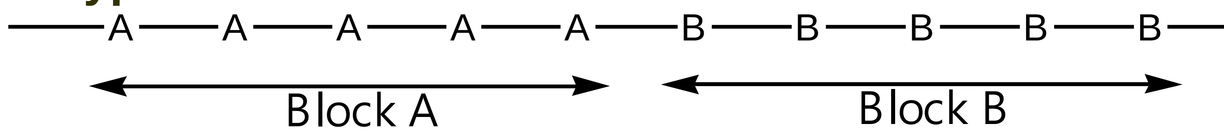
Polymers Based on sequence of Monomers

- **Homopolymer** —A—A—A—A—A—A—A—A—
- **Heteropolymer: Copolymer, terpolymer,...**
- **Copolymer:**
  - **Polymer derived from more than one monomer**
  - **Polymers whose molecules contains two or more different type of repeat units.**
    - **Simplest copolymers: A and B repeat unit.**
  - **Statistical copolymers: copolymers in which the sequential distribution of the repeat units obey known statistical law (Markovion)**
  - **Random copolymers: Here distribution of repeat units is truly random.**

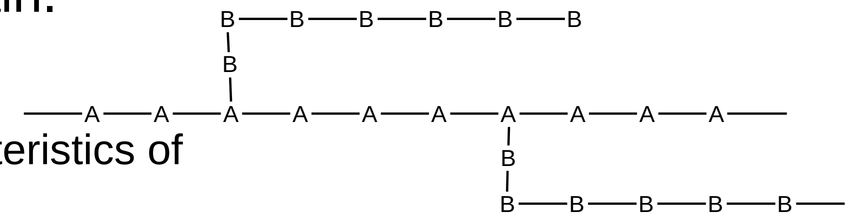
    —A—A—B—B—B—A—B—B—A—A—
  - **Alternating copolymers**

    —A—B—A—B—A—B—A—B—
    - **RC and AC generally have properties intermediate to those of the corresponding homopolymers.**

❖ **Block polymers: where repeat units exist only in long sequences (linear polymers) or blocks of same type.**



❖Graft polymers: Branched polymers in which the branches have a different chemical structure to that of the main chain.



- ❑ BC and GC generally show properties characteristics of each of the constituent homopolymer.

Principles of nomenclature for copolymers

Type of copolymers	Examples of nomenclature
❑ **Unspecified**	**Poly(A-**co**-B)**
❑ **Statistical**	**Poly(A-*stat*-B)**
❑ **Random**	**Poly(A-*ran*-B)**
❑ **Alternating**	**Poly(A-*alt*-B)**
❑ **Block**	**PolyA-*block*-polyB**
❑ **Graft***	**PolyA-*graft*-polyB**

Classification of Polymers

(Based on molecular structure of the polymers)

Polymers

Thermoplastics

Crystalline order Molecular Arrangements

Amorphous (highly coiled)

Can be melt upon the application of heat
Can be processed
Do not crystallize easily upon cooling
Appear simultaneously in both Crys. & Amorphous
Sharp T_m & T_g

Elastomers

(Crosslinked rubbery polymers (rubbery network) can be stretched easily to high extensions(3 x to 10 x to their original dimensions)

And rapidly converts their original dimensions when applied stress is released.

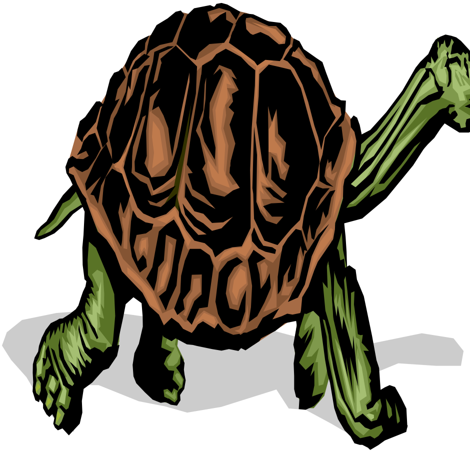
Themosets

Rigid material and are network polymers in which chain motion is greatly restricted by DC
*** Degrade rather melting**

$\uparrow$ Force of intermolecular attraction $T_g \uparrow$ and $T_m \uparrow$

❖In the beginning…

- First natural plastics
  - **Tortoise shell**
  - **Tree resins**
  - **Insect secretion**



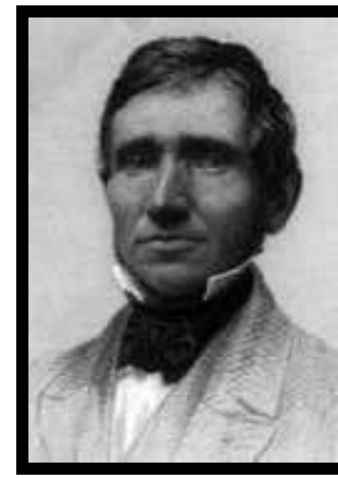
- Opened business with the use of natural polymers
- Made combs out of organic proteins (Keratin and Albuminiod) derived from animal horns, hoofs, an tortoise shells

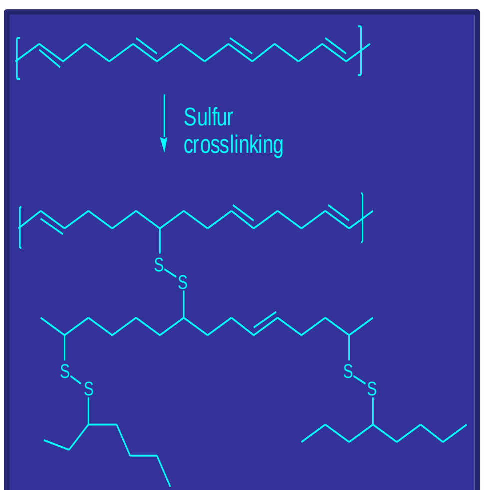
❖Natural rubber:

mainly polyisoprene

- ❑ Tends to be sticky when hot, brittle when warm
- ❑ Does not reform when stretched
- ❑ 1851: Hard Rubber— 20-30% Sulfur

Greatly enhances its elasticity and toughness

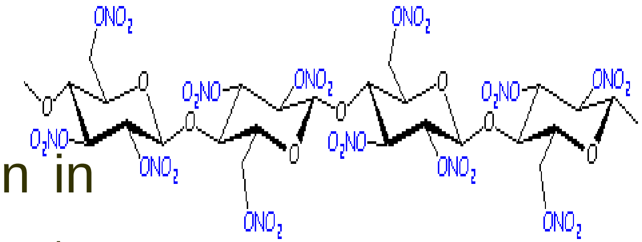




❖Charles Goodyear, 1839

His "sulfurized" rubber, later known
as "vulcanized" rubber, is still widely used today

❖ Cellulose nitrate

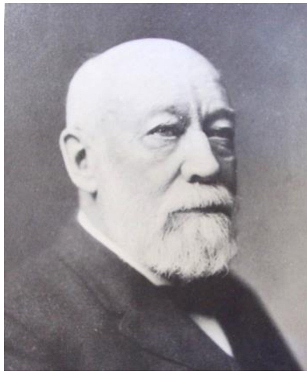


- Semi-synthetic plastic
- Demonstrated in Great International Exhibition in London, England as Parkesine, (cellulose nitrate and a solvent).
- Could be heated, formed, and it retained its shape when cooled.
- Can be molded or carved into products such as buttons, combs, picture frames and knife handles.
- This was never commercialized due its relatively high cost compared to vulcanized rubber.
- Mix of cotton (wife's apron), nitric acid, and sulfuric acid

Examples:Buttons, Combs, Pens

Alexander Parkes, 1862

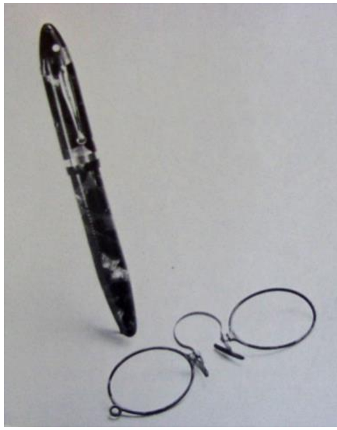
- Blended nitrocellulose with camphor (sap from the laurel tree)
- Produce a durable, colorful, and moldable thermoplastic known as *celluloid*.
- *Celluloid* was the first commercially successful semi-synthetic plastic.



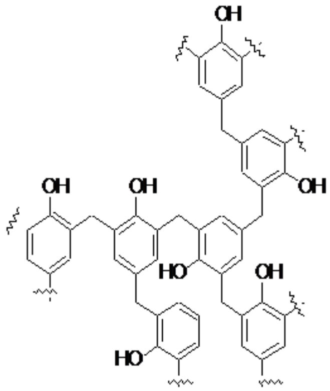
John Wesley Hyatt

celluloid in 1868

***Billiard balls**
***Shirt collars**
***Eyeglass frames**
***Pen housings**

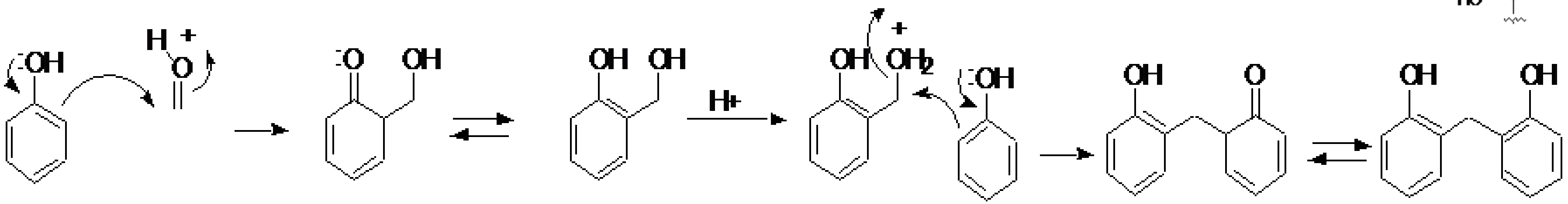


Bakelite (1907)



❖ Dr. Leo Baekeland (Belgian born chemist)

- ❑ First totally synthetic plastic
- ❑ Didn’t throw away his foul glassware



Catalyst: hexamethylenetetramine

❖ Patented in 1909: Right to Kodak Co. (Camera)

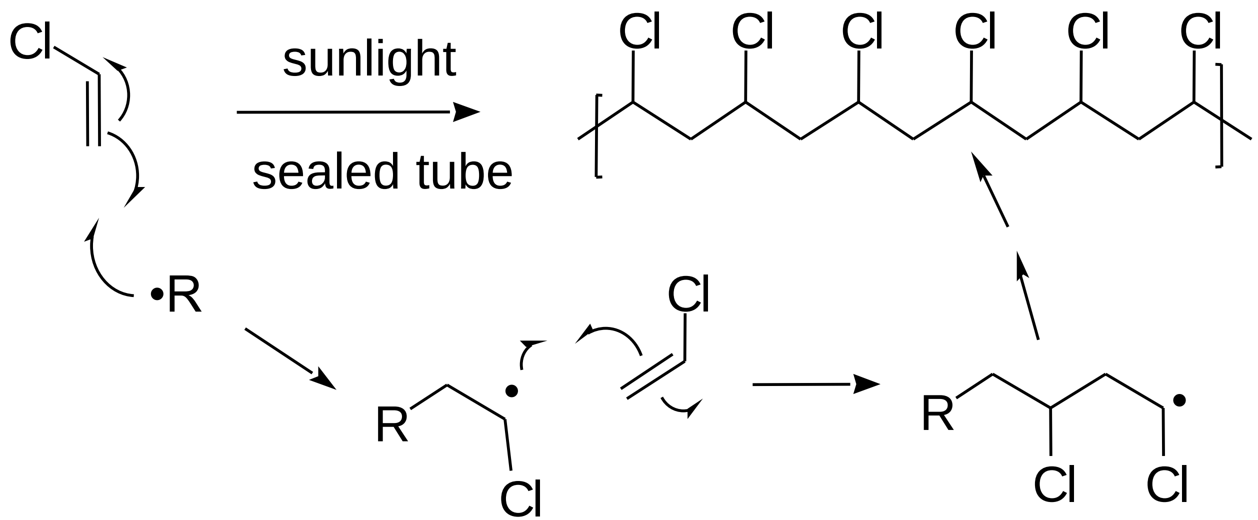
- ❑ Thermoset resin, replaced rubber for insulation in electrics
- ❑ Properties: electrically resistant, chemically stable, heat resistant, rigid, moisture and weather resistant.
- ❑ Hyatt-Burroughs Billiard Ball Company replaced celluloid by Bakelite for their billiard balls due to its superior performance.

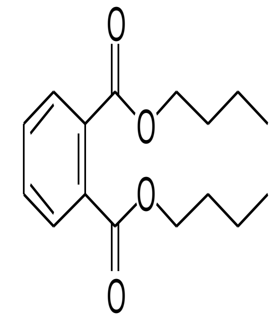
❖Polyvinyl Chloride (PVC)

- Invented by the German chemist Eugen Baumann.
- Waldo L. Semon, invented a way to make polyvinyl chloride (PVC) useful by adding Plasticizer
- PVC formulations can be either rigid or flexible depending their plasticizer concentration.
- Initial application for PVC included foul weather gear and electrical wire insulation.

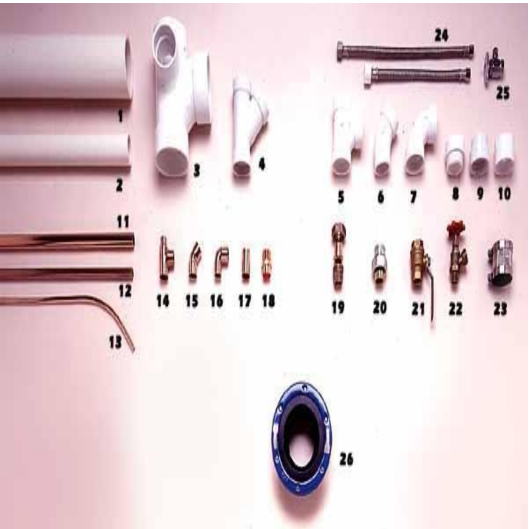



❖Baumann's 1872 experiment



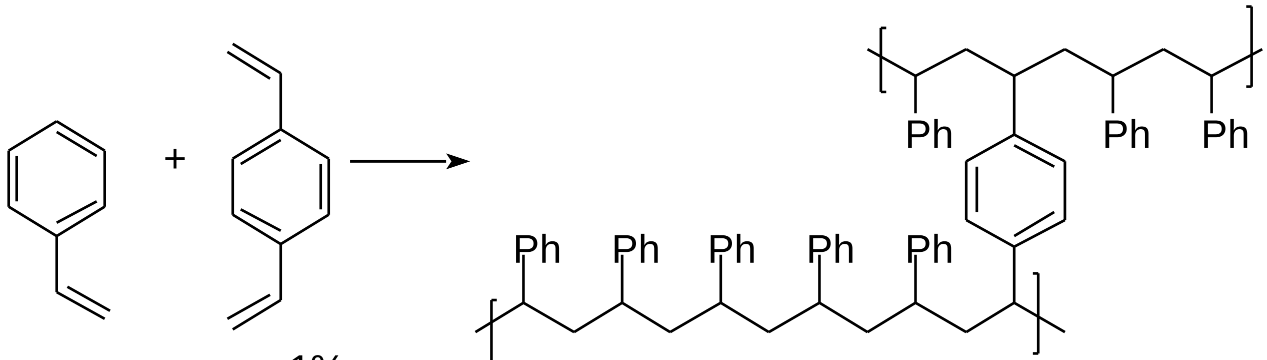


Plasticizers



Polystyrene

- **Scientist from the BASF Corporation developed a commercial process for the manufacture of PS IN 1930.**



1939: Wood TV Cabinet

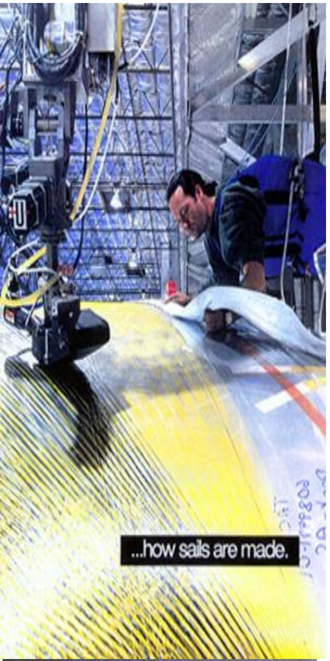
1948: Phenolic TV Cabinet

1970: HIPS TV Cabinet

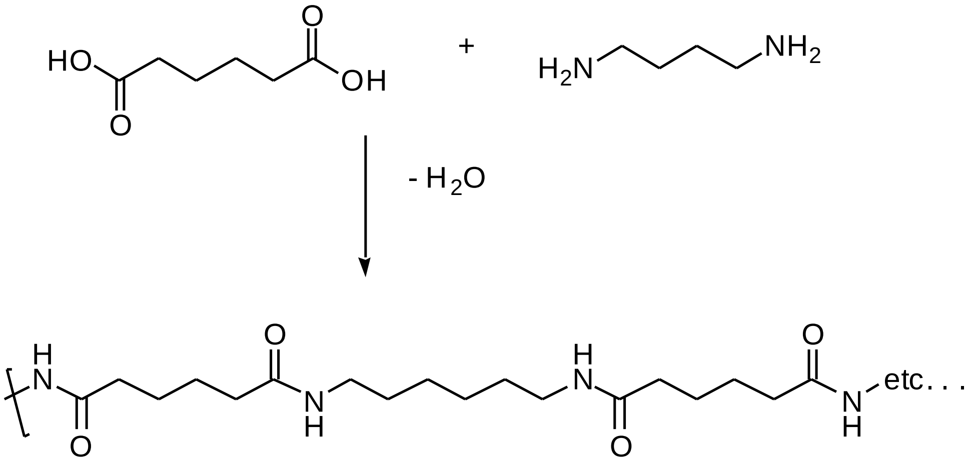
- Toy shark, in Polystyrene, with moving jaw, Made in USA around 1950
- *Dow Chemical* brought polystyrene to the U.S. in 1937
- Foam egg cartons, burger containers, coffee cups , "peanuts" used in packing and the lightweight foam pieces that cushion new appliances and electronics.
  - **Gas is blown in during the polymerization-- 95 % of styrofoam is air (try dissolving in acetone)**
  - **CFC's were used until the 80's: phased out and replaced with pentane or CO_2**

Nylon

- 1930’s research on polymer chains at DuPont Chemical Department Invented Neoprene and Nylon
- Dr. Wallace H. Carothers, pulled the first long, strong, flexible strands of a synthetic polymer fiber out of a test tube & introduced commercially in 1938.
  - **This artificial fiber had properties similar and in many ways superior to natural fibers.**
  - **The material, *poly(hexamethylene adipamide)*, is more commonly known as “nylon 66”. One of the earliest uses of nylon 66 fiber: tooth brush bristles.**
- During World War II, nylon was used for many applications
  - **cargo parachutes,**
  - **tire cord for bombers,**
  - **glider tow ropes,**
  - **flak jackets, mosquito netting,**
  - **Jungle clothing**



- Condensates of aliphatic diacids with aliphatic diamines

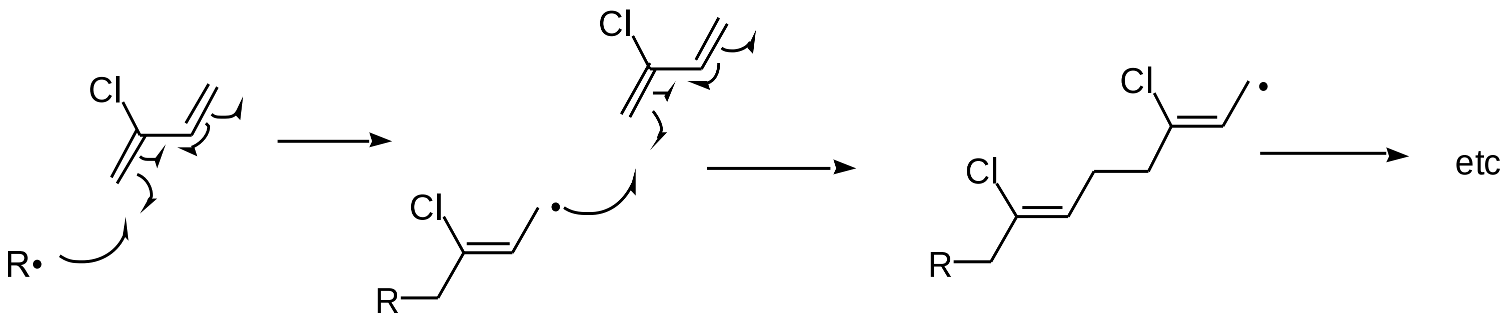


co-crystalline

Nylon 66

❖ Synthetic Rubbers

Neoprene: The first Synthetic Rubber



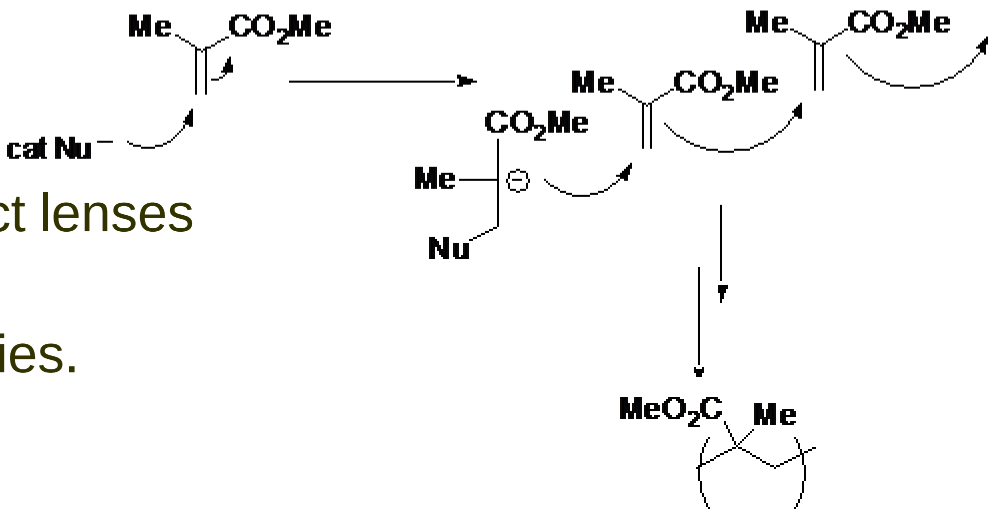
benzoyl peroxide
inititates free radical
polymerization

❖Applications:

- Gasoline pump hoses,
- Hoses for automobile engines

❖ PMMA anionic polymerization (1937)

- PMMA is a very hard material and have superior optical properties
- Transparent than glass
- Used as Hard and soft contact lenses
- Thermoformed aircraft canopies.

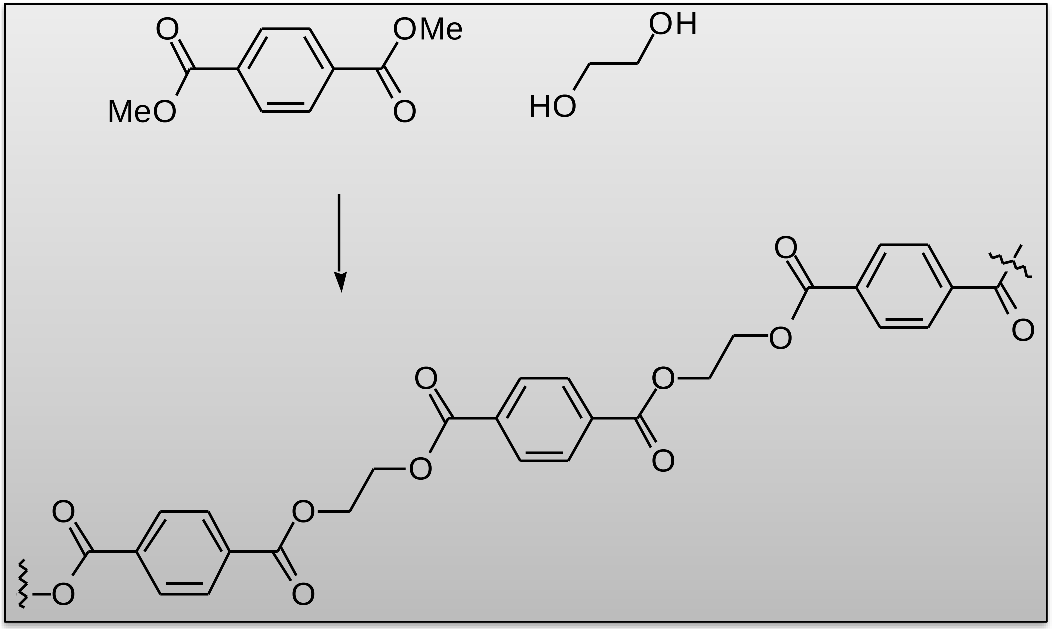


- Automotive tail light lenses due to its, where it is still used today.

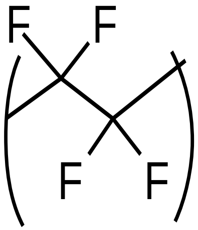
  PMMA is also used as acrylic fibers, paints and coatings, and as a marble replacement for kitchen countertops.

❖ Polyethylene Terephthalate (PET), 1941

- ❑ Extremely versatile thermoplastic
- ❑ Made by the condensation reaction of ethylene glycol and terephthalic acid.
- ❑ Initially used for the production of synthetic textile fiber, know today as Dacron®.
- ❑ Biaxially oriented PET film, known as Mylar®
- ❑ However, largest use for PET is -“stretch blow molded” transparent, lightweight, have good barrier properties, and shatter resistant beverage bottles.
- ❑ PET is recyclable.
- ❑ Recycled PET bottles are reprocessed to form PET textile fiber for clothing.



- Polytetrafluoroethylene (PTFE)
  - Dupont Chemical Department
  - First used for artillery shell covers



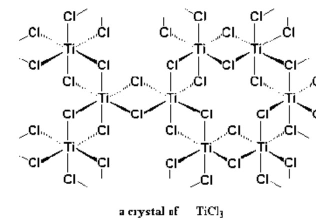
Polytetrafluoroethylene (PTFE), 1938.

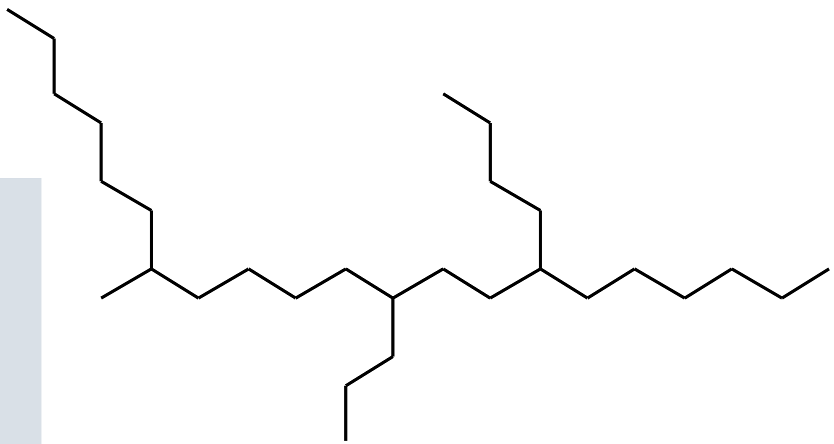
- DuPont scientist Dr. Roy Plunkett, accidentally discovers polytetrafluoroethylene (PTFE).
- An inherently slippery and remarkably chemically resistant plastic. Most slippery substance on earth.
- Commercial introduction of DuPont's Teflon® - 1946.

- Teflon® is most widely known for its widespread use in nonstick cookware
- Cable insulation.
- Teflon® sheet is used as an insulator and lubricant between the copper skin and the stainless steel skeleton of the Statue of Liberty.
- The roof of the Pontiac Silverdome is made of a Teflon® coated woven glass fiber fabric.

❖Polyethylene (1933)

- Imperial Chemical Industries in England
- E.W. Fawcett & R.O. Gibson
- First used for underwater cable coatings and insulation for radar





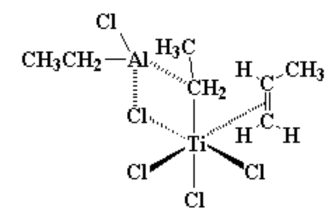
Polyethylene

Low density polyethylene

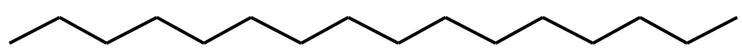
Karl Ziegler changed polymerization of polyethylene

<u>Use of catalysts</u>

Now is most widely produced and perhaps most versatile plastic



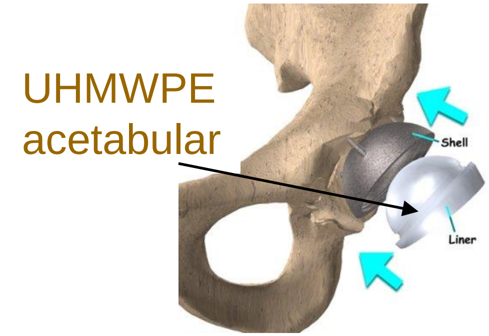
The π-electrons from propylene end up filling titanium's empty orbital.



High density polyethylene
Ziegler-Natta catalysts

❖*Ultra High Molecular Weight Polyethylene (*UHMWPE)

- One of the most interesting medical applications for UHMWPE is the “artificial hip”.
- Each prosthesis is made up of two parts: the acetabular component (socket portion) that replaces the **acetabulum**, and the femoral component (stem portion) that replaces the femoral head.
- The femoral component is made of titanium, while the **acetabular** component is made of a metal shell with a plastic inner socket liner. UHMWPE acts like a bearing. It is extremely **tough**, **abrasion resistant** and has a **very low coefficient of friction.**
- This is a very good example of how plastics and metals work together to enhance our quality of life.



❖ Polyacrylonitrile butadiene styrene ABS (1951)

- “Blend” of SAN & butadiene rubber
- Butadiene act as an impact modifier.
- if the SAN is chemically grafted onto the butadiene rubber “terpolymer”-provide outstanding Impact strength.

❖ Applications

- football helmets, which are now made from polycarbonate.
- Today, ABS is most widely used for consumer electronics and business machine housings.

SAN: polystyrene-acrylonitrile copolymer

Glass Fiber Reinforced Plastic (1953)

- General Motors introduced-Chevrolet *Corvette* in
- Glass fiber reinforced plastic as a body material
- *Car* was available in white body and red
- Interior 1953, and sold for $3,498

2003 50th Anniversary Corvette

Polycarbonate (1953)

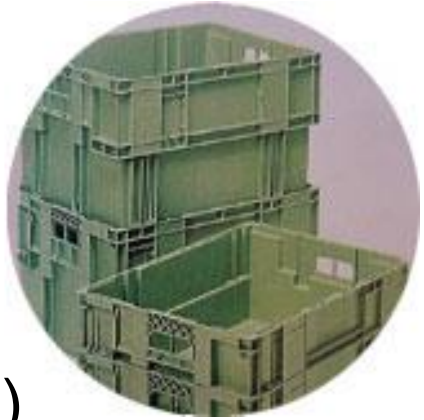
- Hermann Schnell from Bayer A.G. & Daniel Fox from GE-discovered PC
- Optically transparent engineering thermoplastic
- Unique combination having:
  - Stiffness and toughness, heat resistance and electrical insulating properties
- Application
  - Automotive headlights,
  - Tool housings,
  - Helmets and computer enclosures
  - All CD's, CD-ROM's and DVD's

Polypropylene (1957)

❖Guilio Natta continued Ziegler's work

- ❑ Created polypropylene in 1957
- ❑ Substituted for polyethylene where high temperatures were involved
- ❑ Ex. Dishwasher safe dishes
- ❑ Long chain stereo-regular polypropylene molecule.
- ❑ Very good balance of properties include stiffness, toughness, chemical resistance, and translucent optics.
- ❑ Strong ability to form copolymers with most widely used thermoplastics.

Car's front bumper (1978)



Plastic made MOON possible

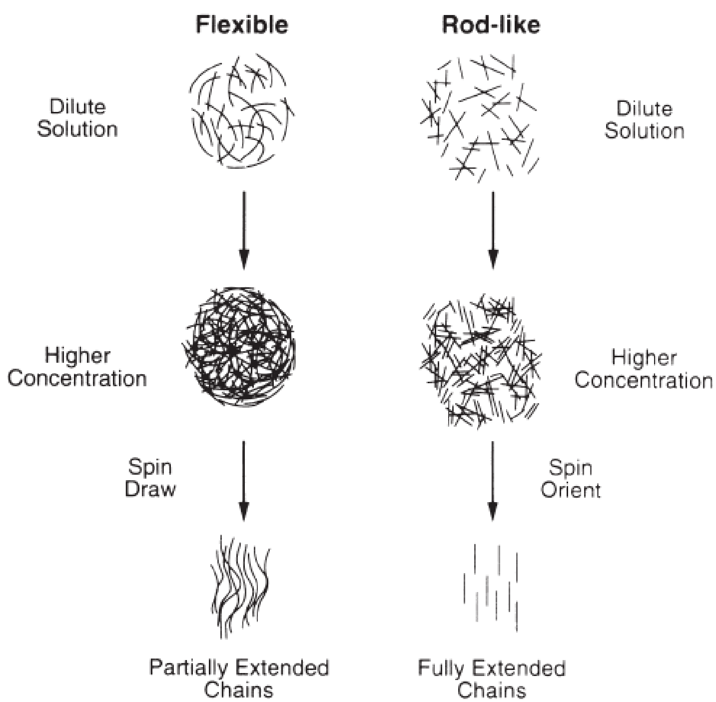
- July 20, 1969 –greatest technological achievement
- when Neil Armstrong set foot on the moon
- Plastics played an important roll.
- *Apollo* A7L space suits were a multi-layer plastic structure c

  - **Nylon fabric,**
  - **Neoprene coated nylon fabric,**
  - ***Dacron*® (PET) fabric,**
  - **Aluminized *Mylar*® (PET) film,**
  - ***Kapton*® (PI) film, and *Teflon*® (PTFE) coated fabric.**
  - **“fish bowl” helmet - polycarbonate.**
  - **Space suits of today make even more extensive use of plastics.**

Kevlar® (1960's)

- Five times stronger than steel (on a strength per weight basis)
- *Kevlar*® is a condensation polymers.
- Bulletproof vests are made;
- In fact, *Kevlar*® has dozens of important applications, including

Stephanie Kwolek



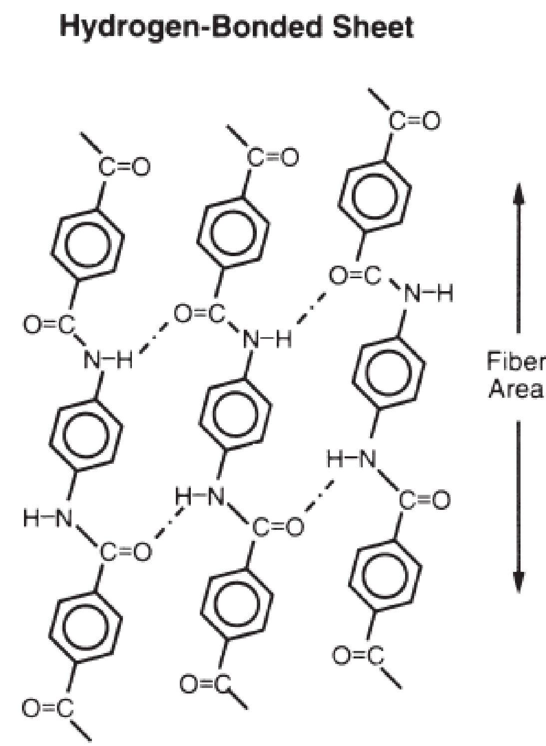
Radial tire cord,

Brake pads,

Racing boat sails,

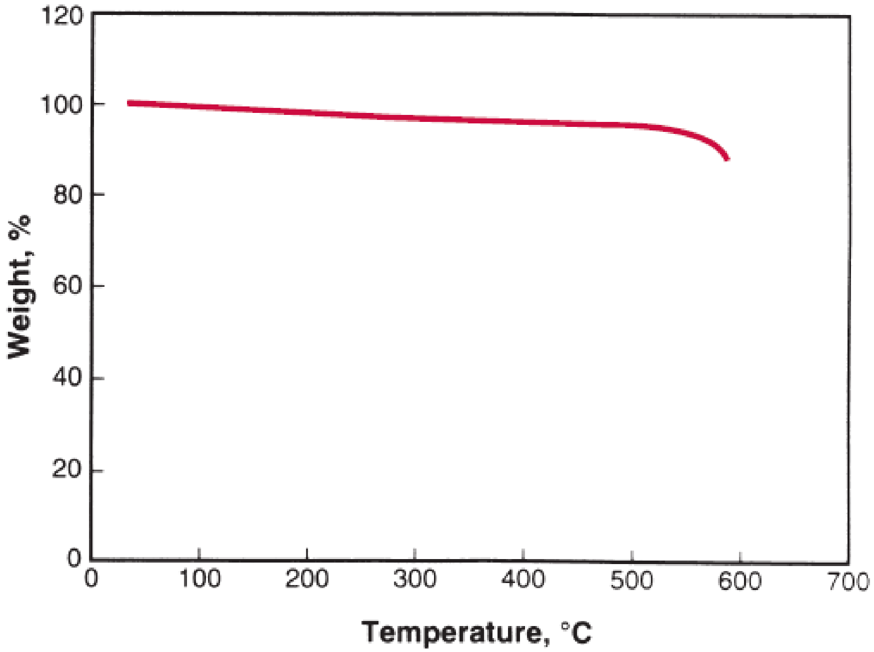
Aircraft components,

Suspension bridge cables.

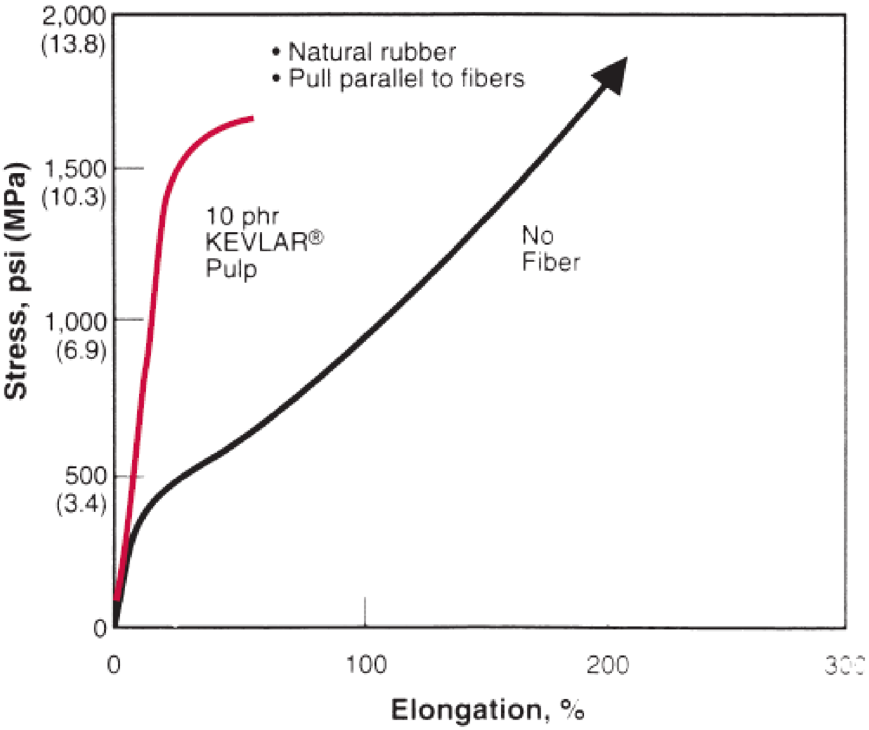


Kevlar® contd..

❖ Thermal Stability



❖ Stress-strain relation



Polyurethane

- Polyurethane- Formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate
- In the presence of suitable catalysts and additives.
- It can be molded, extruded, or cast,
- Available as foams, coatings, specialty adhesives and sealants.
- The first artificial replacement heart, the *Jarvic-7*, was produced from a flexible and fatigue resistant polyurethane.
- The toughness and abrasion resistance of polyurethane make it an ideal material for applications such as in-line skate wheels

- Plastics for telephone housings since the turn of the last century.

  - Thermosetting phenolic thicknesses up to 13 mm.
  - Injection molded ABS phones were introduced in the 1950’s. thicknesses of about 3 mm.
  - ABS has a very high gloss, good impact resistance, and could be molded in a variety of different colors.
  - Polycarbonate & ABS blend (PC/ABS). The compact and lightweight phones of today have wall thicknesses in the range of 1 mm.

  - Telephones are a good example of how plastic products evolve over time.
  - Creative product designers make use of new plastic materials and new plastic processing technologies as they become available in order to improve product performance

The Nobel Prize-Field of Polymers macromolecules

- Hermann Staudinger for his many discoveries in the field of macromolecular chemistry (1953)
- Karl Ziegler and Giulio Natta for their discoveries related to polymer chemistry and new polymerization technologies (1963)
- Paul J. Flory for fundamental achievements, both theoretical and experimental, in the physical chemistry of macromolecules (1974)
- P.G. de Gennes for creating the reptation model of polymer dynamics used to predict polymer properties and viscosity (1991)
- Alan J. Heeger, Alan G. MacDiarmid and H. Shirakawa for the discovery and development of inherently conductive polymers. (2000).
- Atom Transfer Radical Polymerization-2005