UNIVERSITY OF ZAGREB

FACULTY OF CHEMICAL ENGINEERING AND TECHNOLOGY

Polymer science and technology

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Different classification of polymers

1. Properties

- Plastics
  - Thermoplastics
  - Thermosets
- Elastomers
- Fibers

2. Structure

- Linear
- Branched
- Cross-linked

3. Number of monomer

- Homopolymer
- Copolymer
  - Random
  - Alternating
  - Block
  - Graft

4. Configuration

- Isotactic
- Atactic
- Syndiotactic

5. Origin

- Natural
- Synthetic

- World annual production (2022) of plastics is 391 million tons
- ~99% are synthetic polymers

  - ☐ Polypropylene (PP) - 75 mil. t
  - ☐ Low-density polyethylene (LDPE) – 56 mil. T
  - ☐ Poly(vinyl chloride) (PVC) – 50 mil. t
  - ☐ High-density polyethylene (HDPE) - 49 mil. t
  - ☐ Poly(ethylene terephthalate) (PET) – 24 mil. T
  - ☐ Polyurethanes (PUR) – 22 mil. t
  - ☐ Polystyrene (PS) – 21 mil. t
  - ☐ Polyamides (PA) – 8 mil. t

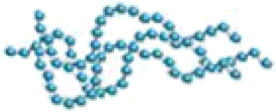
Synthetic polymers

- Classification of synthetic polymers according to **mechanical** and **thermal** properties

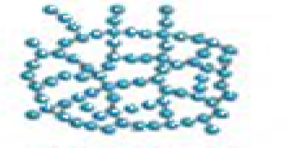
POLYMERS

- PLASTIC
  - Plastic deformation
  - Thermoplastic
  - Thermosets
- ELASTOMERS (RUBBER)
  - Elastic deformation

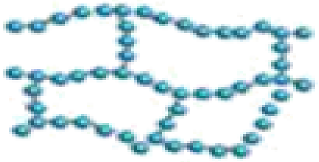
Thermoplastic



Thermosets



ELASTOMERS (RUBBER)



- Plastic deformation is **permanent change in size** of material when forces is applied
- Elastic deformation **is not permanent, it is restorative** after the force is removed

Synthetic polymers

Thermoplastic polymers

- Solid at room temperature
- **Soluble in organic solvents**
- Become soft on heating, flow due to crystal melting or by crossing the glass transition temperature (Tg), turn to melt
- **Upon processing, thermoplastics take the shape of the mould** within which they are poured as melt, and **cool to solidify into the desired shape**
- They can be **melted for several time** without degradation during processing
- Very useful for the recycling of plastic waste
- Thermoplastic polymers are PE, PP, PS, PVC, …

Synthetic polymers

Thermoset polymers

- Thermoset polymers are called also resin, obtained by condensation polymerization, **crosslinked**
- Generally, before crosslinking, a **liquid material at room temperature**
- When **heated**, the thermoset **solidifies** into the specified shape, formation of **crosslinks**
- Thermoset polymers – **can not be soften on heating, can not be melted**
- If crosslinked (cured) the process is irreversible because chains are chemically bonded – crosslinked, forming network, 3D-structure because individual chains are chemically bonded
- During the heating they are subjected to degradation because primary chemical bonds are destroyed
- **Can not be reshaped**, it is a problem during the recycling

Usage of plastics by type

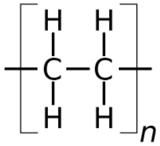
- 80% are thermoplastics
- 20% are thermosets
- Most thermoplastics are commodity (80-85%)

Commodity vs. Engineered Thermoplastics

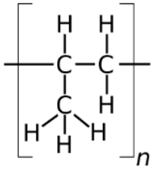
- Commodity thermoplastics < 3 $/kg
- Engineered thermoplastics 3 $/kg to 12 $/kg range but some can be more than 100 $/kg for special plastics
- Engineered plastics used for durable goods, have better mechanical properties or “special” property
- Commodity plastics are used for consumer goods (i.e. food storage), are more readily available and generally have lower mechanical properties

Commodity Thermoplastics

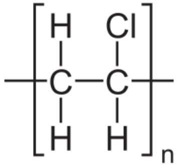
- Polyethylene (PE) (includes LDPE, HDPE)



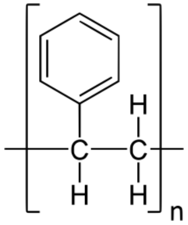
- Polypropylene (PP)



- Poly(vinyl chloride) (PVC)



- Polystyrene (PS)



- These are all ethenic (vinyl) polymers (based on the ethylene molecule)
- Most are linear in structure with minimal branching
- Most are low strength comparable to that of engineering plastics
- Polyethylene (PE) and polypropylene (PP) both have a translucent, waxy texture, and are the **only non-foam plastics that float in water** (density < 1.0 g/cm3)
- Can be amorphous (PS, PVC) or semi-crystalline (PE, PP)

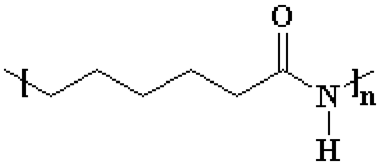
Engineering thermoplastics

- **High thermal stability, excellent chemical resistance, high tensile, flexural and impact strength** → Significantly more expensive, achieve very high performance in one or more area

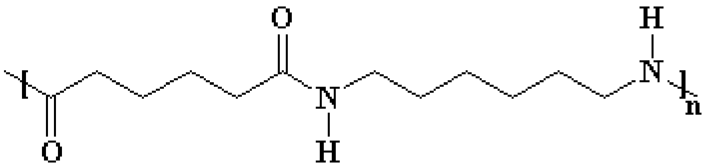
- Replacement for metals, **used where a high strength-to-weight ratio** is important → Automotive and aerospace industry, membranes for gas and liquid separations, flame-retardant textile fabrics for fire fighters and race car drivers, material for surgical implants

1) Polyamides

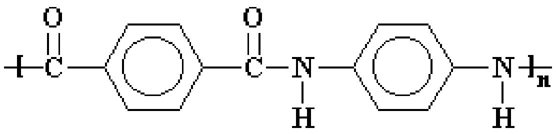
- ☐ Aliphatic (nylon-6 and nylon-6,6) or aromatic backbones (Kevlar^{TM})
- ☐ Used for fibers, Kevlar has higher strength and modulus than steel on an equal weight basis



nylon-6



nylon-6,6

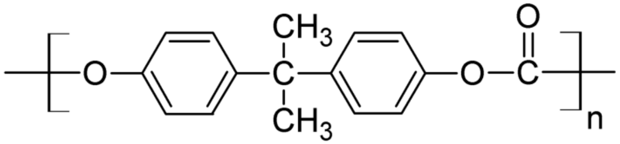


Kevlar^{TM}

Engineering thermoplastics

2) Polycarbonates

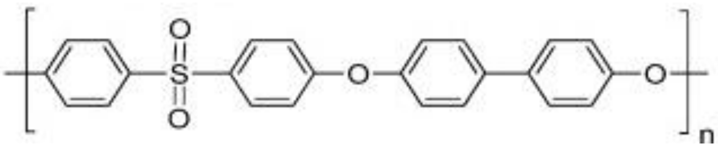
- **High impact strength**, low combustibility, high light transmittance (up to 88%) – **impact resistance substitute for window glass**



Bisphenol-A polycarbonate

3) Polysulfones

- High thermal, oxidative and hydrolytic stability, **high biocompatibility, high permeability and permselectivity**
- **Medical application, membrane polymers in gas separations**

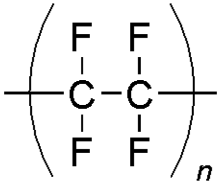


Polyphenylsulfone (PPSU)

Engineering thermoplastics

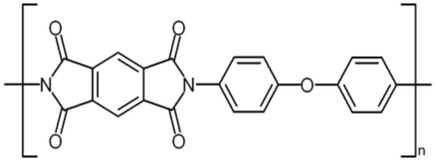
4) Fluoropolymers

- Polytetrafluroethylene (PTFE, Teflon^{TM})
- Highly dense (2.1 to 2.3 g cm^{-3}), high-temperature stability, low-temperature flexibility, low dielectric coefficient, chemical inertness

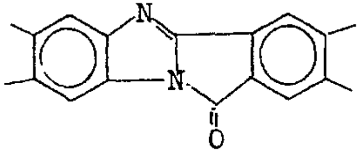


5) Polyimides

- High-temperature solvent-resistant polymers
- Electronics, sleeve bearings, valve seatings, **matrix of graphite composites in jet engines**



Kapton®



Ladder polymer

Highly fused-ring backbone, extreme high-temperature stability, >500 ℃

Engineering thermoplastics

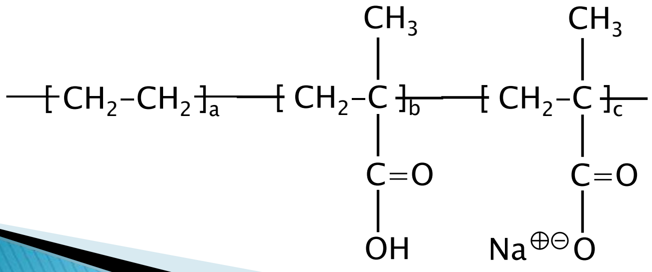
6) Polyolefins

- Ultrahigh-molecular-weight polyethylene (UHMWPE)
- Molecular weight 1 to 6 million
- **Exceptional impact and tensile strength**, tear and puncture resistance, chemical inertness, good fatigue resistance
- **Orthopedic implants**, battery separators

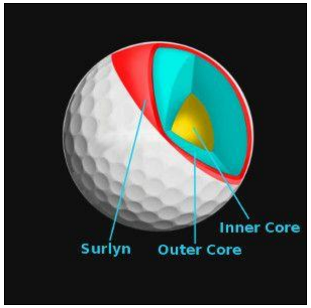
7) Ionic polymers

- **10-15 mol% ionic content *ionomers*, higher content *polyelectrolytes***
- Ionic sites introduced into polymers through chemical modification
- Ion-exchange resins, membranes for liquid and gas separations
- **Nonionic backbones PE or PS**

- Surlyn A™
- Copolymer of ethylene and methacrylic acid, 33% of acid neutralized with NaOH



$$-[CH_2-CH_2]_a-[CH_2-\underset{\substack{|\\C=O\\|\\OH}}{\overset{\substack{CH_3\\|}}{C}}]_b-[CH_2-\underset{\substack{|\\C=O\\|\\Na^{\oplus}\,{}^{\ominus}O}}{\overset{\substack{CH_3\\|}}{C}}]_c-$$



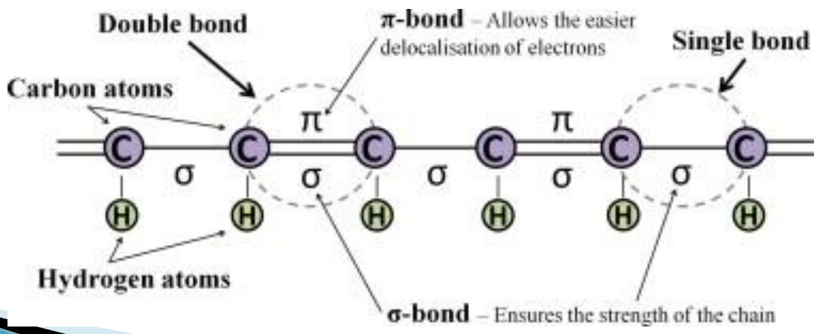
Better toughness, durability, aerodynamics

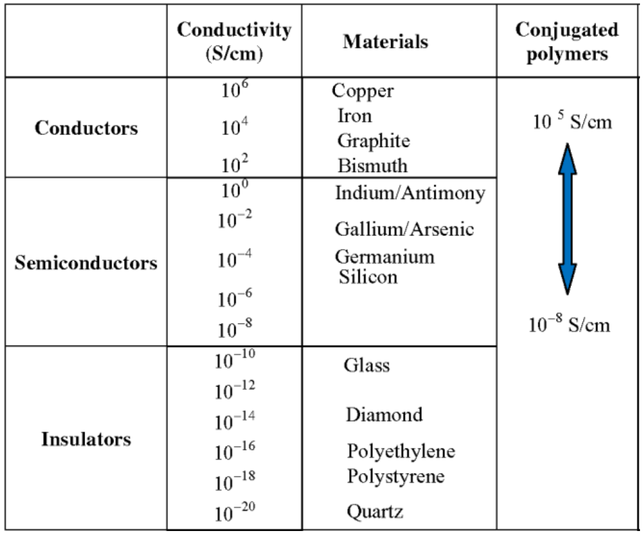
Other engineering polymers (not thermoplastics)

Conductive polymers

- **Organic polymers that conduct electricity**
- **Batteries**, organic solar cells, **organic light-emitting diodes, supercapacitors, chemical sensors and biosensors, flexible transparent displays,** electromagnetic shielding, **microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft**

- Polymers contain conjugated π-electrons backbone, which is responsible for electric charge. Overlapping of orbitals over the entire backbone results in the formation of valence bands and conduction bands, which extends over the entire polymer molecule



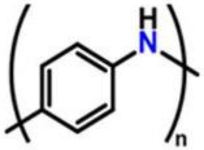


	Conductivity (S/cm)	Materials	Conjugated polymers
Conductors	10^6 10^4 10^2	Copper Iron Graphite Bismuth	10^5 S/cm 10^{-8} S/cm
Semiconductors	10^0 10^{-2} 10^{-4} 10^{-6} 10^{-8}	Indium/Antimony Gallium/Arsenic Germanium Silicon	
Insulators	10^{-10} 10^{-12} 10^{-14} 10^{-16} 10^{-18} 10^{-20}	Glass Diamond Polyethylene Polystyrene Quartz	

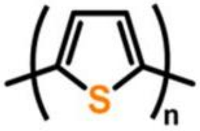
Other engineering polymers (not thermoplastics)

2) Conductive polymers

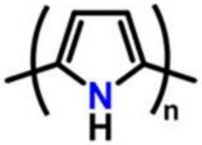
Polyacetylene
(PA)



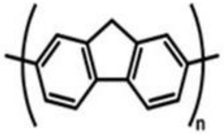
Polyaniline
(PANI)



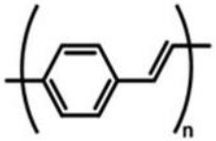
Polythiophene
(PT)



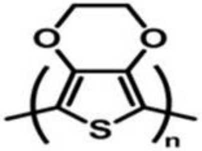
Polypyrrole
(PPy)



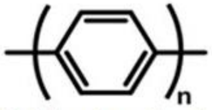
Polyfluorenes
(PF)



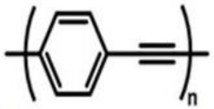
Poly(*p*-phenylene vinylene)
(PPV)



Poly(3,4-ethylenedioxythiophene)
(PEDOT)



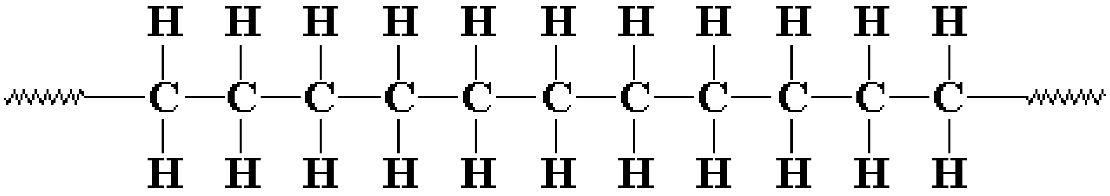
Poly(*p*-phenylene)
(PPP)



Poly(*p*-phenylene ethynylene)
(PPE)

Polyethylene (PE)

- IUPAC name **polyethene** or **poly(methylene)**
- Most common plastic in use today
- One of the first synthesized polymers
- Accidentaly synthesized in 1898, **industrial production started in 1939** (low density PE)
- pure hydrocarbons, **polyolefin** $(CH_2CHR)_n$ group of polymer

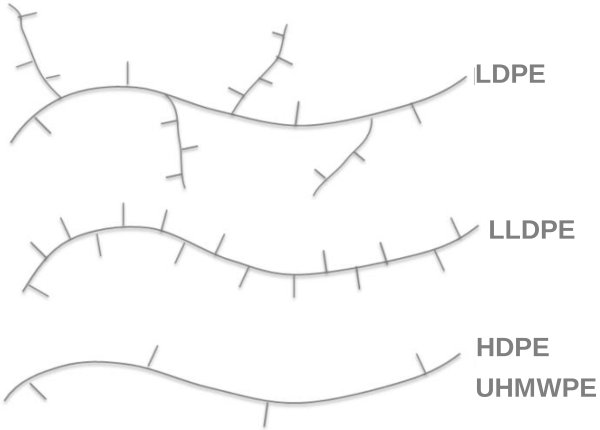


Structural formula of PE

- **Application**
- **Films and foils**
- **Different packaging,** (shampoo, water, containers,…)
- Drainage pipes
- Children's toys and many other products,...

Polyethylene (PE)

- Depending on polymer **chain size and structure**, we distinguish
  - Low-density polyethylene (LDPE)
  - Linear low-density polyethylene (LLDPE)
  - High-density polyethylene (HDPE)
  - Ultra-high-molecular-weight polyethylene (UHMWPE)
  - Crosslinked polyethylene (PEX/XLPE) – **thermoset**



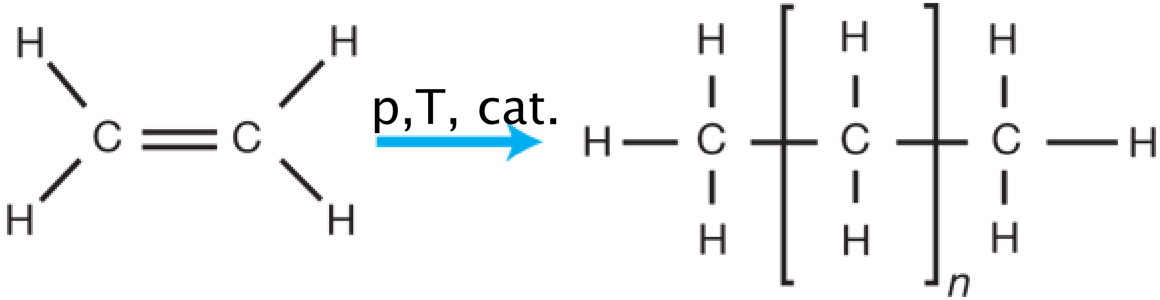
	Mol. weight (1000 gmol^{-1})	Density (g cm^{-3})	Melting point (°C)	Crystallinity (%)
LDPE	<600	0.91–0.93	100–110	30–40
LLDPE	<600	0.92	120–125	40–50
HDPE	200–500	0.94–0.97	130–135	60–80
UHMWPE	3000–6000	0.93–0.94	130–140	60–75

Polyethylene (PE) properties

- **Low strength**, hardness and rigidity, **high ductility and impact strength,** low friction, waxy feel when touched
- Commercial applicability is limited by **low melting point** compared to other thermoplastics
- **Excellent chemical resistance**, not attacked by strong acids and bases, can not be dissolved in organic solvents at room temperature
- **Can be dissolved** (not cross-linked polyethylene) at **elevated temperatures** in aromatic hydrocarbons (toluene or xylene), or in chlorinated solvents (trichloroethane or trichlorobenzene)
- **Absorbs almost no water**
- **Water vapor** permeability is **lower** than for most plastics, **oxygen** and **carbon dioxide can pass it easily**

Polyethylene (PE)

- Polymerization of PE given by schematic equation



Ethylene monomer

Polyethylene polymer

- Free radical polymerization – LDPE
- Ziegler-Natta polymerization - LLDPE
- Ziegler-Natta/Metallocene polymerization – HDPE, UHMWPE

Low-density polyethylene (LDPE)

- First grade of polyethylene produced, process developed in 1933 by Imperial Chemical Industries (ICI) using a **high-pressure process via free radical polymerization** (manufacturing started in 1939), the same method is employed today

- Gaseous ethylene is supplied and mixed with a part of unreacted gas from the process

- An initiator (**organic peroxide**) is into the reactor and the materials are mixed inside the reactor through stirrer

- **Pressure of 100 to 300 MPa, temperature of 200 to 300 °C**

- The unreacted gas is then separated and returned to start of process

- Once the unreacted gas is removed, the polymers can be extruded and pelletized

Low-density polyethylene (LDPE)

- 56 mil tones annual production (2nd after PP)
- **Branched structure**
- It can withstand temperatures of 65 °C continuously and 90 °C for a short time
- It is quite flexible and tough
- **Its most common use is in plastic bags and films**
- For manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic parts for computer components

High-density polyethylene (HDPE)

- **Ziegler-Natta catalysts** to obtain **linear PE chains**
- Ethylene for the synthesis **needs to be very clean**, to contain less then 10 ppm of polar impurities(CO, H_2O, acetylene, CH_3OH), **impurities damage Ziegler-Natta catalysts**

- **Ziegler-Natta catalysts are**:
  - $TiCl_3$ – Titanium (III) chloride
  - $TiCl_4$ – Titanium (IV) chloride
  - VCl_4 – Vanadium (IV) chloride
  - $VOCl_3$ – Vanadium oxytrichloride
  - used together with **co-catalysts** $Al(C_2H_5)_2Cl$ – diethyl aluminum chloride

- **Technological** processes of industrial synthesis are **low pressure methods**
  - **Slurry process**
  - In **solution** *(Du Pont process)*
  - Polymerization in the **gas** phase

High-density polyethylene (HDPE)

- High strength-to-density ratio
- **More crystalline than LDPE**, minimal branching, stronger intermolecular forces and higher tensile strength (38 MPa versus 21 MPa) than LDPE
- **Harder**, less transparent and can withstand higher temperatures (120 °C for short periods)
- **HDPE is resistant to many different solvents**
- Production of **plastic bottles**, corrosion-resistant piping, geomembranes, **chemical containers**, chemical-resistant piping, fuel tanks for vehicles, **water pipes**

Ultra-high-molecular-weight polyethylene (UHMWPE)

- Known as high-modulus polyethylene (HMPE), it has extremely long chains, **molecular mass 3-6 millions**
- The **long chains** of polymers are establishing **strong intermolecular** (bonding),Van der Waals forces between the molecules are relatively weak but because the molecules are very long, with so many Van der Waals forces the intermolecular strength is high
- This causes formation of **tough material**, with the **highest impact strength of any thermoplastic**
- Extremely low moisture absorption, **very low coefficient of friction**, **highly resistant to abrasion**, some forms being **15 times more resistant to abrasion than carbon steel**
- **Very low coefficient of friction**, comparable to polytetrafluoroethylene (PTFE, Teflon), but UHMWPE has better abrasion resistance than PTFE
- Polymerization was commercialized in the 1950s

Ultra-high-molecular-weight polyethylene (UHMWPE)

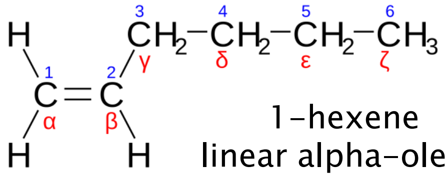
- Application:
- **Fibers**
- Exceptionally strong, **strength-to-weight ratios eight times that of high-strength steels**
- Used in composite plates in **personal armor** (**bulletproof police vests**) and vehicle armor
- The fibers are aligned and bonded into sheets, which are then layered at various angles to give the resulting composite material strength in all directions

- **Sport**
- **Protective clothing** in the fencing, high-performance lines for **sailing and parasailing**, in **archery** widely used as a material for bowstrings, **climbing cords**

- **Medicine**
- **Medical implants, knee joint (low friction coefficient,** self lubricating)

Linear low-density polyethylene (LLDPE)

- **linear** polyethylene, with significant numbers of **short branches**
- Synthesized by copolymerization of **ethylene** with 10 mass% of **comonomer** (**alpha olefins**, butene, hexene, octane)



1-hexene
linear alpha-olefin

- **Ziegler-Nata** catalyst, in solution (comonomer octene), in gas phase (comonomer butene, hexene)
- The result is more regular and **higher crystalline structure, lower index of polydispersity** regarding to LDPE, significantly different melt rheological properties
- **Higher tensile strength** and **higher impact** and **puncture resistance** than LDPE, it can be used to make **thinner films**, with better environmental stress cracking resistance, **not easy to process as LDPE**, lower gloss
- for plastic bags and sheets (thinner than LDPE), plastic wrap, stretch wrap, flexible tubing, geomembranes

Crosslinked polyethylene (PEX/XLPE)

- PEX contains **cross-linked bonds** in the polymer structure, changing the thermoplastic to a **thermoset**
- Used in **pipework systems**, heating and cooling systems, **water piping**, and **insulation for high voltage electrical cab**les, for natural gas and oil applications and transportation of sewage and slurries. Alternative to polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC) or copper tubing for use as residential water pipes
- PEX used **for pipes is made from HDPE**, for wire and **cable applications from LDPE**
- Increased low-temperature impact strength, abrasion resistance, scratch resistance and environmental stress cracking resistance,
- Compared to thermoplastic polyethylene, PEX does not melt (analogous to elastomers) and is thermally resistant (over longer periods up to 120 °C, for short periods up to 250 °C)

Crosslinked polyethylene (PEX/XLPE)

Peroxide crosslinking (PE-Xa) (Engel process)

- The crosslinking using peroxides (e. g. dicumyl peroxide)
- Mixture of **HDPE and** 2% of **peroxide** is mixed in an extruder (**in melt**) and then **crosslinked at high temperatures** (200-250 °C). The peroxide decomposes to peroxide radicals (RO•), which removes hydrogen atoms from the polymer chain, leading to radicals, when these combine, a crosslinked network is formed. The **same process** is used **for LDPE at lower temperature** (160-220 °C)

Silane crosslinking (PE-Xb)

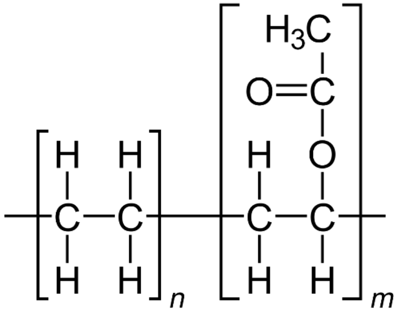
- In the presence of silanes **PE is initially Si-functionalized by irradiation or by a small amount of a peroxide.** Later Si-OH groups can be formed in a hot water bath by hydrolysis, which **condense and crosslink the PE by the formation of Si-O-Si bridges**

Irradiation crosslinking (PE-Xc)

- Crosslinking by a radiation source (usually an electron accelerator)
- Due to high costs minor role compared with the peroxide crosslinking
- In contrast to peroxide crosslinking, the process is carried out **in the solid state**, the cross-linking takes place primarily in the amorphous regions, while the crystallinity remains largely intact

Polyethylene modification by copolymerization

Ethylene-vinyl acetate copolymer (EVA/EVAc)



- **Three** different types of EVA copolymer, which differ in the vinyl acetate (VA) content and the application
- **Low proportion of VA** (< 4%), vinyl acetate modified polyethylene, **thermoplastics material**, properties of a LDPE with increased gloss (useful for film), softness and flexibility
- **Medium proportion of VA** (4 – 30%), **thermoplastic elastomer**, not vulcanized but has some of the properties of a rubber, used as hot melt adhesives
- **High proportion of VA** (greater than 60%) is referred to as ethylene-vinyl acetate rubber, low-temperature toughness, stress-crack resistance, waterproof properties, and resistance to UV radiation

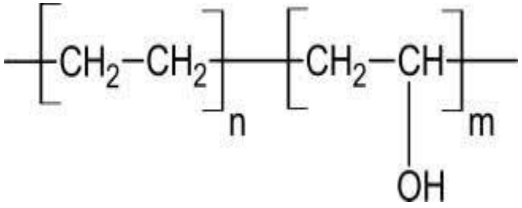
Application

- **Hot melt adhesives**, biomedical engineering as a drug-delivery device, **foam rubber for sports** (ski boots padding, bicycle saddles, hockey pads, boxing gloves)

Polyethylene modification by copolymerization

Ethylene–vinyl alcohol copolymer (EVOH)

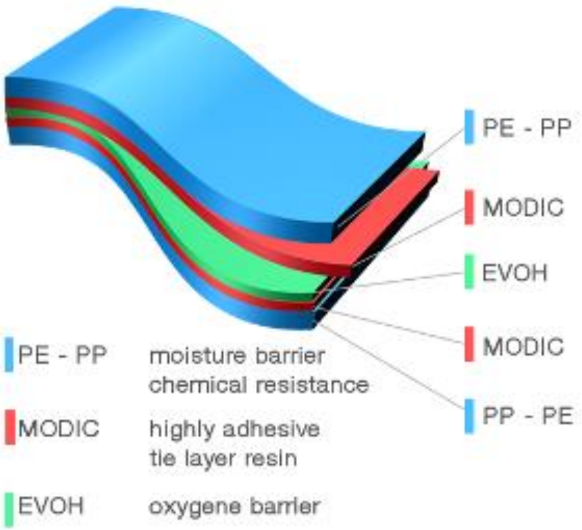
- obtained by hydrolysis of EVA
- excellent barrier properties
- food container
- poor moisture resistance is overcome by coating and lamination with other substrates



$$-\!\left[CH_2-CH_2\right]_n\!-\!\left[CH_2-\underset{OH}{\underset{|}{CH}}\right]_m\!-$$

	Permeation rates ($g/24\ h/100\ in^2$)		
	O_2	CO_2	H_2O
HDPE	110	300	0.5
EVA	170	180	0.9
EVOH	0.01	0.03	2000

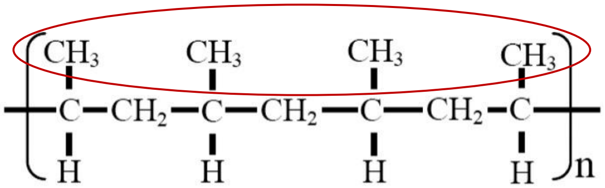
TYPICAL BUILD-UP MULTILAYER BARRIER FILM



Polypropylene (PP)

- First time synthesized in 1951, commercial production from 1957
- **Semicrystalline** and non-polar, properties similar to PE, but slightly harder and more heat resistant
- Second-most widely produced polymer (after PE – all grades)
- **Linear isotactic** polymer was obtained by **Ziegler-Natta** catalysts
- **Ziegler & Natta** obtained Nobel Prize (1963) for that achievement to discover the catalysts for the synthesis for PP polymer

Isotactic:



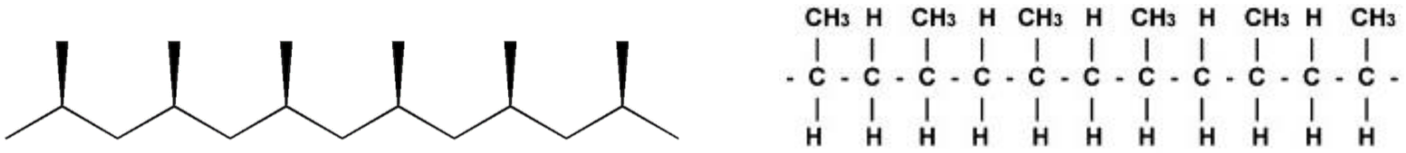
$$\left[\begin{array}{ccccccc} CH_3 & & CH_3 & & CH_3 & & CH_3 \\ | & & | & & | & & | \\ C & -CH_2- & C & -CH_2- & C & -CH_2- & C \\ | & & | & & | & & | \\ H & & H & & H & & H \end{array}\right]_n$$

side group

Polypropylene (PP)

Isotactic PP

- The head-to-tail configuration, in which **$-CH_3$ groups all on the same side** of the chain



$$\begin{array}{ccccccccccc} CH_3 & H & CH_3 & H & CH_3 & H & CH_3 & H & CH_3 & H & CH_3 \\ | & | & | & | & | & | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | & | & | & | & | & | \\ H & H & H & H & H & H & H & H & H & H & H \end{array}$$

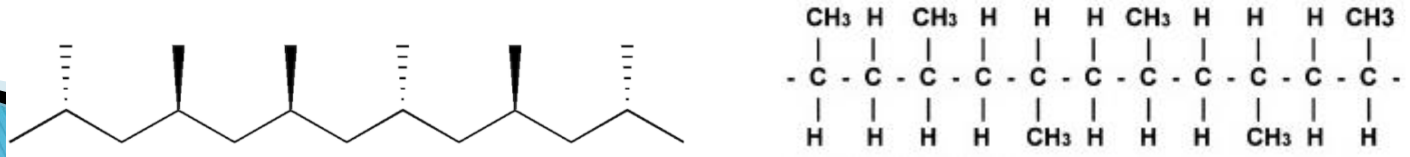
Syndiotactic PP

- **$-CH_3$ groups are in alternating fashion**

$$\begin{array}{ccccccccccc} H & H & CH_3 & H & H & H & CH_3 & H & H & H & CH_3 \\ | & | & | & | & | & | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | & | & | & | & | & | \\ CH_3 & H & H & H & CH_3 & H & H & H & CH_3 & H & H \end{array}$$

Atactic PP

- **Arrangement of $-CH_3$ groups is random** around the main chain



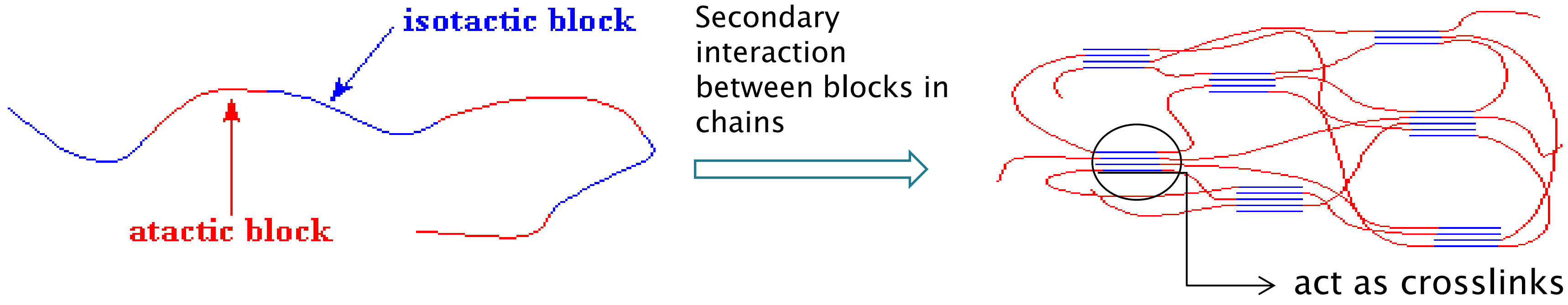
$$\begin{array}{ccccccccccc} CH_3 & H & CH_3 & H & H & H & CH_3 & H & H & H & CH3 \\ | & | & | & | & | & | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | & | & | & | & | & | \\ H & H & H & H & CH_3 & H & H & H & CH_3 & H & H \end{array}$$

Polypropylene (PP)

- **Commercial PP is usually isotactic**
- As the methyl group is consistently located at the same side, it forces the macromolecule in a **helical shape**
- An isotactic structure leads to a semi-crystalline polymer, **the higher the isotacticity (the isotactic fraction), the greater the crystallinity**, and thus the softening point, rigidity, E-modulus and hardness
- Isotactic polypropylene has a **degree of crystallinity 30-60%**
- **Syndiotactic polypropylene** can only be prepared by using metallocene catalysts, has a lower melting point than isotactic
- **Atactic polypropylene** is **amorphous**, has no crystal structure
- It readily soluble even at moderate temperatures, which allows to separate it as by-product from isotactic polypropylene by extraction

Polypropylene (PP)

- PP obtained by **Metallocene** catalysts – possible to synthesize the chains with **isotactic** and **atactic** blocks



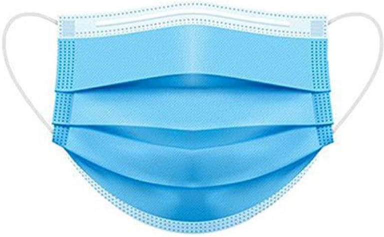
- This PP is named **thermoplastic elastomer** (**TPE**), has the properties of **plastic and rubber**
- At room temp. **elastic** (like rubber)
- At higher temp is **melting** like a plastics
- **Atactic** blocks create **amorphous domains,** and **isotactic** blocks create **crystal domains,** which act as crosslinks

Polypropylene (PP)

- **Application**

- In the household (**containers, packaging, furniture**,…)
- Many **plastic items for medical or laboratory use** can be made from PP because it can withstand the heat in an autoclave

- **Roofing membranes** as the waterproofing top layer
- Manufacture of loudspeaker drive units
- **Concrete additive** to increase strength and reduce cracking and spalling
- **Fibers for carpets, technical fibers, ropes** (PP rope is similar in strength to polyester rope, but costs less)
- In 2020, the demand for PP has increased significantly – vital raw material for producing **fabric for facial masks**



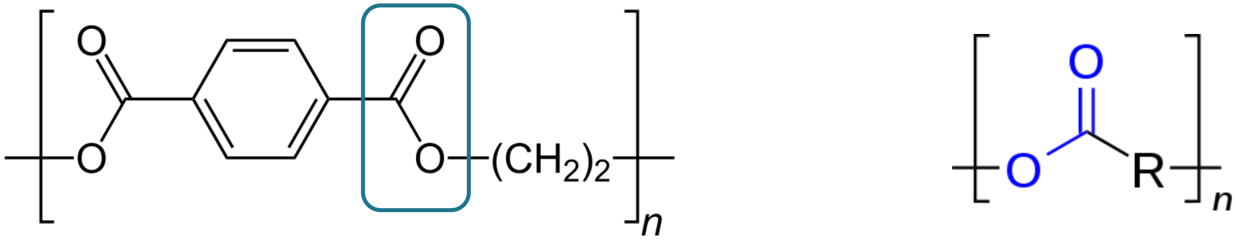
Polypropylene (PP)

- Expanded polypropylene (EPP or XPP)
- Obtained in 2001, manufactured using melt processing with either **chemical or physical blowing agents**
- EPP foam is a structural material in hobbyist radio control model aircraft, it can **absorb impacts without breaking**, retain its original shape, exhibits **memory form characteristics** which allow it to return to its original shape in a short amount of time (Expanded PS breaks easy)

- Biaxially oriented polypropylene (BoPP)
- When PP film is extruded and **stretched in both the machine direction and across machine direction,** biaxial orientation increases **strength and clarity**
- Widely used as a packaging material for snacks and fresh produce. It is easy to coat, print and laminate to give the required appearance and properties for use as a packaging material. **It is one of the most important commercial polyolefin films**

Poly(ethylene terephthalate) (PET)

- PET is most common polymer from polyester family



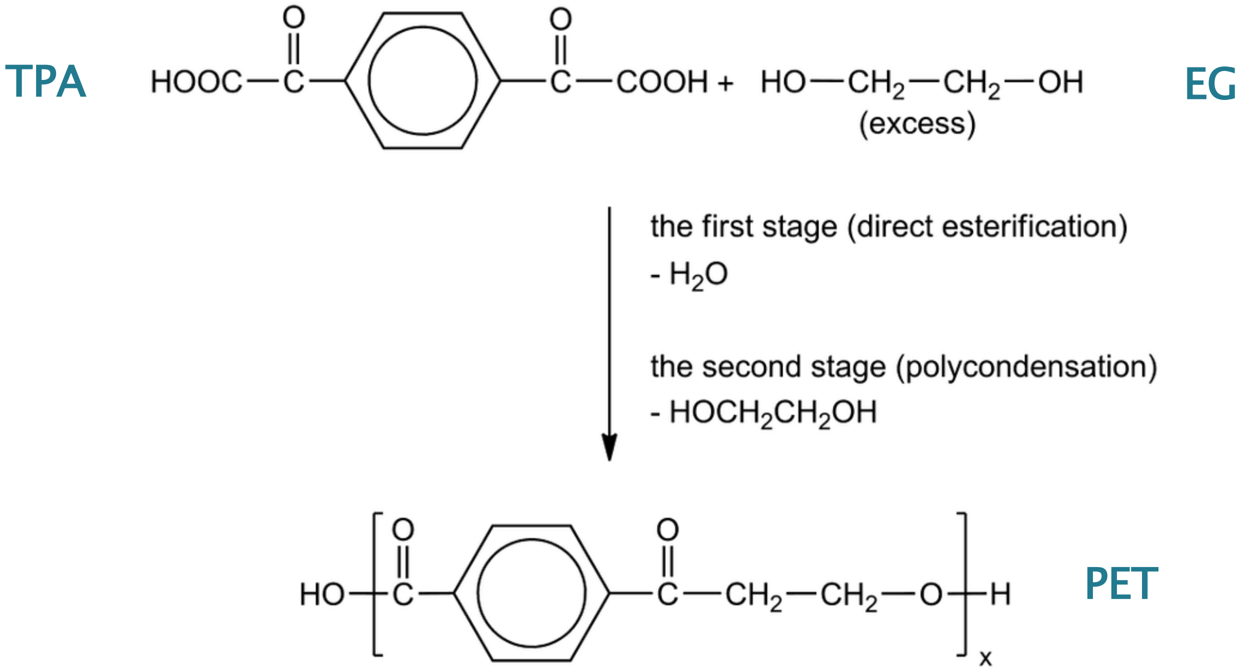
Ester group

- First time synthesized in 1941; mass production started in 1950s

- PET can be synthesized by:
- ❑ Esterification reaction of **ethylene glycol (EG)** and **terephthalic acid (TPA)**
- ❑ Transesterification reaction of **dimethyl terephthalate (DMT)** and **ethylene glycol (EG)**

Poly(ethylene terephthalate) (PET)

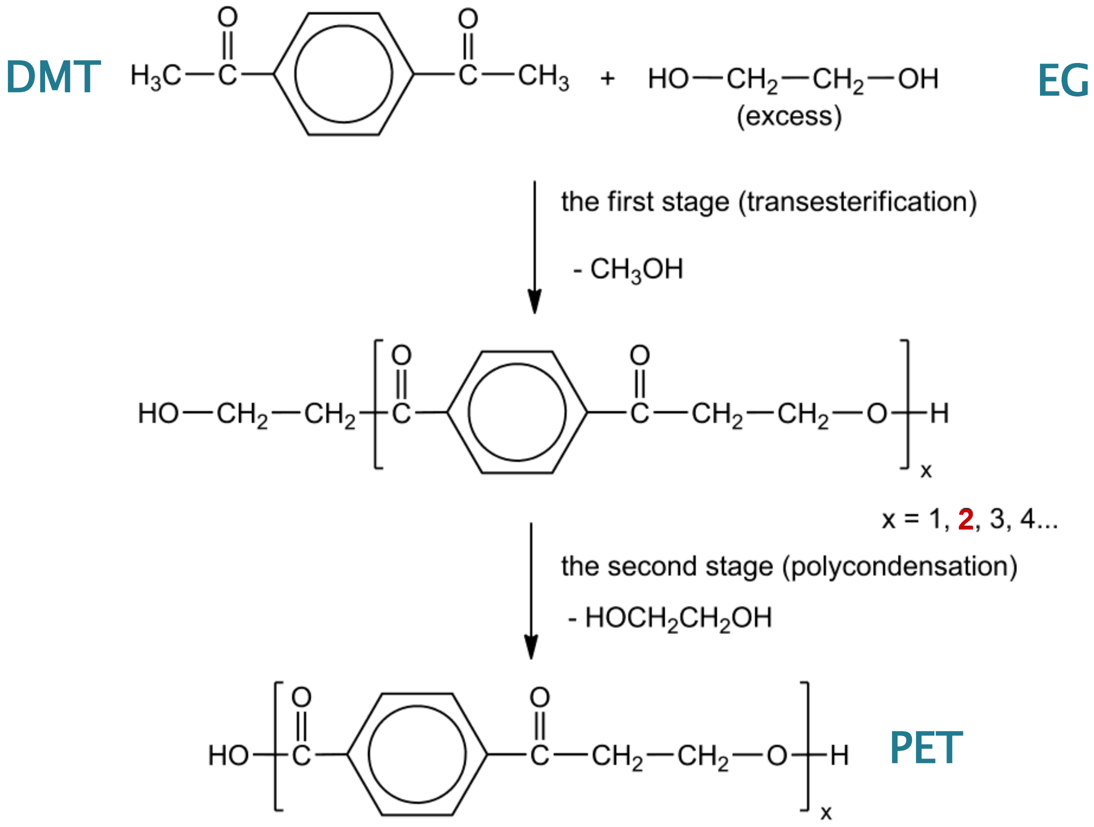
- **Synthesis from TPA & EG**



- **Addition of a catalyst is not required** since the acid group of TPA self-catalyzes the reaction
- When the concentration of acid groups decreases, metal catalysts could be used to maintain the reaction rate

Poly(ethylene terephthalate) (PET)

Synthesis from DMT and EG



conversion of the methyl ester groups of DMT into bis(2-hydroxyethyl)terephthalate (**BHET**), 1 atm, 150–210 °C

High-vacuum (10–50 Pa), 270–280 °C

- **Long reaction times (5–10 h)**, can be decreased by catalyst (acetates of Mg, Zn, Ca in the first step of reaction, antimony trioxide in second)
- Advantages in production from DMT, compared to TPA, is that no aggressive chemicals are used (such as bromides or acetic acid), which eliminates the need for expensive, high corrosion resistant reaction vessels

Poly(ethylene terephthalate) (PET)

- Properties
- Depending on its processing and thermal conditions, PET may exist both as **amorphous** and as **semicrystalline** polymer
- **Transparent** when molten polymer is **rapidly cooled below glass transition temperature** (Tg, 70–80 °C) to form an **amorphous**, glass-like, solid
- When **cooled slowly**, molten polymer forms **more crystalline** material, light tends to scatter on crystallites, scattering means that **crystalline PET is opaque and white**
- **High barrier properties** (CO_2, O_2), fair moisture barrier, and solvents. It is strong and impact-resistant
- **High melting point** (250–260 °C)
- **Hygroscopic**, it absorbs water from its surroundings. When "damp" PET is heated, the **water hydrolyzes the PET**, causing degradation. Before processing in a molding machine, it must be dried
- **Soluble** only in a rather **specialized organic solvents**, such as *o*-chlorophenol, tetrachloroethane, phenol

Poly(ethylene terephthalate) (PET)

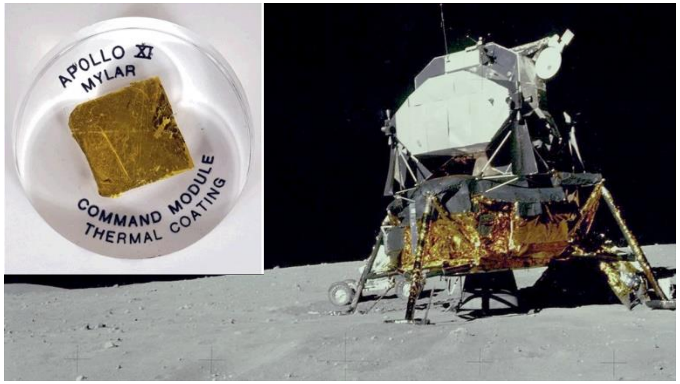
- **Intrinsic viscosity [η]**
- One of the **most important characteristics** of PET
- The intrinsic viscosity of the material is found by extrapolating to zero concentration of relative viscosity to concentration (dL/g)
- **Depends on the length of polymer chains**, the longer the chains the more entanglements between chains and therefore the higher the viscosity

- Fibers
  - ☐ 0.40–0.72, textile
  - ☐ 0.72–0.98, technical, tire cord
- Films
  - ☐ 0.60–0.70, biaxially oriented PET film
  - ☐ 0.70–1.00, sheet grade for thermoforming
- Bottles
  - ☐ 0.73–0.78, water bottles (flat)
  - ☐ 0.78–0.85, carbonated soft drink grade

Example, Intrinsic viscosity (η) of recycled PET (RPET) can be from 0.45 to 0.80 dl/g, **bottles are produced from RPET when [η] is 0.73 dL/g and higher**

Poly(ethylene terephthalate) (PET)

- Application
- **Synthetic fibers** (60% of produced PET) – first time synthesized in 1949
- **Fibers for clothing**, microfiber towels and cleaning cloths
- **BoPET** (biaxially-oriented PET), **high tensile strength,** chemical and dimensional stability, **transparency, reflectivity**, **gas and aroma barrier** properties
- Used for **flexible packaging** and food contact, in balloons, **high performance sails** for sailboats, paragliders, carrier for **flexible printed circuits**
- „Mylar" fabric (made by DuPont)is **metallized** (evaporated Al, Au) **BoPET**, used for **reflecting thermal radiation**, radiation resistant NASA's spacesuits, **emergency blankets** to conserve a shock victim's body heat, **fire shelters** for firefighters

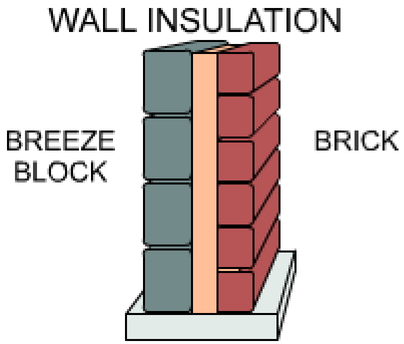


Descent stage of the Apollo's lunar module

fire shelters

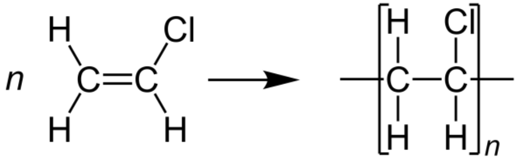
Poly(ethylene terephthalate) (PET)

- Application
- **Bottle production** (30% of produced PET) – first bottle produced in1973
  - ❑ For certain drinks, such as those designated for beer, additional polyvinyl alcohol (PVOH) layer is added between PET layers to further reduce its oxygen permeability
- **Films and foils packaging**
- Containers
- Constructional materials



Poly(vinyl chloride) (PVC)

- Third-most widely produced synthetic plastic polymer (after PE and PP)
- **Known since 1872**, discovered by German chemist Eugen Baumann
- Production was limited by its **extreme rigidity**
- In 1926 commercial application, B.F. Goodrich company developed **method to plasticize PVC** by blending with additives, resulting in **more flexible and easily processed material**



- **Free radical polymerization** (dioctanoyl peroxide, dicetyl peroxydicarbonate)
- **Suspension polymerization (80%)**
- **Emulsion polymerization (12%)**
- **Bulk polymerization (8%)**
- Weight average molar mass 100.000-200.000

Poly(vinyl chloride) (PVC)

- Naturally white and **very brittle**
- Before PVC can be made into finished products, it always requires **incorporation of additives** (**plasticizers**, heat stabilizers, UV stabilizers, thermal modifiers, fillers, flame retardants,…)

- Today is produced with **12 to 50 % of plasticizers**
- **Rigid** or unplasticized polymer (RPVC or uPVC)
- **Flexible** plastic

- **Plasticizers**
- Flexible vinyl products contain **plasticizers which make material softer and more flexible**, and lower Tg, they **increase the space** and act as a lubricant between the polymer chains
- The most common class of **plasticizers used in PVC are phthalates**, which are diesters of phthalic acid

Poly(vinyl chloride) (PVC)

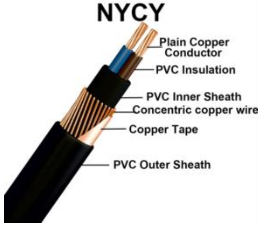
- Properties
- **High hardness**, increased with the molecular weight increasing
- **Very poor heat stability**, addition of a heat stabilizer is necessary, **maximum operating temperature around 60 °C**, good flame retardancy (due to Cl content)
- Good insulation properties but **inferior to PE and PP** (used for medium or low voltage)
- **Resistant to acids, salts, bases,** fats, and alcohols, making it **resistant to the corrosive effects of sewage**, which is why it is extensively **utilized in sewer piping systems**
- **uPVC** (unplasticized PVC) **resistant to some solvents**, **plasticized PVC less resistant** to solvents

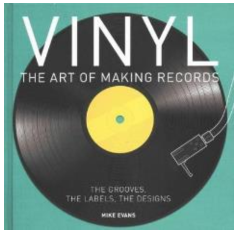
Poly(vinyl chloride) (PVC)

	Rigid PVC	**Flexible PVC**
Density (g/cm^3)	1.3–1.45	1.1–1.35
Yield strength (MPa)	31–60	10–24.8
Elastic modulus (MPa)	1500–3000	1.5–15

- **Rigid**:
- In the **construction**, its **rigidity** and **low flammability** are useful
  - **Pipes (50% of produced PVC)**
  - Window frames
  - Door frames

- **Flexible**
- In combination with plasticizer (as high as 50 %)
  - **Electric cable insulation**
  - Imitation of **leather**
  - Shower curtains
  - Hoses
  - Vinyl records





Poly(vinyl chloride) (PVC)

- Health concerns
- **Plasticizers (phthalates)**
- **Not covalently bound to the polymer matrix, highly susceptible to leaching.** Low molecular phthalates are generally being phased out, high-molecular-weight phthalates such as are generally considered safer
- Alternatives are adipates and esters

- **Heat stabilizers**
- They **minimize loss of HCl**, a degradation process that starts above 70 °C, once it starts, it is autocatalytic
- **Tin mercaptides and derivatives of heavy metals** (Pb, Cd) are widely used in rigid PVC applications

- **Vinyl chloride monomer**
- Vinyl chloride monomer (VCM) was linked to cancers in workers in the polyvinyl chloride industry, technology for removal of VCM from products has become stringent and highly regulated

- **Dioxins**
- PVC is a significant contributor to the formation of both dioxin in incinerators, modern incinerators operate in conditions minimizing dioxin formation

Poly(vinyl chloride) (PVC)

Modification

- **Chlorinated PVC (CPVC)**
- Modified by chlorination of PVC, which **increases its chlorine content to 67-74% (normal PVC 57%)**
- Produced by free radical chlorination reaction of PVC
- Chlorine gas is decomposed into free radical chlorine by exposure to UV light which initiates chlorination of aqueous suspension of PVC particles
- Used in **hotter and more corrosive environments than PVC**
- CPVC can withstand corrosive water at temperatures 40-50 °C higher than PVC
- CPVC is significantly more ductile, allowing greater flexure
- Thermoplastic and has greater insulation than that of Cu pipes, better maintains temperature for both hot and cold water