SYNTHETIC MACROMOLECULAR SUBSTANCES

History:

1. Materials made by chemical modification of natural polymers:

EBONITE (Ch. Goodyear, 1851) = hard rubber made by ..... (treatment with sulphur) of natural rubber, originally – electric insulator
Todays use: bowling balls, mouthpieces for smoking pipes, for demonstrativ .... in physics

NITROCELLULOSE (Parkes, 1856), made by ..... of cellulose, explosive (gun cotton) of limited use (spontaneous explosions)
Nitrocellulose + camphor (plasticizer) (Parkes) = CELLULOID (trade name), more flexible, used for X-rays films and motion picture film base (flexible enough was developed by Goodwin and Kodak) – dangerous, fires during projections, when it burns it does not need oxygen
Nitrocellulose with very low esterification level – table tennis balls, guitare picks

GALALITH = casein (..... protein) + formaldehyde, button industry

CELLULOSE-ACETATE – replaced nitrocellulose in making films, safer

2. Fully synthetic polymers
   FORMALDEHYDE RESINS:
   Phenol-formaldehyde resins (1907, L.H. Baekeland), electric insulator, ebonite substitute
   Urea-formaldehyde – adhesive, moulded objects
   Melamine - cookware

   From 1930: PVC, LD-PE, PS, PTFE, PET, PAD, PAN, Silicones, polymethylmetacrylate
   After WWII: PP, HD-PE
   Polyacetylene

PLASTICS = materials that can be easily shaped and moulded

- **Thermoplastics** = when heated, they can be shaped, this process can be repeated many times
- **Thermosetting plastics** = heated, shaped, when cooled down, they get hard and thermally resistant to any change of shape

POLYMERIZATION

Many monomer units combine to make one long chain, no byproduct is formed, usually molecules with a ..... bond.

Homopolymers = polymers made from monomers of one kind.

Copolymers = polymers made by connecting different monomer units

Plastics made by polymerization:

Polyethene (.....)

Most widely used plastics, packaging

1. *Write the equation for making polyethene*

There are several types of PE:

LD-PE: highly branched, made at high *t* and *p*, with a peroxide initiator, the mechanism is ...., used for e.g. containers and plastic bags

HD-PE: linear or slightly branched, chains packed closely – higher density and withstands higher temperatures, made at lower *p* and *t*, with the help of a catalyst, used for containers, water pipes, ...

Polypropene (.....)

2. *Write the equation for making polypropene.*

There are three types according to the positions of the methyl groups:

- Isotactic
- Syndiotactic
- Atactic

3. *Put these types of polypropene in order with respect to their softness and melting point.*

Properties and uses: tough, flexible, packaging, textiles (ropes, carpets), auto parts,...

Poly vinylchloride (.....)

4. *Write the equation for the polymerization of vinylchloride (chloroethene).*

Properties:cheap, durable, may be made softer and more flexible by adding plasticizers – phthalates (esters of phthalic acid), they are harmful, softened PVC cannot be used for making toys or food containers.

Uses: sewerage pipes, upholstery, electric cable insulation, flooring, window frames,...

5. *Write the formula of phthalic (benzene-1,2-dicarboxylic) acid.*

6. *Use the internet to find the health effects of phthalates.*

Polystyrene (.....)

7. *Write down the equation for the polymerization of styrene (vinylbenzene, phenylethene).*

8. *Polystyrene has two forms: syndiotactic and atactic. Compare their structures. Which one has a higher degree of crystallinity?*

Properties and uses: thermoplastic, hard, brittle, colourless plastic with limited flexibility and low thermal conductivity, used for food and dairy containers, CD cases, drinking cups.

Foam polystyrene: made by adding pentane (or other blowing agents) into polystyrene beads and heating it by steam, light, excellent thermal insulator – used for building insulation, packing, hot drink cups, floating devices,..

9. *Originally CFC's were used to foam polystyrene. Why were they replaced by pentane?*

Polytetrafluroethene (.....) = ...

10. *Write down the equation for the polymerization of tetrafluoroethene.*

Properties and uses: strong plastic with very low friction and very high thermal resistance, used for non-stick coating for cookware or irons, as a lubricant (bicycle chains).

Polyacrylonitrile (.....)

11. *Write down the equation for the polymerization of acrylonitrile (propenonitrile)*

- Homopolymer (acrylonitrile monomers only) - fibrous polymer, used in sails for yachts, awnings,...
- Copolymer (with e.g. vinylchloride or methylacrylate) – knitting yarn (textiles), tents
- Production of carbon fibre

Polybutadien

= synthetic rubber made by polymerization of buta-1,3-diene, used for making car tyres, golf balls,...

12. *Write down the equation for the polymerization of buta-1,3-diene.*

ABS = acrylonitrile butadiene styrene

= copolymer of the three monomers, very strong and light, used for automobile body parts, Lego bricks, pipes,...

Poly(methylmethacrylate) = plexiglas = perspex

13. *Write down the formula of the monomer knowing that its systematic name is methyl 2-methylpropenoate.*

14. *Write down the segment of poly(methylmetacrylate).*

= strong, light material, used as a non-brittle substitute for glass, for making dentures, dental fillings, artificial eye lenses,...

Polyacetylene = polyethyne

15. *Write down the segment of polyethyne.*

16. *Write down the part of the chain of:*
    a. *cis-polyacetylene*

    b. *trans-polyacetylene*

invented in 1970 by Shirakawa, Nobel Prize in 2000 – conductive polymer, when oxidised by I_2, the same conductivity as Ag

<u>POLYCONDENSATION</u>

As well as the molecule of a polymer, small molecules (usually that of water) are released.

Plastics made by polycondensation:

Polyamides

= polymeric substances containing ..... link, natural polyamides = ...

- <u>Aliphatic polyamides:</u>

PA6: $[NH–(CH_2)_5–CO]_n$ Silon, made from caprolactam,

PA66: $[NH–(CH_2)_6–NH–CO–(CH_2)_4]_n$ Nylon

- Aromatic polyamides = aramides: n NH_2 – Ar – COCl →
  Strong, heat resistant fibres – bulletproof vests, asbestos substitute

textile fibres, carpets, sportswear
complete el. insulators→generate static electricity (C, Ag added)

Polyesters

= mainly thermoplastic substances made by polycondenzation of ..... and ....

17. Write down the equation for the polycondenzation of terephthalic acid and ethyleneglycol.

Textile fibres, ropes, safety belts, plastic bottles (PET)

Phenol-formaldehyde resins

= the first commercially used synthetic plastics – Bakelite (1907, Baekeland)
Molecules of phenol are connected by methylene bridges in the positions ortho and para forming a 3D network. Thermosetting plastics, used as circuit boards. Novolacs, resols.

Urea-formaldehyde resins

= non-transparent thermosetting plastics made by polycondensation of urea and formaldehyde used for making adhesives and moulding objects,..

Melamine resins

Thermosetting plastics made by polycondensation of formaldehyde and melamine used mainly for making kitchen utensils or laminate flooring.

Silicones

The most common: polydimethylsilicone (PDMS): $Si(CH_3)_2Cl_2 + H_2O$ →

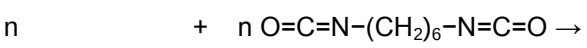
Thermally stable, good electric insulators, resistant to light and oxygen, non-toxic
Side alkyl groups and crosslinking affect the consistency – may be liquids, gels, rubbers or hard solids.
Uses: greases, sealants, bakeware (moulds for muffins), dry cleaning solvents, lubricants, breast implants,...

POLYADDITION

Is similar to polycondensation, i.e. there is a reaction between the functional groups, but there is no side product, there is a transfer of hydrogen atoms only.

Polyurethane

butane-1,4-diol + hexamethylenediisocyanate



$$n \quad + \quad n\ O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O \rightarrow$$

It is used for the production of synthetic leather, fibres and polyurethane foams (molitan).