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Medicinal Chemistry

Marek Bryjak, Irena Gancarz

POLYMERS IN MEDICINE

Wrocław 2011

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PREFACE

It would be a difficult task to imagine the modern world without polymers or plastics. Polymers are everywhere - and this statement is not an exaggeration. Polymers are inside us (proteins, nucleic acids) as well as everywhere around us. The natural polymers were used by people for ages for heating, food, clothing, and in at that time medicine. The 20^{th} century discovered the first synthetic polymers and for this reason it is called the "polymer age". Since the first discovery thousands of new polymeric materials have been developed and applied in all branches of modern technology.

Huge possibilities in synthesis and modification of polymers, ease of their processing, flexibility in design (they can be formed in almost any shape!) and low cost made polymeric materials the most important and of the highest level application in modern biomedicine. Every day, plastics are involved in critical surgery, life-saving efforts, and routine medical procedures. Most of them can be sterilized hundreds of times without degradation, many show biocompatibility and biofunctionality, hence do not cause allergic, mutagenic or inflammatory reactions.

Thanks to easy processing polymers are used to manufacture disposable labware (syringes, medical containers) and elements of medical equipment. Polymers able to form fibers are applied for production of sutures, wound dressing and protective clothing (surgical and isolation gowns, face masks). Polymeric materials are applied on a wide scale for manufacture of all kinds (tissues and whole organs, soft and hard) including prostheses. Biodegradable polymers are used as resorbable sutures, as scaffolding for tissue engineering or in controlled drug release. In pharmacy polymers are used as shells of drugs, allowing for slow release of active substances. Some polymers are themselves used as drugs.

To apply the proper polymer for the particular case knowledge of polymer properties is necessary, hence the first part of this book is an introduction to polymer science.

This part is based on the following sources:

Allcock H.R., Lampe F.W. Contemporary polymer chemistry, 2^{nd} ed., Prentice Hall, Inc. 1990

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Nicholson J.W. The chemistry of polymers, The Royal Society of Chemistry, 2006

Nicholson J.W. The chemistry of medical & dental materials, Royal Society of Chemistry 2002

Odian G.G. Principles of polymerization, 4th ed. John Wiley & Sons, Inc. 2004

Ratner B. D. Biomaterials science: an introduction to materials in medicine, Academic Press, 2004

Rodriquez F. Principles of polymer systems, 4th ed. Taylor & Francis 1996

Stevens M.P. Polymer chemistry. An introduction, Oxford University Press, 1999

In the second part examples of biomedical application of polymers are given. They show the most spectacular use of polymers in medicine and address several questions that need to be answered before applying polymers to these cases. The authors have used the following sources when preparing this chapter:

D.Klee, H.Höcker, Polymers for Biomedical Applications: Improvement of the Interface Compatibility, Adv Polym Sci, vol 149, 2000

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I. INTRODUCTION TO POLYMER SCIENCE

1. DEFINITIONS

Many terms used in polymer chemistry are not known in the other branches of chemistry and for this reason it seems to be necessary to introduce them and define.

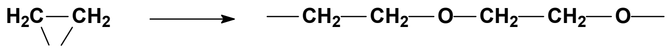
Monomers

A monomer is any substance that can be converted into a polymer. It has to be at least bifunctional, posses multiply C-C bonds, at least two groups that are able to react i.e. OH, NH_2, COOH, or a heterocyclic ring. From bifunctional monomers one usually obtains linear polymers while from tri- or higher functional monomer the crosslinked, tridimensional molecules are formed. The examples of monomers:

ethylene $H_2C{=}CH_2 \longrightarrow$ **polyethylene** $-CH_2-CH_2-CH_2-CH_2-$

amino acid $H_2N-R-COOH \longrightarrow$ **polyamide** $-NH-R-CO-NH-R-CO-$

ethylene oxide

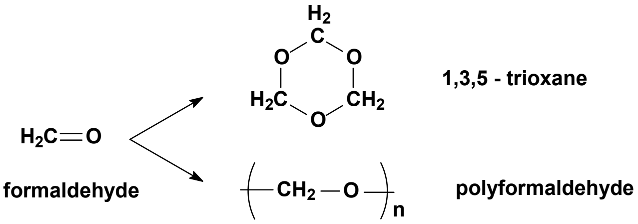


H_2C-CH_2 (with O bridging) $\longrightarrow -CH_2-CH_2-O-CH_2-CH_2-O-$

poly(ethylene oxide)

Oligomers

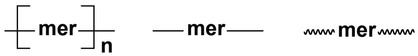
The low-molecular-weight polymerization products are called oligomers. These are for example dimers (the product of two molecules), trimers (three molecules), tetramers (four molecules) and so on. Dimers are usually the linear molecules while the others can be both linear and cyclic:



The degree of polymerization of oligomers is usually from 2 to 20, and molecular weight usually below 10 000 Da. Their properties are different from these of the corresponding high-molecular-weight compounds.

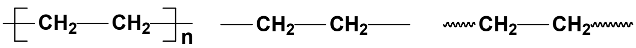
Polymers

A polymer is a large molecule built from many identical elements called monomer units or mers. There are a few ways in which we write down the structure of polymers:



$$\left[\!-\text{mer}-\right]_n \qquad -\text{mer}- \qquad \sim\text{mer}\sim$$

For example the polyethylene can be written as:



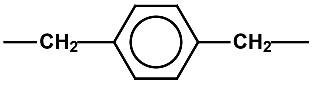
$$\left[\!-CH_2-CH_2-\right]_n \qquad -CH_2-CH_2- \qquad \sim CH_2-CH_2\sim$$

Polymer is a collection of many macromolecules which are not identical chemical compounds; they can differ in molecular weight and chemical structure.

How big has to be a molecule to call it macromolecule or polymer?

The line between oligomer and polymer is not sharp and is set by the material behavior. We can find in the literature such a description as ***low polymers*** *and* ***high polymers***. The former are characterized by molecular weight (M) of 10 000-20 000 Da while for the latter M is higher and sometimes reaches even several million. This distinction is however arbitrary.

The process of polymer synthesis is called polymerization and from the mechanism point of view one can distinguish ***chain-reaction*** and ***step-reaction*** polymerization. ***Linear polymers*** consist of a long chain of skeletal atoms to which are attached the substituent groups. They are linear only in the topological sense, their real shape can be very complicated. The representative of this group of polymers are polyethylene, poly(methyl methacrylate), or poly(vinyl chloride). There are also special types of linear polymer – ***cyclolinear,*** polymers – which are formed by linking together ring systems. Introducing the ring in the chain makes polymer more rigid and thermally stable. The poly(p-xylen) is an example of such polymers:

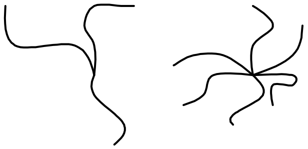


Some polymers have branched chains which are often the result of side reactions during polymerization. A few types of ***branched polymers*** are known:

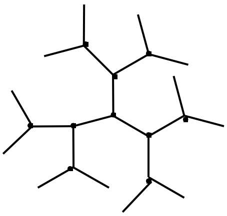
with ***random branches***

comblike polymer

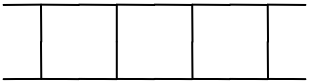
star polymer

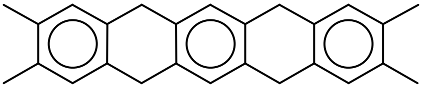


dendrimer

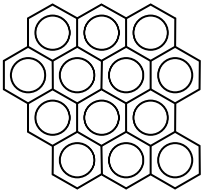


Ladder polymers, as the name suggests, resemble the ladder in which two skeletal strands are linked together in a regular sequence. In practice the aromatic rings may constitute the linking, as illustrated below:

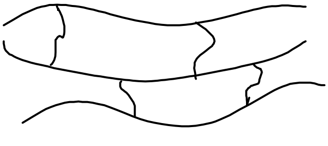




Cyclomatrix polymer it is a system of connected rings that form a tridimensional matrix. Such polymers are rigid, insoluble and thermally stable. The special example of such polymer is graphite.



Crosslinked or ***network polymers*** are ones in which chemical linkages exist between the chains.



Crosslinking can happen during the polymerization reaction when the monomers of functionality higher than 2 are used or in the post-polymerization process, for example vulcanization.

The crosslinking bonds are usually covalent therefore those of the highest bonding energy. The obtained polymer is then dimensionally stable, it is swelled by solvents but does not dissolve, it does not melt and can not be formed.

When the distance between two points of crosslinks is big the net is **loose**, its swelling in the solvents is significant and polymer shows the elastomeric behavior (vulcanized rubber). Crosslinks between the chains prevent the macromolecules from slipping past each other and thus prevent the macromolecules from becoming permanently elongated when held under tension. The opposite case – **dense network** – are rigid and their swelling in the solvents is insignificant.

Homopolymer is a product of polymerization with the use of only one type of monomer.

Copolymers are polymers synthesized from two or more various monomers. The sequence of monomer units along a copolymer chain depends on a method and mechanism of the synthesis. Three different types of sequencing arrangements can be found:

- ***random copolymers*** in which no definite sequence of monomer units exists:

-A-B-B-B-A-A-B-A-A-A-A-B-A-B-B-B-

- ***alternating copolymers*** containing regular, alternating sequence of two monomer units:

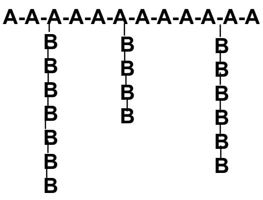
-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

- ***block copolymers*** contain a block of a one kind of monomer connected to a block of another:

-A-A-A-A-A-A-B-B-B-B-B-B-B-B- diblock

-A-A-A-A-A-A-A-B-B-B-B-B-A-A-A-A-A- triblock

A different structure have ***graft copolymers***, in which side polymer chains are built from a different polymer than the main polymer chain:



Degree of polymerization and molecular weight of polymer

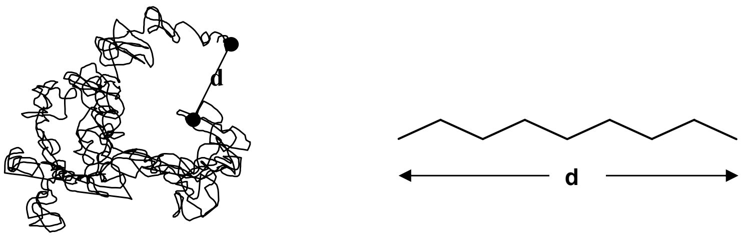
The structure of typical linear polymer can be written as Y – M_n – Y; where Y is an end group, n is the degree of polymerization (DP). For long chains the end groups do not play any role and often their nature is not known. The molecular weight of such a molecule equals n x M (M = molecular mass of the mer). In the process of polymerization molecules of various length (hence molecular weight) are produced hence the values of ***average molecular weight*** and ***molecular weight distribution*** are in use.

Configuration, conformation

The geometric arrangement of the atoms in a polymer chain can be divided into two categories:

- ***configurations*** – arrangements fixed by the chemical bonding (for example *cis* and *trans* isomers); they cannot be altered unless chemical bonds are broken and reformed,
- ***conformations*** – arrangements arising from the rotation about single bonds; it is the real shape of the polymer molecule.

In a flexible macromolecule the rotation of bonds in the main polymer chain is easy and frequent and such a chain has the conformation of ***Gaussian coil*** (Fig.1.1a) which is characterized by ***end-to-end distance*** (d - much lower than the length of a totally extended molecule) and ***radius of gyration***. The rigid macromolecule is extended and its conformation reminds rather a bent rod (Fig.1.1 b) and the average end-to-end distance is close to the molecule length.



a

b

Fig. I/1.1. Polymer conformations: a – coil. b - extended chain

Tacticity

Some monomers that contain one unique group (for example propylene, styrene) yield polymers that possess an asymmetric center on each monomer residue. The tacticity of a polymer describes the sequencing of these asymmetric centers along the chain. One can distinguish three main possibilities – ***isotactic, syndiotactic*** and ***atactic*** (heterotactic) sequencing. The tacticity of a polymer strongly influences its properties.

Polymer morphology

Polymers exhibit two types of morphology in the solid state: ***amorphous*** and ***semicrystalline (microcrystalline)***. In an amorphous polymer the molecules are oriented randomly and are intertwined, much like cooked spaghetti; the arrangement of molecules has no long-range order or form in which the polymer chains arrange themselves. Amorphous polymers are generally transparent. In semicrystalline polymers, the molecules pack together in ordered regions called ***crystallites***. Polymers are never crystalline in 100% (hence the name semicrystalline).

Linear polymers, having a very regular structure, and these possessing polar groups are more likely to be semicrystalline. Semicrystalline polymers tend to form very tough materials because of the strong intermolecular forces associated with close chain packing in the crystallites. Also, because the crystallites scatter light, they are more opaque. The crystallinity of the polymer is a necessary condition to use it for fiber manufacture.

Resins

It is polymer that is useful only after crosslinking. Epoxy resins or phenol-formaldehyde resins can serve as examples.

Thermoset - thermoplast

Thermoset resin are polymers which exist initially as liquids but which, on heating, undergo a hardening process to form a solid, highly crosslinked matrix (for example resol – phenol-formaldehyde resin). There is also a group of polymers in which curing is affected by the reaction with some chemical compounds (for example epoxy resins). The curing process creates a chemical bond that prevents the material from being remelted.

Thermoplastic polymer always softens (and finally become a viscous liquid) when it is heated, and solidifies when cooled.

Elastomer

Any material, such as natural and synthetic rubber which has the ability to undergo deformation under the influence of a force and quickly regain its original shape once the force has been removed.

Polymers - plastics

Polymers are rarely used in a pure form, usually they are mixed with various additives to improve or tailor their properties. These mixtures from which the definite products are formed are named ***plastics***. Among ***additives*** one can find:

- plasticizers - the compounds that soften some rigid polymers,
- stabilizers - antioxidants, thermal and photo-stabilizer,
- other modifiers - impact strength modifiers, antistatics, antiadhesives, antipirens.

Polymer composites are products made from polymer and other constituent material with significantly different physical and/or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. Well known are the composites of epoxy resin with glass or carbon fiber.

Polymer biocompatibility

The term "biocompatibility" describes the suitability of a material for the exposure to the human body or body fluids. The polymer is biocompatible if its contact with the living organism does not cause allergic reaction, chronic inflammation, cell disruption, thrombosis and is not toxic to the cells.

2. BASIS OF POLYMER PHYSICS

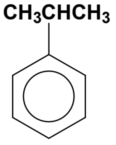
2.1. POLYMERS IN SOLUTION

To determine the molecular weight of polymer and other polymer properties it is necessary to find the proper solvent and dissolve the polymer in it. The dissolution of a polymer in a solvent takes place in two distinct stages:

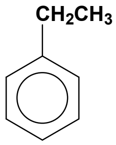
- the polymer "takes up" a solvent, and expands to a swollen gel; this first stage is common for all amorphous (linear, branched and lightly crosslinked) polymer samples,

- the swollen gel breaks-down giving the solution of polymer molecules in the given solvent; this stage never occurs for crosslinked polymers and may not be shown by microcrystalline polymers.

The old rule says that "like dissolves like". According to this rule cumene (1) and ethylbenzene (2) should be good solvents for polystyrene (3):



1



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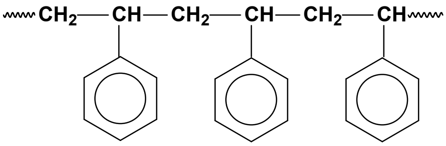


3

It means that a liquid should be a good solvent for polymer if the molecules of the liquid chemically and physically resemble the structural units of the polymer. In this case the adhesive forces between the solvent and the polymer are similar to the cohesive forces that exist between the solvent molecules or between the polymer molecules. Hence the exchange of a solvent molecule by a polymer structural unit goes with little or no change in the interaction forces that exist between solvent and polymer molecules. Heat of mixing is then negligibly small.

The more scientific way to find the solvent for the chosen polymer uses the **solubility parameter** δ which is defined as square root of ***cohesive energy density***:

$$\delta = \sqrt{\frac{E_0}{V_0}}$$

where E_0 – is the energy of vaporization for a molar volume V_0 of the substance in question. The enthalpy change per unit volume during mixing (that is a necessary clause of dissolution) is given by Hildebrand's equation:

$$\Delta H_m = \phi_1 \phi_2 V_m (\delta_1 - \delta_2)^2$$

where ϕ_1 and ϕ_2 are volume fractions of solvent and polymer in solution respectively, V_m is the volume of the system. To dissolve polymer ΔH should be close to zero hence cohesive energy densities of the polymer and the solvent should be very close. It is believed that dissolution is possible when this difference is not higher than 3.5-4 $[\text{cal/cm}^3]^{1/2}$. However, this clause is necessary but not sufficient as solubility of polymer depends also on other parameters as for example, its crystalline degree.

The other measure of the possibility of polymer dissolution is the value of the ***interaction parameter*** χ. It comes from Flory-Huggins theory according to which the enthalpy of mixing solvent and polymeric solute can be expressed as:

$$\Delta H_m = RT\chi \phi_1 \phi_2$$

The interaction parameter is the energy change (in units of RT) that occurs when a mole of solvent molecules is removed from the pure solvent (where $\phi_2=0$) and is immersed in an infinite amount of pure polymer (where $\phi_2=1$). χ is positive (dissolution of a polymer in a solvent is an endothermic process) and depends on temperature. Usually when χ for the pair of polymer-solvent is equal or lower than 0.5, polymer is soluble in this solvent.

2.2. MOLECULAR WEIGHT OF POLYMERS

Definitions

The molecular weight is the one of the most important features of polymers which is necessary to understand the relations between the structure and properties. Many properties and applications of polymers are the consequence of their long chains. The length of the polymer chain is a control factor in solubility, elasticity, mechanical properties, ability of fibres production and other properties of polymers. The determination of polymer molecular weight however is not as easy as for the low-molecular-weight organic molecules. The problems come from choosing the right solvent, from polydispersity of polymer molecules and from the fact, that various determination methods give different values of M.

Because of the existence of the distribution in any finite sample of polymer, the experimental measurements of molecular weight can give only an average value. Several different averages are important.

Number-average molecular weight $\overline{M}_n$

$$\overline{\boldsymbol{M}}_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \sum_i x_{ni} M_i$$

where: N_i – number of molecules of the i^{th} kind, M_i – mass of the molecule of the i^{th} kind, x_{ni} –number of fraction.

The number-average-molecular-weight of polymer is determined by methods that “count” the number of molecules in known mass of the material. This average is used mainly for the kinetic investigations.

Weight-average molecular weight $\overline{M}_w$

$$\overline{\boldsymbol{M}}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \sum_i x_{wi} M_i$$

Here each molecule contributes to molecular weight in proportion to the square of its mass.

Heavy molecules contribute more than light ones hence for polydispersive polymers M_w is always greater than M_n. This average is very important as it informs about the possible application of polymers.

Viscosity-average molecular weight $\overline{M}_\eta$

$$\overline{M}_\eta = \left[\frac{\Sigma_i N_i M_i^{1+\alpha}}{\Sigma_i N_i M_i}\right]^{1/\alpha}$$

α is not a universal constant; it depends on the kind of polymer and solvent.

Viscosity-average molecular weight lies between the number- and weight-average molecular weight but is closer to M_w.

$$\overline{M}_n < \overline{M}_\eta < \overline{M}_w$$

When $\boldsymbol{\alpha}$ equals 1, viscosity-average and weight –average-molecular-weights are equal.

Polydispersity degree – width of molecular weight distribution (**MWD**) - is defined as

$$\mathbf{M_w/M_n}$$

MWD is equal: 1 – for monodisperse polymer,
1.5 - 2 – for chain polymerization,
2 – for polycondensation,
2 - 5 – for high monomer conversion,
20-50 – for highly branched polymer.

For monodispersive polymers (for example some biopolymers):

$$\overline{M}_n = \overline{M}_\eta = \overline{M}_w$$

Methods of determination

Two fundamentally different approaches are used for the measurement of polymer molecular weights – the absolute (end group analysis, ebuliometric and crioscopic methods, osmometry, light scattering, ultracentrifugation) and the secondary (solution viscosity, gel permeation chromatography) methods. The absolute methods provide a direct estimation of molecular weight while the secondary methods must be calibrated by the reference to a system which M was determined by the one of the absolute methods.

Analysis of the end groups

The method is useful only for low-molecular-weight polymers ($\overline{M}$ below 25 000 Da), those, which end groups are known. Hydroxyl and carboxyl groups are the most often determined for this purpose.

Ebullioscopy - measurements of the boiling point elevation and ***cryoscopy*** – the freezing point depression. Both methods are used for polymer of rather low molecular weight but the real limit of the determined molecular weights depends on the accuracy of measurement of the temperature difference. With the use of thermistors this difference of 0.0001°C can be measured and $\overline{M}$ up to 50 000 can be determined. The molecular weight is calculated from the formula:

$$\lim_{c \to 0} \frac{\Delta T}{c} = \frac{RT^2}{\rho \Delta H} \frac{1}{\overline{M}_n}$$

where:

ΔT – difference between the temperature of boiling (freezing) of solvent and solution,

c – solute concentration g/cm^3, ρ – solvent density,

ΔH – enthalpy of vaporization (fusion) of the solvent per gram

Osmometry – osmotic pressure measurements

This is the most important method to measure a number-average-molecular-weight of polymer. The method can be used in the range of $\overline{M_n}$ 3x10^4 to 1x10^6 Da of polymer. Two techniques of osmometry are known – the membrane osmometry and the vapor-phase osmometry.

Membrane osmometry

When the solution and solvent are separated by a semipermeable (only solvent is able to penetrate through it) membrane (Fig. 2.2.1) a hydrostatic pressure called osmotic appears. It is caused by the diffusion of solvent molecules into the polymer solution to get equilibrium of the solvent activity in these two compartments. The long time to establish the equilibrium and problems with choosing the right membrane are main disadvantages of the method.

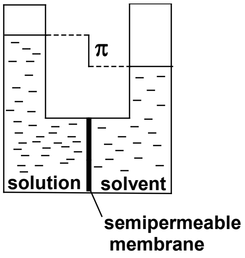


Fig.2.2.1. The scheme of membrane osmometer

From the osmotic pressure values measured for a few polymer solutions of several concentrations, the number-average-molecular-weight can be calculated:

$$\lim_{c \to 0} \frac{\Pi}{c} = \frac{RT}{\overline{M}_n}$$

where: Π – osmotic pressure of the solution

Vapor-phase osmometry is used to measure $\overline{M}_n$ of samples too low in molecular weight to be measured in a membrane osmometer (up to 40 000 Da). In this method the temperature difference resulting from different rates of solvent evaporation from and condensation onto droplets of pure solvent and polymer solution is measured. The method is rapid and only a few milligrams of a sample is required.

Light scattering

When a beam of the monochromatic light traverses a system and no absorption of light occurs, the transmission is still not complete. A fraction of the incident light is scattered and a resultant attenuation of the intensity of the incident light occurs. The decrease in the intensity of a beam of light because of scattering is used to define the turbidity of a solution.

From the turbidity data of several polymer solutions of varying concentration one can calculate the weight-average-molecular-weight of polymer. The knowledge of refractive index differences between solutions and pure solvent is necessary. The solution has to be carefully cleaned from all suspended dust particles which may produce greater scattering.

Ultracentrifugation

The sedimentation rate of polymer from solution under the influence of gravity is vanishingly small. Elaborate ultracentrifugation techniques must be used to supply the much larger acceleration needed.

Two techniques are used – sedimentation velocity and sedimentation equilibrium. In the ***sedimentation equilibrium*** experiment, the ultracentrifuge is operated at a low speed of rotation for times up to 1 or 2 weeks (the major disadvantage of the method) under constant condition. A thermodynamic equilibrium is reached in which the polymer is distributed in the cell solely according to its molecular weight and molecular-weight distribution.

In the ***sedimentation velocity*** experiment, the ultracentrifuge is operated at high speed so that the solute is transported to the bottom of the cell. The knowledge of the sedimentation constant and diffusion coefficient is necessary.

Both techniques allow for the estimation of weight-average molecular weight. Although ***ultracentrifugation*** is the most elaborate, expensive, and time-consuming technique for the determination of polymer molecular weights, it is perhaps the most versatile of all the absolute methods. It has been used very extensively for molecular weight determination of **biological polymers such as proteins**.

Viscometry

It was observed that even a low concentration of a dissolved polymer markedly increased the viscosity of a solution relative to that of the pure solvent. This increase is caused principally by the unusual size and shape of the dissolved polymer and by the nature of solutions of high polymers. The shape of most polymers reminds random, statistical coils which in diluted solutions are completely solvated by the solvent molecules. On the basis of the size of these solute ‘particles”, polymer solutions are correctly classified as *colloidal dispersions*.

The base of the method is the measurement of viscosity of a few polymer solutions of various concentrations. In the most commonly used Ostwald or Ubbelohde viscometers the time required for the determined volume of liquid to flow through the capillary is measured.

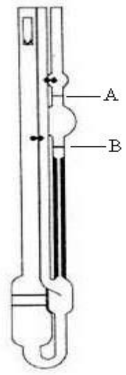


Fig. 2.2.2.
Ubbelohde viscometer

The following parameters are calculated:

- relative viscosity – $\eta_r = t/t_0$ where t, t_0=time of the polymer
- solution and solvent flow, respectively
- specific viscosity - $\eta_{sp} = \eta_r - 1$
- reduced viscosity = η_{sp}/c

Intrinsic viscosity [η] is defined as the limit of the reduced viscosity as the concentration approaches zero, and is given by:

$$[\eta] = \lim (\eta_{sp}/c)_{c \to 0}$$

Molecular weight of the polymer is calculated from the equation:

$$[\eta] = K M^{\alpha} \qquad \text{with} \qquad 0{,}5 < \alpha < 1$$

K, α- are the function of solvent, polymer and T and for most polymers can be found easily.

It is the easiest and cheapest method of molecular weight determination, willingly used in the industry.

Gel permeation chromatography

The gel permeation chromatography (GPC) method is essentially a process for the separation of macromolecules according to their size. The principle of the method is as follows. The polydispersive polymer (containing molecules of different size) is eluted in a solvent through a column filled with porous particles. The small molecules can enter the pores and be retarded, whereas the large ones are swept through relatively unhindered. The smaller molecule is the more pores it penetrates and its retention time is longer. The molecules will emerge from the column in sequence, distributed according to molecular size.

The molecular weight cannot be determined directly, but only after calibration that requires the establishment of a relationship between the retention volume and molecular weight of monodisperse fractions of polymer. As such monodisperse polymers are not generally available, lately the ***universal calibration*** ([η]M as a function of retention volume) is often used. GPC allows for the determination of the molecular weight distribution.

2.3. MACROMOLECULES IN A CONDENSED STATE

Morphological changes in polymers

Elementary physics divides matter into three quite distinct categories: solids, liquids, and gases. Most polymers however are neither classical solids nor liquids. They are ***viscoelastic*** materials that show characteristics of both the solid and liquid states.

Viscous materials resist shear flow and strain linearly with time when stress is applied. ***Elastic*** materials strain instantaneously when stretched and just as quickly return to their original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, the ***exhibit time dependent relationship between the stress and strain***.

The source of such behavior of polymers are the conformational properties of a polymer chain and counteract among them. In low temperatures polymer behave as hard and brittle as glass – in material dominate elastic elements (***glassy state***). Molecular motions in such conditions – oscillation of atoms, chemical bonds or small groups - are of short distance. With the raising temperature molecular motion of chains' fragments become possible what leads to retrievable deformation. Polymer goes into flexible, ***rubbery state***. In a high enough temperature the elasticity disappears and polymers become the ***viscous liquid***. The molecular motions in such conditions include the movement of whole macromolecules what causes the unlimited and irretrievable polymer deformation (flowing liquid).

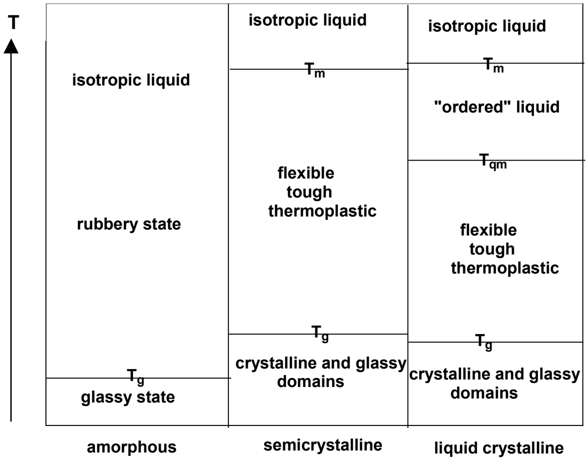


Fig.2.3.1.

Changes undergoing in polymers when heated

T_g – glass temperature,

T_m –melting temperature,

T_{qm} – quasi melting transition

Most of long-chain synthetic polymers show a characteristic sequence of changes as they are heated (Fig.2.3.1). These changes are different for ***amorphous, semicrystalline*** and ***liquid crystalline*** polymers. However all polymers are glass at low temperatures. The point at which the polymer changes from glass to rubber is known as ***glass temperature*** T_g.

The glassy state

Both amorphous and crystalline polymers in low temperatures are in a glassy state. Typical polymers used in their glassy state are polystyrene, polycarbonate or poly(methyl methacrylate). They are dimensionally stable and do not creep. As thin films they are flexible, but they are not elastomeric. They are used mostly as structural materials hence high impact strength is highly desirable. However polymer in the glass state are easy to shatter for example by a sharp blow with a hammer. This brittleness is connected with the fact that even a small fracture is propagated through polymer. The breaking bonds is the only mechanism of dissipation of the impact energy.

There are some methods to overcome this problem:

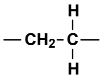
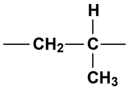
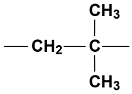
- crosslinking – it increases the number of bonds which have to be broken to destroy polymer,
- addition to the polymers' fine particles – they are able to interrupt the propagation of cracks
- preparation of a system that possesses both glassy and elastomeric domains for example a block copolymer of glassy (polystyrene) and elastomeric (polybutadiene) polymers.

The ***glass transition temperature*** is characteristic of a particular polymer in much the same way that the melting point is characteristic of an ordinary low-molecular-weight compound. To a high degree the properties and the practical utility of polymers depend on their glass temperatures.

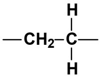
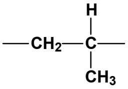
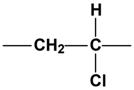
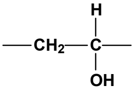
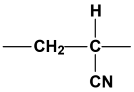
There is a close connection between T_g and the flexibility of the polymer chain. The flexibility on a macroscopic scale depends by turns on torsional mobility at the molecular level. If the chain is rigid, the T_g value will be high, and otherwise, if the chain is flexible, one can expect low value of glass temperature. The torsional mobility hence T_g will depend also on the presence, size, and polarity of side groups. Even the chain length has an effect – T_g raises with increasing molecular weight until a limiting value is reached. Crosslinking, chain branches, orientation of polymer and the presence of plasticizer also increases T_g.

The presence of one side group causes the rise of T_g but the effect of symmetry of the repeated units is opposite (Table 2.3.1a). The effect of polar group is significant in raising Tg of polymers (Table 2.3.1b).

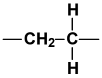
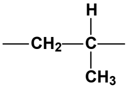
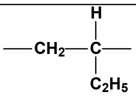
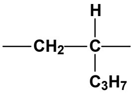
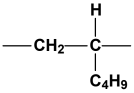
Table 2.3.1. Dependence of glass temperature of polymers on their structure

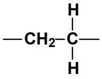
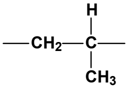
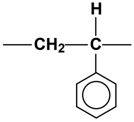
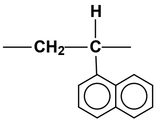
symbol	structure	T_g
PE - polyethylene	 $-CH_2-\overset{H}{\underset{H}{C}}-$	**- 80**
PP - polypropylene	 $-CH_2-\overset{H}{\underset{CH_3}{C}}-$	**- 20**
PiBu - polyisobutylene	 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$	**- 73**

a

symbol	structure	T_g
PE - polyethylene	 $-CH_2-\overset{H}{\underset{H}{C}}-$	**- 80**
PP - polypropylene	 $-CH_2-\overset{H}{\underset{CH_3}{C}}-$	**- 20**
PVC - poly(vinyl chloride)	 $-CH_2-\overset{H}{\underset{Cl}{C}}-$	**+ 80**
PVA - poly(vinyl alcohol)	 $-CH_2-\overset{H}{\underset{OH}{C}}-$	**+ 85**
PAN - polyacrylonitrile	 $-CH_2-\overset{H}{\underset{CN}{C}}-$	**+ 105**

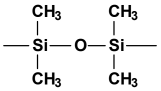
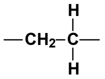
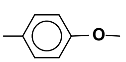
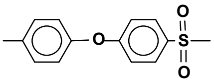
b

symbol	structure	T_g, °C
PE - polyethylene	 $-CH_2-\overset{H}{\underset{H}{C}}-$	**- 80**
PP - polypropylene	 $-CH_2-\overset{H}{\underset{CH_3}{C}}-$	**- 20**
poly(butene-1)	 $-CH_2-\overset{H}{\underset{C_2H_5}{C}}-$	**- 24**
poly(pentene-1)	 $-CH_2-\overset{H}{\underset{C_3H_7}{C}}-$	**- 40**
poly(hexene-1)	 $-CH_2-\overset{H}{\underset{C_4H_9}{C}}-$	**- 50**

symbol	structure	T_g, °C
PE - polyethylene	 $-CH_2-\overset{H}{\underset{H}{C}}-$	**- 80**
PP - polypropylene	 $-CH_2-\overset{H}{\underset{CH_3}{C}}-$	**- 20**
PS - polystyrene		**+100**
poly(a-vinyl naphtalene)		**+135**

d

c

symbol	structure	T_g, °C
PDMS **polydimethylsiloxane**	 $-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-$	**-123**
PB **cis 1,4- polybutadiene**	$-CH_2-CH{=}CH-CH_2-$	**-108**
PE - polyethylene	 $-CH_2-\underset{H}{\overset{H}{C}}-$	**- 80**
PEO **poly(ethylene oxide)**	$-CH_2-CH_2-O-$	**- 67**
PPO **poly(phenylene oxide)**		**+83**
PSU- polysulfone		**+250**

e

At the beginning, with the size of the side group effect of increasing T_g is observed; later on the opposite trend takes place (Table 2.3.1c). Aromatic rings both as side groups (Table 2.3.1d) and present in the main chain (Table 2.3.1e) make the chain much stiffer and more rigid and this is the reason for higher values of T_g.

A single double bond and oxygen in the main chain makes the chain very flexible what gives very low T_g (Table 2.3.1e).

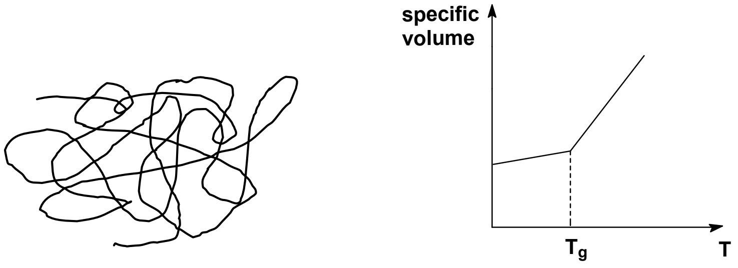
There are several methods of T_g determination:

- penetrometer – sharp point rests on the sample surface which temperature is raised; in T_g it penetrates the surface as material from hard and glassy becomes soft and flexible,
- torsional rigidity method – the resistance to torsion and the energy loss of the polymer is measured as a function of temperature; a drastic loss in rigidity hence a sharp maximum in the damping curve is observed in T_g,
- broadline NMR – the NMR line width dramatically changes in T_g of the material,
- dilatometry – change of a slope of volume versus temperature plot is used to identify T_g,
- DTA and DSC – the most popular technique for the measurements of glass temperature; both are based on the fact, that in T_g, the specific heat of polymer rapidly changes.

Polymers between glassy and liquid state

Amorphous polymers

An amorphous polymeric material contains randomly entangled chains without any degree of ordering (Fig. 2.3.2a).



a b

Fig. 2.3.2. Amorphous polymer: a – polymer chain, b – dependence of specific volume of polymer on temperature

Below the glass temperature they have many of the properties associated with ordinary inorganic glasses, including hardness, stiffness, brittleness, and transparency. Amorphous polymers heated above T_g pass successively through rubbery, gumlike and finally liquid states with no clear demarcation between the different phases (Fig. 2.3.1. and 2.3.2b). The amorphous polymers used above their T_g are named ***elastomers*** or sometimes rubbers.

The pure elastomers are usually too soft and extensible for any applications and have to be lightly crosslinked. Crosslinks between the chains prevent the macromolecules from slipping past each other and thus prevent the material from becoming permanently elongated when held under tension. They behave like liquids – they change the shape or flow easily under even small stress but unlike liquids return to its original length immediately after the release of stress (Fig. 2.3.3). Such behavior is a consequence of high torsional mobility of the backbone bonds of the polymer. As a response on the external force they change their conformation from coiled to extended and when the tension is released - the chains revert to the highly coiled state to assure the maximum entropy for the system.

Elastomers are characterized also by two other features – they are ***resilient*** and ***swell*** in solvents to a remarkable degree.

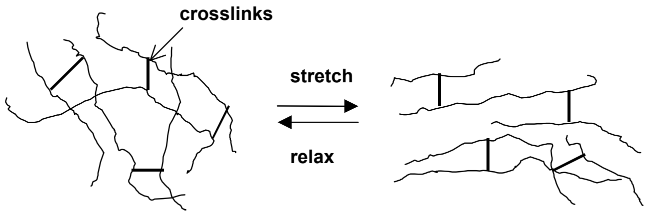


Fig.2.3.3. Behavior of the crosslinked elastomer under the stress

Microcrystalline polymers

There is a difference between the polymers described as “crystalline” and the crystals formed by low-molecular-weight substances. In the latter the crystalline order results from a regular packing of molecules or ions in a three-dimensional lattice. In the microcrystalline polymers, on the other hand, the crystallinity results from the ***regular packing of chains*** (Fig. 2.3.4a).

Such regular packing arrangements usually exist only in small domains (called **lamellae**) within the polymer. Hence, a microcrystalline polymer consists of micro crystallites embedded in a matrix of amorphous polymer (Fig.2.3.4b). Typically, 30-70% of the polymer may remain in the amorphous state. A single polymer chain may traverse several microcrystalline and amorphous regions (Fig.2.3.4c).

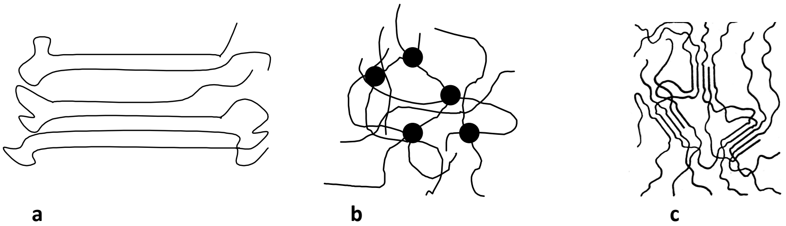


Fig. 2.3.4. Microcrystalline polymer

The micro-crystallites play the role of temporary crosslinks that give the polymer toughness and limit its tendency to creep. Too high crystalline degree might however increase the material fragility.

Crystalline polymers above T_g are flexible and thermoplastic. They are dimensionally stable and much tougher than an amorphous polymer in the rubbery phase. A microcrystalline polymer melts to a viscous liquid at a sharply defined temperature (Fig. 2.3.1 and 2.3.5).

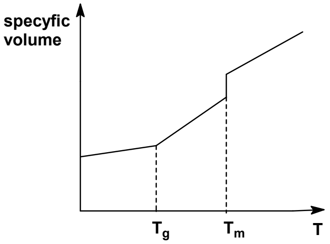


Fig. 2.3.5. Dependence of specific volume of microcrystalline polymer on temperature

One can enhance a degree of the order in the process that is known as ***orientation*** in which crystallites themselves are lined up on the same axis. The amorphous polymer may also be subjected to the orientation (Fig. 2.3.6). The simplest way of orientation used for polymer foil or fibers is stretching and annealing (heating and cooling) of the stretched material.

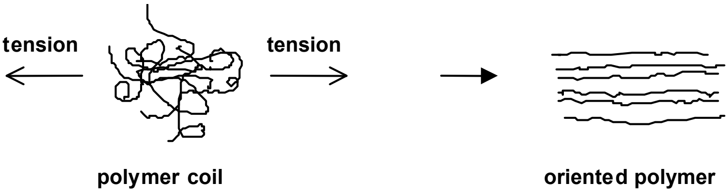


Fig. 2.3.6. Orientation process of amorphous polymer coil

Microcrystalline polymers have a higher density than forms of the same material that are totally amorphous. They are also usually tougher, more resistant to the temperature and solvent (lower swelling). Characteristics of microcrystalline polymer should contain such features as :

- crystalline degree,
- crystallites size and degree of their perfection (presence of structure defects),
- crystallization morphology (presence of higher order for example spherulites),
- degree of orientation.

Nearly all methods for the measurement of glass transition temperature can be used to measure crystalline melting temperature. However two methods are leading in detection and measurement of crystallinity – optical birefringence and X-ray crystallography. The first one makes use of a polarizing microscope. Through crossed polarized lenses a microcrystalline polymer is seen as a bright speck (coming from the crystalline domains) on a dark background.

X-ray diffraction pattern (Fig. 2.3.7) is different for amorphous polymer (diffuse scattering rings resembling patterns obtained for liquids), unoriented microcrystalline polymer (sharp rings) and oriented microcrystalline polymer (diffraction spots or arcs). At T_m the patterns from crystalline domain disappear.

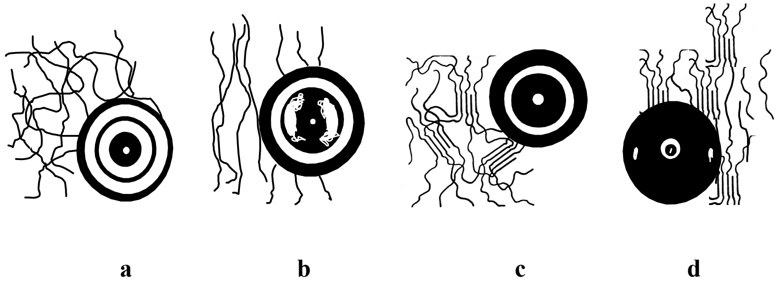


Fig. 2.3.7. X-ray diffraction pattern for:
a – unoriented amorphous polymer, b – oriented amorphous polymer,
c – unoriented microcrystalline polymer, d - oriented microcrystalline polymer

Liquid-crystalline polymers

The liquid-crystalline polymers (LCPs) show an additional phase transition between the glass transition temperature and the formation of a true isotropic liquid (Fig.2.3.1). A liquid-crystalline polymer, when heated, passes through the normal glass and microcrystalline phases but undergoes a quasi melting transition T_{qm} at a temperature below the final liquefaction point T_m. Between these two temperatures polymer is in a molten state but in which some structural order is retained.

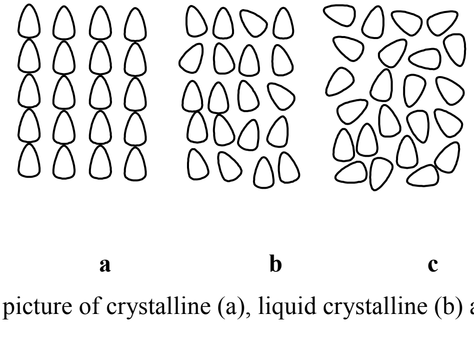


Fig. 2.3.8. The picture of crystalline (a), liquid crystalline (b) and liquid substances (c)

The liquid crystalline (***mesomorphous*** – intermediate state) substances (Fig.2.3.8b) lay between the perfectly ordered crystals (Fig.2.3.8a) and isotropic liquids (Fig.2.3.8c). In order for normally flexible polymers to display liquid crystal characteristics, rod-like or disk-like elements (called ***mesogens***) must be incorporated into their chains.

Mesogens may be placed in the main chain or as side groups (Fig. 2.3.9).

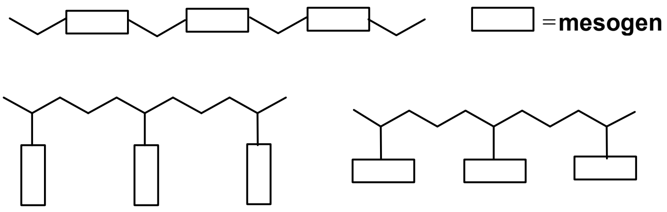
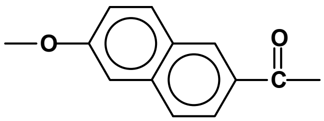
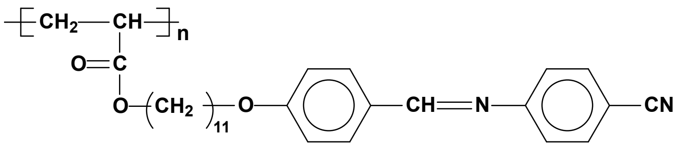


Fig. 2.3.9. The placement of mesogens in the liquid-crystalline polymer

Below is given an example of a main chain mesogen:



and a side-group mesogen:



LCPs may be divided into two broad categories, according to the principal means of achieving fluidity. ***Lyotropic LCPs*** result from an action of solvent and hence are multicomponent polymer solutions. ***Thermotropic LCPs*** are produced by heat and may be single or multicomponent melts. Within each category three distinctive supramolecular structural classes of LCPs have been identified (Fig. 2.3.10):

- ***nematic*** – the phase of liquid crystal characterized by arrangement of the long axes of the molecules in parallel lines but not layers; disk-shaped LC molecules can orient themselves in layer-like fashion known as the ***discotic nematic phase***,
- **smectic** - the phase of a liquid crystal characterized by the arrangement of the molecules in layers with the long axes of the molecules in a given layer being parallel to one another and perpendicular to the plane of the layer,

- ***cholesteric*** (twisted nematic) - is a type of liquid crystal with a helical structure. They organise in layers with no positional ordering within layers, but a director axis which varies with layers.

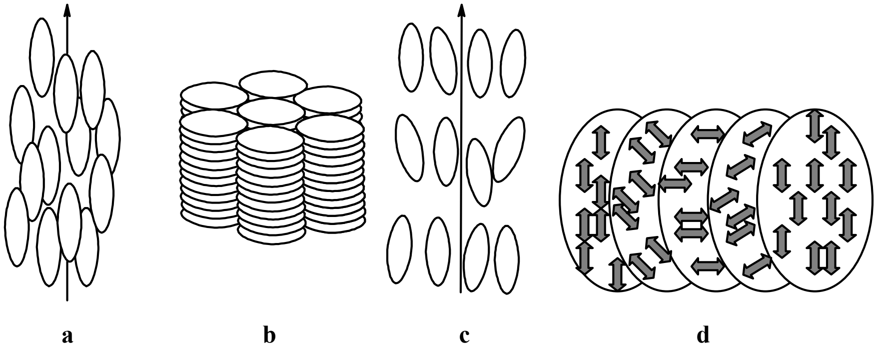


Fig. 2.3.10. Structural classes of liquid-crystalline polymers:
a – nematic, b – dyscotic nematic, c – smectic, d – cholesteric

The LCPs show very interesting mechanical, optical, electrical and magnetic properties. Kevlar, which is used to make such things as helmets and bullet-proof vests, is an example of high strength fibers made of LCP. A twisted nematic polymer liquid crystal cell can be used to make energy efficient displays. Side chain polymer liquid crystals exhibit good properties for applications in optically nonlinear devices including optical waveguides and electro-optic modulators in poled polymeric slab waveguides.

The most common application of the liquid crystal technology is in liquid crystal displays (LCDs). From the ubiquitous wrist watch and pocket calculator to an advanced VGA computer and TV screens, this type of a display has evolved into an important and versatile interface.

3. POLYMERIZATION REACTIONS

3.1. CHAIN VERSUS STEP POLYMERIZATION

Based on reaction mechanism, polymerization can be divided into the ***step reaction*** and ***chain reaction***, the latter being named also the additional polymerization. This classification does not take into account the loss of a small molecule or type of interunit linkage. The main differences between these two mechanisms are listed in the Table 3.1.1.

Table 3.1.1. The main differences between the step and chain polymerization

	Chain polymerization	**Step-growth polymerization**
1.	Repeating units are added to the chain only one at a time.	Any two present molecules can react
2.	Monomer concentration decreases steadily throughout reaction.	Monomer disappears in the early stage of reaction
3.	From the very beginning the high-molecular weight product is formed; polymer M remains nearly constant throughout reaction	Molecular weight of polymer rises steadily with reaction time
4.	Long reaction time is necessary to obtain high yields of product	Long reaction time is necessary to obtain high molecular weight
5.	Only polymer and monomer is present in the reaction mixture; part of growing chains is very small, about 10^{-8}	At any stage all molecular species are present in a calculable distribution

Depending on the type of active centers that initiate and propagate the polymerization process in chain polymerization one can distinguish four types of chain polymerization: free radical, anionic, cationic, and coordination.

In case of the step-growth polymerization polycondensation (involving the formation of low molecular mass species) and polyaddition can be distinguished.

3.2. CHAIN POLYMERIZATIONS

In the process of polymerization we may recognize four distinct types of processes. They are:

- ***chain initiation*** – the process in which highly reactive transient molecules or active centers are formed
- ***chain propagation*** – the addition of monomer molecules to the active chain end, with the regeneration of the terminal active site,
- ***chain transfer*** – the transfer of the active site to another molecule;
- ***chain termination*** – the reaction in which the active chain centers are destroyed.

Free radical polymerization

In the free radical process, the radical is the agent initiating the process of chain growth.

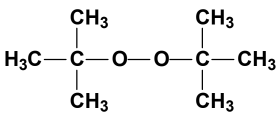
Free radicals are the chemical compounds with unpaired electrons. If they are not stabilized by a particular substituent, their life time is extremely short due to very high reactivity. They are generated by the homolytic rupture of covalent bonds being a result of either physical (thermal, radioactive) excitation or chemical (oxydo-reduction) means.

Free radicals initiators used are then unstable molecules that can homolytically dissociate due to the presence of a weak covalent bond. However these compounds have to be stable in storage temperature, should decompose in the temperature range 60-150^{o}C with the half-life time of several hours. Value T_{10} usually given to characterize initiators is the temperature in which half-life time equals 10 hours and that is close to the best polymerization temperature.

The main groups of initiators include:

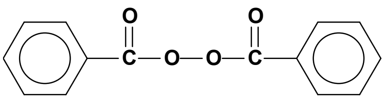
- organic (dialkyl-, diaryl-, diacyl-,) ***peroxides***

$$R{-}O{-}O{-}R' \longrightarrow R{-}O\bullet + \bullet O{-}R'$$



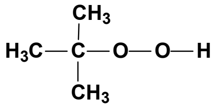
$$H_3C{-}C(CH_3)_2{-}O{-}O{-}C(CH_3)_2{-}CH_3$$

di-t-butyl peroxide



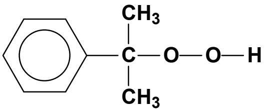
benzoyl peroxide

- *hydroperoxides*, $R-O-O-H \longrightarrow R-O\bullet + \bullet O-H$



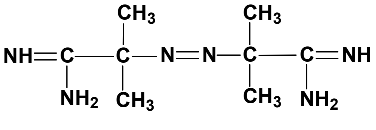
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O-O-H$

t-butyl hydroperoxide

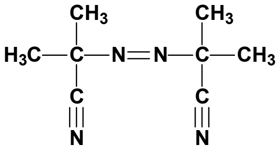


cumyl hydroperoxide

- *azo compounds* $R-N-N-R' \longrightarrow R\bullet + N\equiv N + \bullet R'$

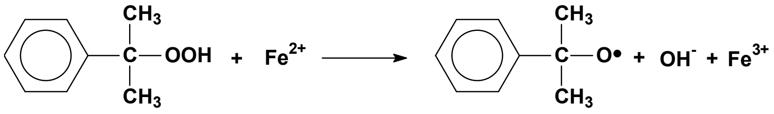


2,2'-azobis(2-methylpropionamidine)

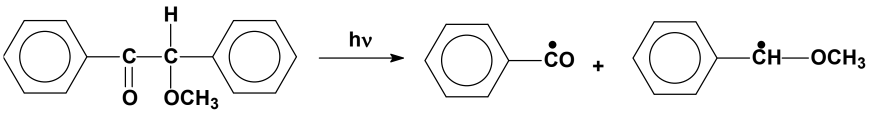


azobisisobutyronitryl (AIBN)

When it is necessary to generate free radicals at low temperatures ***oxydo-reduction reaction*** are used:



Photochemical initiation resulting from the activation of monomer molecules by photons usually needs the presence of an activator, like the benzoin ether:



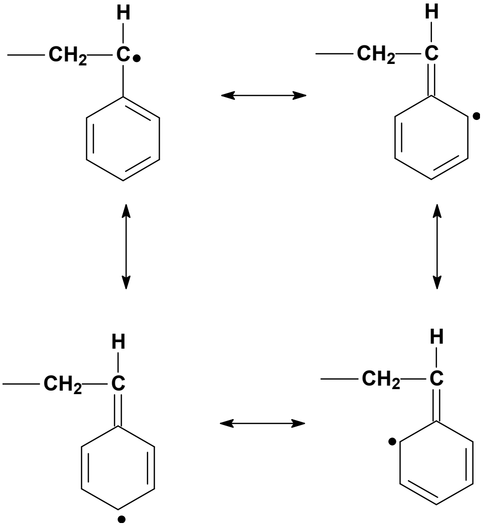
Benzyl, benzoin, organic disulfides and many others UV activators are used. Such initiation has many advantages:

- its kinetic does not depend on temperature,

- the process of control is easy (using light of a narrow range of a wavelength, regulation with the intensity of light),
- instantaneous breaking with the turning off the light,
- great diversity of attainable activators.

Direct thermal initiation or high-energy radiation (electrons, γ rays, x-rays, slow neutrons) initiation are sometimes also used.

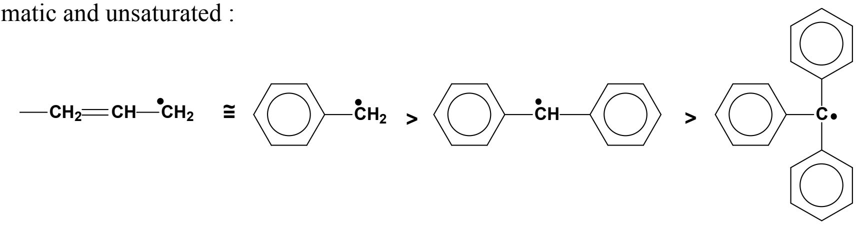
Radicals show a very wide range of reactivity. They can be stabilized by resonance or electron - withdrawing effects. The stabilization of styrene radicals is shown on the scheme beside:



The reactivity order of radicals is as follows:

aliphatic: $H^{\cdot} > CH3^{\cdot} > CH3CH2^{\cdot} > (CH3)2CH^{\cdot} > (CH3)3C^{\cdot}$

aromatic and unsaturated :



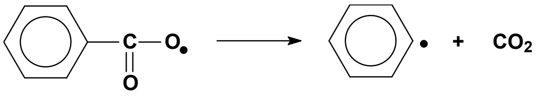
The last of radicals is so stable that even its dimerization reaction is not complete. What is very important – ***the more stable the radical the slower is its addition to the monomer***.

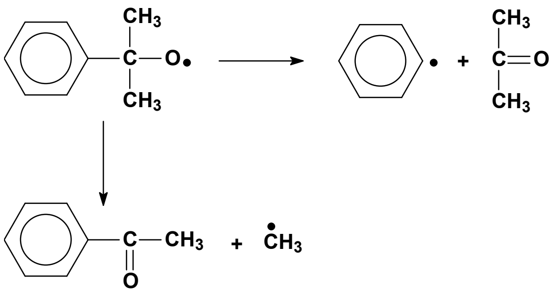
Reactions of radicals

Only a fraction of generated radicals initiate the polymerization and the rate of initiating is always lower than the rate of radicals generation. This happens because of other radicals reactions (except addition to the monomer) take place in the reaction medium. There are six reactions in which free radicals can be involved:

- ***fragmentation*** $RM^{\bullet} \longrightarrow R^{\bullet} + M$

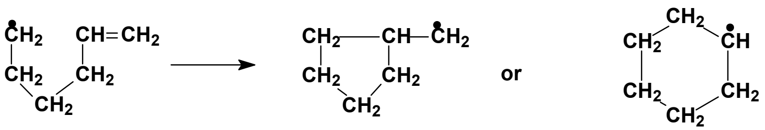
The examples of such reactions are given below:





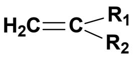
- ***rearrangement*** $R_1^{\bullet} \longrightarrow R_2^{\bullet}$

Some radials undergo isomerization via intermolecular reactions of addition or substitution:



- ***addition*** $R^{\bullet} + M \longrightarrow RM^{\bullet}$

Usually it is addition to double bonds. The most of compounds able to undergo polymerization have a structure:

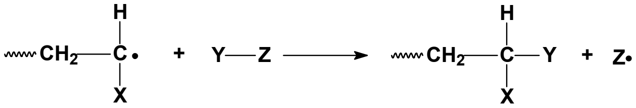


$H_2C{=}C\begin{matrix}R_1\\R_2\end{matrix}$

A radical most often attacks from the CH_2 side which creates a more stable new radical. This leads to addition named ***head-to-tail***.

The addition reaction begins the polymerization process and makes the chain propagate.

- ***abstraction / transfer*** $R\bullet + HM \longrightarrow RH + M\bullet$

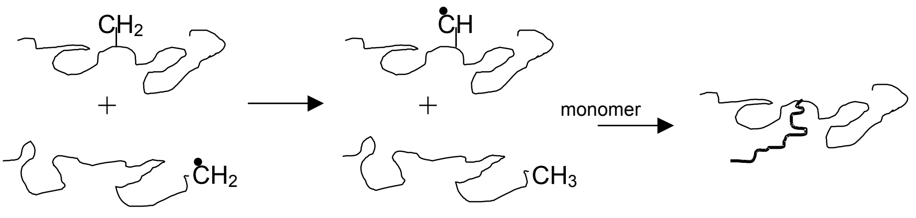


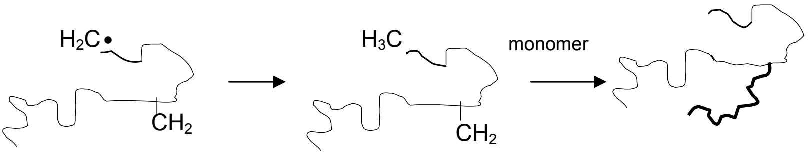
$$\sim\sim CH_2-\overset{H}{\underset{X}{C}}\bullet + Y-Z \longrightarrow \sim\sim CH_2-\overset{H}{\underset{X}{C}}-Y + Z\bullet$$

A radical can abstract a single atom or group of atoms from the molecule and generate a new radical on this molecule. If this new radical Z· is sufficiently reactive it can start a new polymeric chain. This process is described as a kinetic chain transfer. In this case the only consequence is the decrease of molecular weight of the formed polymer. If the radical Z is less reactive or unreactive, the YZ substance is a retarder or an inhibitor respectively.

The phenomenon of a transfer of the growing active centers onto other species present in the reaction medium is extremely frequent in the radical polymerization. The transfer can take place to:

- initiator – it consumes molecules of the initiator and thus decreases its efficiency,
- monomer – especially prone to transfer are monomers $CH_2{=}CHCH_2$ X, where X = halogen, ester or ether
- solvent,
- transfer agents – substances prone to transfer, added to the reaction medium to regulate (lower) molecular weight of polymer and sometimes also introduce the desired end groups into the polymer; as transfer agents sulfides, disulfides, and alkyl halides are commonly used,
- polymer chain (a) or its own growing chain (b) – it results in long or short branches in the obtained polymer: **(a)**

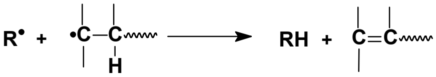




(b)

- *combination* (coupling) $R_1^{\bullet} + R_2^{\bullet} \longrightarrow R_1-R_2$

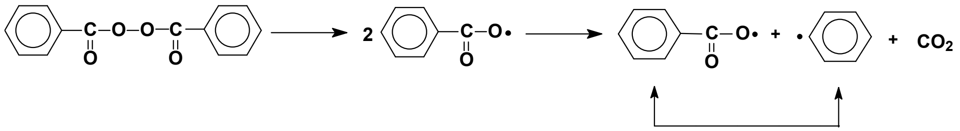
- ***disproportionation***



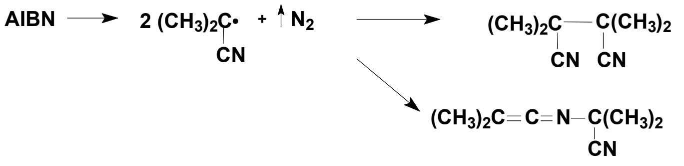
$$R^{\bullet} + {}^{\bullet}\overset{|}{\underset{|}{C}}-\overset{|}{\underset{H}{C}}\sim\sim \longrightarrow RH + \overset{|}{\underset{|}{C}}=\overset{|}{C}\sim\sim$$

The **collision of two free macroradicals** can result in two different processes, both being a termination step. Combination doubles the molecular weight of a polymer while competitive disproportionation leaves the molecular weight unchanged and both “dead” chains posses different end groups. Which mechanism of termination prevails depends on the kind of monomer, and temperature (in low temperatures – combination is more important).

The collision of primary radicals may occur immediately after the dissociation of an initiator, when they are in the “cage” made of solvent and other reaction molecules. In this case radicals combination often gives unreactive products, lowering the efficiency of an initiator. The examples of such a situation are shown on the scheme below:



These radicals recombine
giving unreactive compound



$$\text{AIBN} \longrightarrow 2\,(CH_3)_2\underset{CN}{C^{\bullet}} + \uparrow N_2 \longrightarrow (CH_3)_2\underset{CN}{C}-\underset{CN}{C}(CH_3)_2$$

$$\searrow (CH_3)_2C=C=N-\underset{CN}{C}(CH_3)_2$$

Polymerization rate and molecular weight of polymer

Schematically, a free-radical polymerization can be represented by the sequence of the reactions:

initiation:

$$\text{initiator} \longrightarrow 2R'^\bullet$$

$$R'^\bullet + M \longrightarrow R_1^\bullet$$

propagation:

$$\begin{array}{c} R_i^\bullet + M \longrightarrow R_{i+1}^\bullet \\ \hdashline R_n^\bullet + M \longrightarrow R_{n+1}^\bullet \end{array}$$

chain transfer:

$$R_n^\bullet + YZ \longrightarrow R_nY + Z^\bullet$$

termination:

$$R_n^\bullet + R_m^\bullet \longrightarrow P_{n+m}$$

$$R_n^\bullet + R_m^\bullet \longrightarrow P_n + P_m$$

Rate of polymerization r_p is proportional to monomer concentration [M] and initiator concentration $[I_2]$ to the power of 0.5:

$$r_p = (k_p / k_t^{1/2})(f \cdot k_d [I_2])^{1/2} [M]$$

where: k_p, k_t, k_d – rate constant of propagation, termination and initiator decomposition, respectively, f – initiator efficiency; usually $0.5 < f < 0.7$

Molecular weight distribution of free-radical polymerization depends on the way of chain termination. M_w/M_n for combination equals 1.5 and for disproportionation equals 2.

Technology of radical polymerization

Free radical polymerization is extensively utilized in industry for the preparation of a variety of polymeric materials. Five main techniques are commonly utilized, namely polymerization in bulk, solution polymerization, dispersion polymerization, suspension polymerization, and emulsion polymerization.

Polymerization in bulk seems to be the simplest and the most economical for it requires neither sophisticated equipment nor any special chemicals except a monomer and initiator. The initiator and formed polymer are soluble in the monomer. The problem however appears when the reaction yield increases; viscosity of solution becomes very high and kinetics is accelerated by the gel effect (or Trommsdorf effect). The rate constant of termination became diffusion-controlled – long chain radicals lost their mobility and ability of finding other radicals - hence a pronounced decrease of its value is observed. At the same time diffusivity of small molecules (monomer, initiator) though lower is still significant, then processes in which they take part (initiation, propagation) are fast. The total rate of polymerization dramatically increases, and system looses its fluidity (hence gel effect). For this reason polymerization in bulk is rarely used in the industry. The exceptions are PMMA sheets that are solely produced by this method.

Polymerization in bulk can be carried in the continuous mode that is more complicated but assures better heat control and narrower molecular weight of the produced polymer.

Solution polymerization is commonly used in laboratories but seldom applied in the industry. The reason is the cost of the solvent and problems with environmental requirements. Exceptions are processes when water can be used as a solvent (as in case of acrylamide or acrylic acid) or when a polymer solution is a final product.

In a ***dispersion (precipitation) polymerization***, the initial reaction medium (monomer, solvent, initiator, additives) is homogenous, but the polymer formed is insoluble and precipitates progressively as the polymerization proceeds. That provokes a limitation of the sample molar masses. This process can be carried out either in bulk or in the presence of a solvent and is industrially utilized to polymerize vinyl chloride, acrylonitrile, and vinylidene chloride.

The term ***suspension polymerization*** refers to polymerization in an aqueous system with the monomer as a dispersed phase, resulting in a polymer as a dispersed solid phase. The polymerization initiator is dissolved in the monomer. Polymerization goes in the droplets as in the small blocks. To prevent the agglomeration of blocks the water-soluble “suspending agents” such as poly(vinyl alcohol) with small amount of surfactant are dissolved in water. Stirring of the system is necessary. The Polymer is obtained in the form of beds of size between 3 and 30 μm. By this method the polymers and copolymers of vinyl chloride, styrene, tetrafluoroethane, methyl methacrylate are produced.

In ***emulsion polymerization***, that proceeds also in water medium, an important role plays soap. It exists in the form of micelles; part of the monomer enters the micelles, but most of it exists as droplets. The polymerization initiators are dissolved in water. Free radicals generated in the aqueous phase enter the micelles and start polymerization. As polymer is formed, the micelles grow by the addition of a monomer from the aqueous phase. Such a process results in polymer latex with particles size ranging between 0.05 and 5 μm. Such polymers as poly(vinyl chloride), poly(vinyl acetate), butadiene, styrene are often produced as emulsions.

The compact comparison of the polymerizing system is given in Table 3.2.1.

Table 3.2.1. Advantages and disadvantages of various radical polymerization processes

Type	**Advantages**	**Disadvantages**
Bulk	High-purity polymer, simple equipment.	Difficulties with heat transfer (gel effect), broad molecular weight distribution.
Solution	Easy heat control, solution may be directly usable.	Solvent cost and environmental requirements, difficulties with solvent removal if dry polymer is demanded.
Dispersion	Gel effect is avoided, narrower MWD.	Limitation of molecular weight.
Suspension	Easy heat control, granular polymer ready to use.	Continuous agitation is necessary, polymer contaminated by stabilizers, granules have to be washed and dried after process.
Emulsion	Easy heat control, fast polymerization, polymer of high molecular weight and relatively low MWD, emulsion may be directly used.	Inevitable polymer contamination by emulsifier, process if disruption of latex is necessary if dry polymer is demanded.

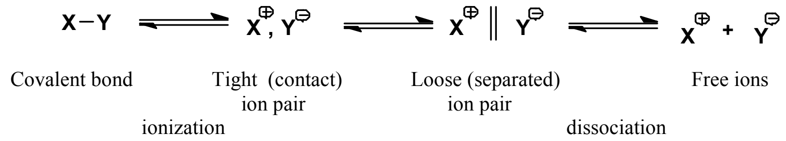
Ionic polymerization

At the first glance the ionic polymerization looks like a radical one – it also consists of the same stages: initiation, propagation and termination. There are however very essential differences between these two types of polymerization. They are listed in the Table 3.2.2.

Table 3.2.2. Comparison of radical and ionic polymerizations

Radical polymerization	**Ionic polymerization**
Propagating species are radicals.	Propagating species are anion or cation.
Almost all monomers containing C=C undergo this polymerization.	This process is highly selective. A monomer has to posses electron-releasing (for cationic) or electron-withdrawing groups (for anionic).
Radicals are always separated, they do not interfere with themselves during the chain propagation up to its termination.	Counterions are always in close neighbourhood of an active center and have significant influence on all process stages; polymerization depends strongly on the nature of counterion.
Active chains are terminated by the reaction with other radicals which are always present in the system.	Ionic chains are terminated by the species that are avoided in the propagation step, then they are absent in the system; hence polymerization has often “living” character.
Kinetics of polymerization is practically independent of the solvent present in the system.	The polymerization is much faster and is highly solvent-dependent.
Reaction temperature depends only on the initiator chosen.	Temperature influences the polymerization rate. Reaction proceeds well in very low (below $0^{o}C$) temperatures.

Two last characteristic features of ionic polymerization are connected with the heterolytic break of a covalent bond:



Ionization of XY compound results in formation of an internal ion pair in which the cation and anion are adjacent (tight or a contact ion pair). The internal ion pair can undergo further dissociation to loose the (solvent separated) ion pair and finally free ions. The different types of propagating species have different reactivity. The free ions are of course the most reactive. The equilibrium state between these species depends strongly on the solvent and temperature. Both processes – ionization and dissociation are exothermic then lowering the temperature increases amount of more reactive species. Additionally, low temperatures suppress termination, transfer and various side reactions.

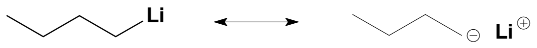
Ions of different signs have a tendency to be as close to each other as possible, to lower the enthalpy of the system. The counterweight of this tendency may be solvent of a high dielectric constant (increase solubility) and able to solvate ions (make the ionization and dissociation easier).

Anionic polymerization

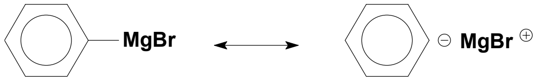
To be polymerized by anions the monomer has to possess electron-withdrawing groups such as nitrile, cyano, carbonyl, phenyl, and vinyl. Heterocyclic monomers - ethers, lactams aldehydes – are also able to undergo anionic polymerization.

A variety of basic (nucleophilic) initiators have been used in anionic polymerization. These include: ***alkali metals*** (Na, Li, K), ***organometallic*** compounds of these metals (butyllithium, sodium naphthalenide), ***amides*** (KNH_2, $NaNH_2$), ***alkoxides*** (CH_3ONa), or ***Grignard reagents***.

The structure of a monomer depends on how strong nucleophile has to be used to initiate the polymerization. A monomer such as methyl-α-cyanoacrylate (used in many so called “super glues”) with two electron-withdrawing substituents can be polymerized with very mild nucleophiles, even by OH^- from water.



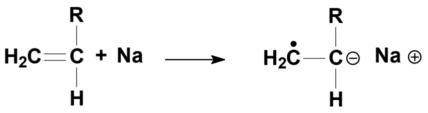
strong - initiates styrene, isoprene



middle - initiates methyl methacrylate

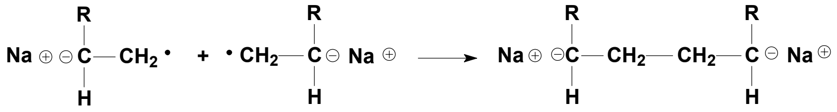
$H_3C—ONa \longleftrightarrow H_3C—O^{\ominus}\ Na^{\oplus}$ **weak - initiates cyanoacrylates**

Two types of reactions can be utilized to generate primary active centers. The first one is an ***electron transfer from a metal atom to a monomer*** to generate a radical anion.



$$H_2C{=}C(R)(H) + Na \longrightarrow H_2\dot{C}—C(R)(H)^{\ominus}\ Na^{\oplus}$$

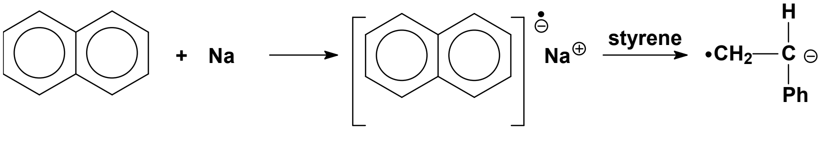
Dimerization of the radical anion takes place to form a dianion.

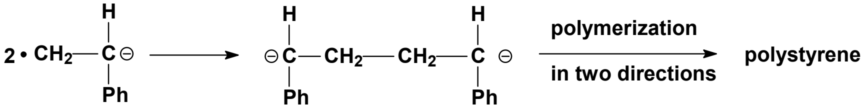


$$Na^{\oplus}\ {}^{\ominus}C(R)(H)—CH_2^{\bullet} + {}^{\bullet}CH_2—C(R)(H)^{\ominus}\ Na^{\oplus} \longrightarrow Na^{\oplus}\ {}^{\ominus}C(R)(H)—CH_2—CH_2—C(R)(H)^{\ominus}\ Na^{\oplus}$$

Propagation occurs at both ends of the dimer.

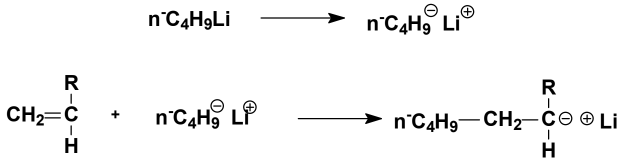
The direct initiation is rarely utilized for it is very slow. To overcome this limitation, an organic intermediate that cannot polymerize itself but can accommodate electrons by transfer is generally utilized. Naphthalene is commonly used for this purpose:





$$2\,{}^{\bullet}CH_2—C(H)(Ph)^{\ominus} \longrightarrow {}^{\ominus}C(H)(Ph)—CH_2—CH_2—C(H)(Ph)^{\ominus} \xrightarrow[\text{in two directions}]{\text{polymerization}} \text{polystyrene}$$

The second way is an ***addition of a negative ion to the monomer*** with the opening of a bond or ring and growth at one end.



$$n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_9^{\ominus}\,Li^{\oplus}$$

$$CH_2{=}\underset{H}{\overset{R}{C}} + n\text{-}C_4H_9^{\ominus}\,Li^{\oplus} \longrightarrow n\text{-}C_4H_9{-}CH_2{-}\underset{H}{\overset{R}{C}}{}^{\ominus}\,{}^{\oplus}Li$$

The initiation is very fast, the initiator added to the monomer reacts with it quantitatively in a few seconds. The equilibrium between various types of a growing anion chain is established very fast. ***Propagation*** of all chains occurs in these same conditions hence the ***length of all chains is almost identical***. As a result polymers of small molecular weight distribution are obtained ($M_w/M_n<1.1$).

In anionic polymerization ***termination*** usually involves transfer, and the kinetic chain is broken only if the new species is too weak to propagate. By careful purification of all ingredients of a reaction system to eliminate all species to which transfer can occur, the termination step is effectively eliminated and the growing chains remain active indefinitely. Such situation is referred to as "***living polymerization***". The chains are growing as long as a monomer is in the system and remain "living"; adding new portions of a monomer makes chains grow further.

Termination ("killing of the polymer") can be done by reactions resulting in anions that are not sufficiently active to propagate chains. It might be a reaction with water or alcohol for alcoxide that is too weak to polymerize C=C monomers.

Application of anionic synthesis in polymer chemistry

Synthesis of polymers of demanded molecular weight and low dispersity index. Regulation of M in anionic polymerization is relatively easy. Taking into account that all initiator molecules [I] start the chain growth and monomer conversion [M] reaches 100%, average polymerization degree can be calculated as:

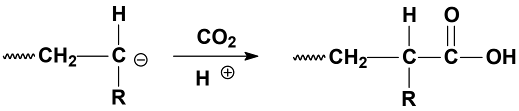
$$\overline{DP} = \nu_{\infty} = \frac{[M]_0}{[I]} \qquad\qquad \overline{DP} = 2\,\nu_{\infty} = \frac{[M]_0}{0.5\,[I]}$$

a **b**

for monofunctional (a), and difunctional (b) initiator, respectively.

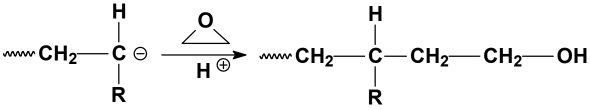
- Synthesis of polymers with **functional end group(s)**

Choosing the proper terminating agent one can introduce various groups as the polymer end-group. For example, reaction with CO_2 gives carboxyl end group:



$$\sim CH_2-\underset{R}{\overset{H}{C}}{}^{\ominus} \xrightarrow[H^{\oplus}]{CO_2} \sim CH_2-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

and the addition of ethylene oxide chain ends with hydroxyl:



$$\sim CH_2-\underset{R}{\overset{H}{C}}{}^{\ominus} \xrightarrow[H^{\oplus}]{\overset{O}{\triangle}} \sim CH_2-\underset{R}{\overset{H}{C}}-CH_2-CH_2-OH$$

- Synthesis of **block copolymers**

Because in living polymerization when a monomer has been consumed the chain ends remain “alive”, the chain growth can be restarted by the addition of more of the same monomers or a different monomer. In the latter case a copolymer is formed. When the monofunctional initiator is used, ***diblock copolymer*** AAAABBBB is obtained, in the case of the difunctional initiator - ***triblock copolymer*** BBBBAAAABBBB. Triblock copolymer may be synthesized also using the monofunctional initiator in the three-step process (sequential addition of monomers) or in two step anionic polymerization followed by a coupling reaction of AB chains.

Triblock copolymers comprising a central of polybutadiene (elastomer) and two external blocks of polystyrene (glassy polymer) was the first synthesized ***thermoplastic elastomer*** i.e. material that behaves as crosslinked elastomer but can be processed as thermoplastic. The morphology of such materials is shown in the Fig.3.2.1 – polystyrene spheres are distributed in an elastomeric matrix of polybutadiene.

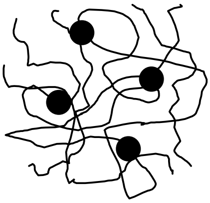


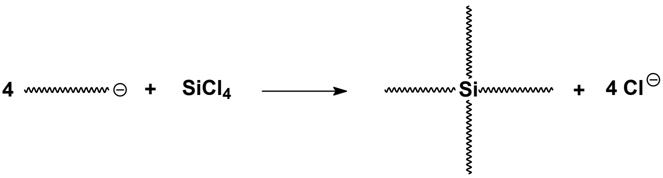
Fig. 3.2.2.1.

The picture of triblock PS-PB-PS thermoplastic elastomer. ● polystyrene domains

At the service temperature the polystyrene (T_g~ +100°C) domains are in the glassy state, whereas the polybutadiene chains (T_g~ -108°C) connecting them are in the elastomeric state. Rigid domains of PS play the role of physical crosslinks, which are responsible for the deformation undergoing in the sample. When the sample is heated the above T_g of polystyrene, the material becomes plastic and can be processed as viscous liquid. Subsequent cooling restores elastomeric character of the material.

- Synthesis of **star polymers**

Coupling of living chains with a multifunctional coupling agent is applied also for the synthesis of ***star polymers.*** The scheme below shows the synthesis of the four-arm polymer:



Star polymers show different crystalline, mechanical, and viscoelastic properties in comparison with their corresponding linear analogues.

Cationic polymerization

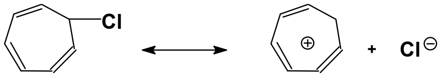
In cationic polymerization the growing chain end bears a positive charge. Monomers that polymerize under the influence of cationic initiators usually contain electron-supplying substituent groups. They can form stable carbenium-ion salts. Isobutylene, vinyl ethers, α-methylstyrene, aldehydes are examples of such monomers. The typical catalysts for cationic polymerization include:

- aprotonic acids (Lewis acids and Friedel-Crafts halides) – BF_3, $AlCl_3$, $SnCl_4$, $TiCl_4$, $ZnCl_2$,
- protonic acids - H_2SO_4, HCl, $HClO_4$, CF_3SO_3H (triflic, strong acid soluble in many organic solvents),
- other compound that can be easily ionized:

- iodine $2 I_2 \longleftrightarrow I^{\oplus} + I_3^{\ominus}$

- chlorotriphenylomethane $(C_6H_5)_3CCl \longleftrightarrow (C_6H_5)_3C^{\oplus} + Cl^{\ominus}$

- chlorocycloheptatrien

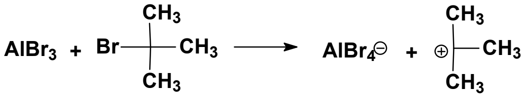


All these are strong electron acceptors. The first step of the polymerization is the generation of the proton or other cation. Strong protonic acids in nonaqueous media liberate protons by the conventional ionization process, for example:

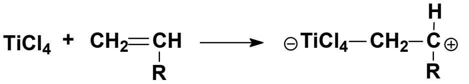
$$H_2SO_4 \longrightarrow \overset{\oplus}{H} + \overset{\ominus}{HSO_4}$$

Lewis acids require a cocatalyst to initiate polymerization :

$$BF_3 + H_2O \longrightarrow H^{\oplus}(BF_3OH)^{\ominus}$$

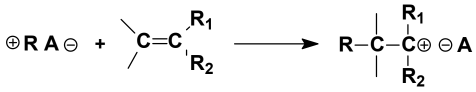


$$AlBr_3 + Br-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow AlBr_4^{\ominus} + \oplus\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$



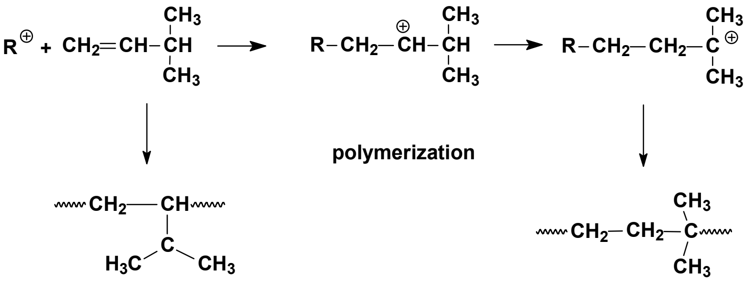
$$TiCl_4 + CH_2=\underset{R}{CH} \longrightarrow \ominus TiCl_4-CH_2-\overset{H}{\underset{R}{C}}\oplus$$

Initiation of a monomer molecule involves the addition of the catalyst ion pair to the monomer:

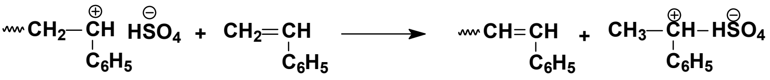


Propagation takes place by successive insertion monomer molecules into the cation-anion “bond”. The chain growth takes place rapidly, especially in low temperatures. Reactivity of monomer depends on stability of the formed carbocation – the more stable carbocation the faster polymerization reaction.

Carbonium ions are very reactive and can undergo many side reactions. To form more stable species the ***isomerization of the growing chain is possible***. In the case below a more stable tertiary cation is formed and the obtained polymer is different from the one that was expected.

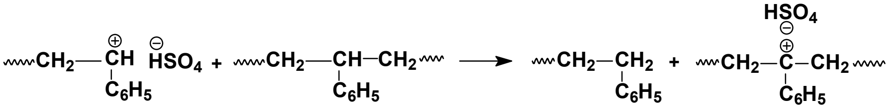


Transfer of an active chain is frequent in cationic polymerization, and resulting species are sufficiently reactive to reinitiate the polymerization. The examples of transfer to a monomer (a) and polymer (b) are shown below:



$$\sim CH_2-\underset{C_6H_5}{\overset{\oplus}{C}H}\ \overset{\ominus}{HSO_4} + CH_2{=}\underset{C_6H_5}{CH} \longrightarrow \sim CH{=}\underset{C_6H_5}{CH} + CH_3-\underset{C_6H_5}{\overset{\oplus}{C}H}-\overset{\ominus}{HSO_4}$$

a



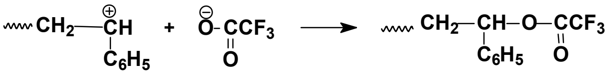
$$\sim CH_2-\underset{C_6H_5}{\overset{\oplus}{C}H}\ \overset{\ominus}{HSO_4} + \sim CH_2-\underset{C_6H_5}{CH}-CH_2\sim \longrightarrow \sim CH_2-\underset{C_6H_5}{CH_2} + \sim CH_2-\underset{C_6H_5}{\overset{\overset{HSO_4}{\ominus}}{\overset{\oplus}{C}}}-CH_2\sim$$

b

In the last case the branched polymer is obtained.

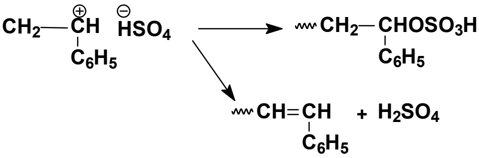
The reactions that result in the deactivation of carbonium ions are numerous.

- The end of the chain can react with the counterion and change the ionic bond on the covalent bond (a); the termination is real and the restart of polymerization is not possible.



$$\sim CH_2-\underset{C_6H_5}{\overset{\oplus}{C}H} + \overset{\ominus}{O}-\underset{\underset{O}{\|}}{C}CF_3 \longrightarrow \sim CH_2-\underset{C_6H_5}{CH}-O-\underset{\underset{O}{\|}}{C}CF_3 \quad (a)$$

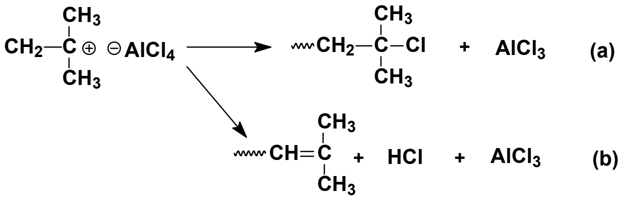
- In the case shown below a formed compound can start a new reaction (b). The growing end eliminates the proton and forms a double bond (c).



$$CH_2-\underset{C_6H_5}{\overset{\oplus}{C}H}\ \overset{\ominus}{HSO_4} \longrightarrow \sim CH_2-\underset{C_6H_5}{C}HOSO_3H \quad (b)$$

$$CH_2-\underset{C_6H_5}{\overset{\oplus}{C}H}\ \overset{\ominus}{HSO_4} \longrightarrow \sim CH{=}\underset{C_6H_5}{CH} + H_2SO_4 \quad (c)$$

- Complexes of Lewis acids with cocatalyst can eliminate the cocatalyst fragment which will combine with the growing chain (a); a cocatalyst can also detach β-proton from the growing chain regenerating the initiator (b):



The kinetics of cationic polymerization is complicated for multiplicity of initiation and termination reactions involved in it. However the assumption of existence of steady-stade, in which the initiation rate r_i equals the termination rate r_t leads to the equation:

$$r_p = (k_i k_p / k_t)\left[H^+ I^-\right]\left[M\right]^2$$

in which: r_p - propagation rate,

k_i, kp and k_t are initiation, propagation and termination rate constants, respectively,

[HI] – concentration of initiating complex,

[M] – monomer concentration.

Estimation of an average degree of polymerization being the ratio of propagation (r_p) and (r_t) termination rates gives the equation:

$$\overline{DP} = r_p / r_t = k_p / k_t\left[M\right]$$

from which is clearly seen that the average polymerization degree, hence average-molecular-weight of cationic polymer does not depend on initiators concentration. The polymerization rate increases with the increase of an initiator and monomer concentration (the latter to the power of two). In special conditions cationic polymerization can show a “living“ character.

Coordination polymerization

The term suggests that the essential feature of this type of polymerization is the presence of coordination complex of the monomer with the catalyst. This coordination not only influences the monomer polymerizability but can also determine the configuration - in particular, the stereochemistry of the insertion. The first known coordination catalysts were those known as "Ziegler Natta" and "Phillips". Since then, many other systems have been developed.

The characteristic features of coordination polymerization are:

- the mechanism of reaction lays somewhere between anionic and cationic,
- the active complex is not ionized even to a tight ionic pair,
- a monomer is first coordinated to an active complex, then through the rearrangement inserted into the growing chain.

Many coordination catalysts have the capability to yield unbranched and stereospecific polymers. α-olefins, cycloolefins, and dienes are the monomers for coordination polymerization. The mechanism of coordination polymerization and the nature of its catalysts are still not sufficiently known and clear.

Ziegler-Natta catalysts

A Ziegler-Natta catalyst is made from two components:

- a transition metal compound from groups IVB to VIIIB of the periodic table, usually a halide or oxyhalide of titanium, vanadium, chromium, molybdenum, or zirconium, and
- an organometallic compound, usually derived from a group IA to IIIA metal, often alkyl, aryl, or hydride of aluminum, lithium, magnesium, or zinc.

The catalyst system may be heterogeneous or soluble (homogeneous). Various catalyst systems or their additives (like amines) result in a polymer of various molecular weight and a degree of stereoregularity. The best known systems are those derived from $TiCl_4$ or $TiCl_3$ and aluminum trialkyl. It is not a simple coordination adduct of these two compounds. A critical "aging" period for the catalyst is often needed before it achieves its highest activity. During this time many complex reactions occur like the exchange of substituent groups between the two metals.

$$AlR_3 + TiCl_4 \longleftrightarrow AlR_2Cl + RTiCl_3$$

$$R_2AlCl + TiCl_4 \longleftrightarrow RAlCl_2 + RTiCl_3$$

$$AlR_3 + TiRCl_3 \longleftrightarrow AlR_2Cl + TiR_2Cl_2$$

The organotitanium halides are unstable and can undergo reductive decomposition processes:

$$RTiCl_3 \longrightarrow R^{\bullet} + TiCl_3$$

$$R_2TiCl_2 \longrightarrow R^{\bullet} + RTiCl_2$$

In all these systems one of the most important steps is the reduction of the transition metal to a low-valence state in which the metal possesses unfilled ligand sites.

Two general mechanisms have been proposed:

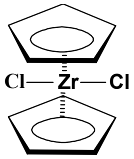
- "monometallic" mechanism - involving coordination of the monomer to a vacant site on the transition metal,
- "bimetallic" mechanism – supposing a participation by both metals present in the catalyst.

Ziegler-Natta polymerization is used to produce high-density polyethylene (HDPE – highly crystalline PE), isotactic polypropylene, ethylene copolymers such as linear low-density polyethylene (LLDPE), ethylene/propylene elastomer (EP), ethylene/propylene/diene terpolymer (EPDM) and the stereospecyfic polybutadienes and polyisoprenes.

Phillips catalysts

Catalysts consisting of metal or metal oxides adsorbed on or complexed with the surface of a solid carrier. Common catalysts include the oxides of vanadium, titanium, chromium, cobalt, nickel, and tungsten supported on silica, alumina, or activated carbon. Polymerization with such a catalyst process under the middle pressure (40-70 at) is used in the industry for the synthesis of ideally linear polyolefins.

Metallocene-based systems

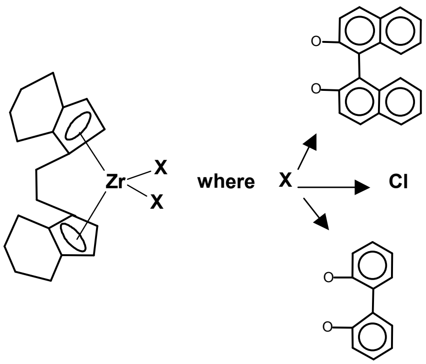


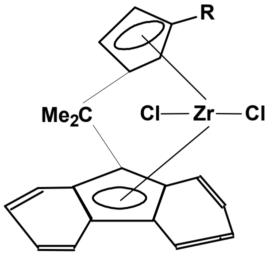
bis-chlorozirconocene

Metallocene are complexes whose transition metal (mainly from IVB group) is sandwiched between two aromatic rings, most generally of the cyclopentadienyl type.

Metallocenes themselves are not active for polymerization. Usually, a cocatalyst is required to activate the metallocene. Methylaluminoxane (MAO) or borate compounds are used to activate the metallocene. The activated metallocene catalysts can be used for olefin polymerization.

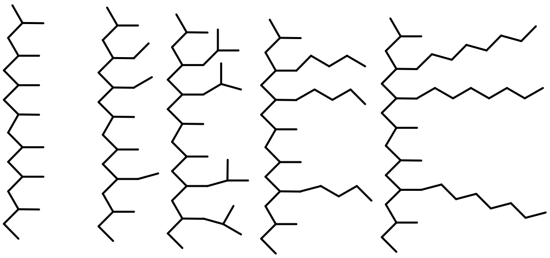
Some derivatives of *bis*-chlorozirconocene can be taken to make polymers:



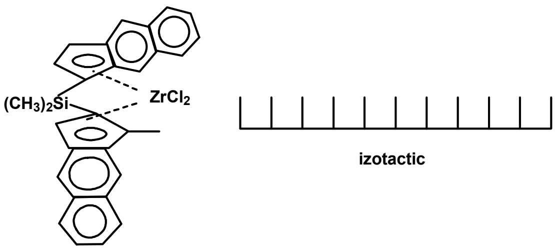


Metallocene-based systems exhibit many advantages compared to other coordination catalysts:

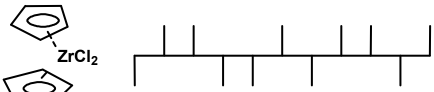
- high productivity of the catalyst;
- narrow molecular weight distribution of the formed polymers;
- controlled comonomer distribution along the chain;
- better tailoring of the polymers to the special demands. For example it is possible to obtain branched polymers of a controlled number and length of branches:



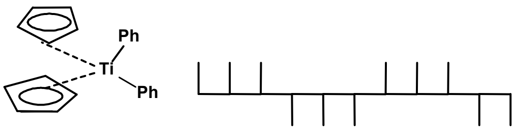
- high degree of stereoregularity and various stereo-isomer obtained for different catalysts, for example:



izotactic



atactic

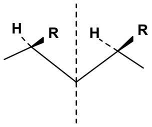


izotactic stereoblocks

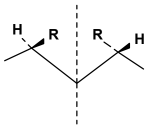
Metallocene catalysts are capable of producing a polymer with varying molecular weight and comonomer incorporation, also of producing homo- and copolymers that were economically unfeasible before. Polymers and copolymers of cyclic olefins are good examples of such polymers.

Stereochemistry of polymers

Monosubstituted vinyl monomers form polymers containing a series of asymmetric carbon atoms along the molecule. Two parts of the main chain coming out from any carbon atom could be taken as identical, but important is the configuration of the two close, neighboring centers. There are two possible configurations of such two units (diads):

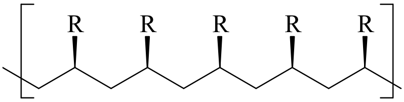


izotactic diad with the symmetry plane (meso)

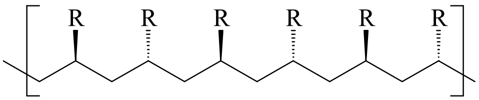


syndiotactic diad with no symmetry element (racemic)

When all possible diads adopt identical configuration, the resulting polymer is described as ***isotactic***.



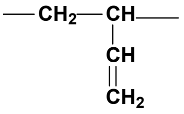
Where there is a regular alternating arrangement of asymmetric carbon (all diads are racemic), the polymer is named ***syndiotactic***.



Where there is no regularity at all in the arrangement – both types of diads are present and statistically placed, the polymer is known as ***atactic***.

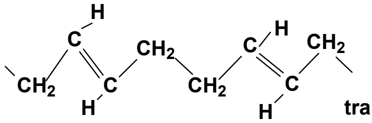
For some polymers more complicated arrangements are possible.

The polymer tacticity is not the only source of variation in the polymer configuration. ***Geometric isomers*** concern configurations involving a carbon-carbon double bond, present in the polymers of 1,3 dienes. For a polybutadiene the following structures are possible:

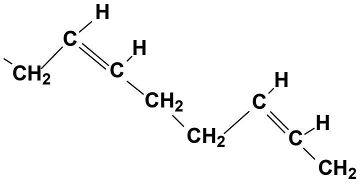


$$—CH_2—\underset{\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}}{CH}—$$

1,2-polybutadiene

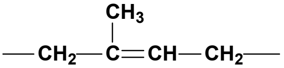


trans -1,4 polybutadiene



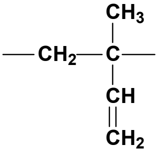
cis-1,4 polybutadiene

The polymer of a monosubstituted butadiene such as isoprene, has even more possible configurations:



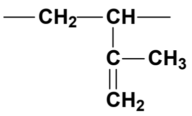
$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

1,4-polyisoprene, cis or trans



$$-CH_2-\underset{\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}}{\overset{\overset{CH_3}{|}}{C}}-$$

1,2-polyisoprene



$$-CH_2-\underset{\underset{\underset{CH_2}{\|}}{C-CH_3}}{\underset{|}{CH}}-$$

3,4-polyisoprene

For polybutadiene -1,2 , polyisoprene-1,2 and –3,4 various types of tacticity (iso-, syndio and a-tactic) are possible.

The one more configuration that can be met in polymers is head-to-head, head-to-tail configurations what is shown below for PVC. This is connected with the addition of a monomer to the growing chain. Usually dominates the head-to-tail addition what gives more stable intermediates.

$-CHCl-CH_2-CHCl-CH_2-CHCl-$ **head - to - tail**

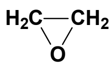
$-CH_2-CH_2-CHCl-CHCl-CH_2-$ **head - to - head**

Polymerization of cyclic organic compounds

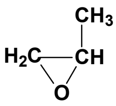
Generally as examples of chain polymerization, the compounds with double bonds were shown as monomers. The cyclic compounds are the other group of monomers that are able to form polymers. The driving force of the polymerization of unsaturated compounds is the loss of unsaturation whereas in the case of cyclic monomers polymerization it is releasing the strain by the ring opening. The example of a highly strained structure is 3-membered ethylene oxide. The polymerization enthalpy ΔH of a 3-4 membered cyclic are comparable to those for alkenes, but their entropy ΔS is smaller, so these compounds undergo the most exothermic polymerization. ΔH values for the longer-sized cyclic monomers are much lower than those for alkenes. Six-membered rings are the least strained, and hence are the most stable.

Heterocyclic monomers (ethers, lactones, lactams, etc.) undergo polymerization under both anionic and cationic conditions (depending on the monomer). Only a few examples of ring-opening polymerization are known to take place via radical pathways.

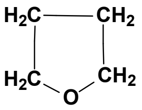
The main representative of polymerizable cyclic ethers are epoxides: ethylene oxide (1) and propylene oxide (2) which polymers and copolymers are of considerable technological importance, tetrahydrofuran (3) (gives polymer of high elasticity even in very low temperatures) and trioxane (4) (its polymerization yields polyformaldehyde).



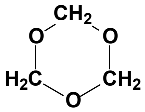
(1)



(2)

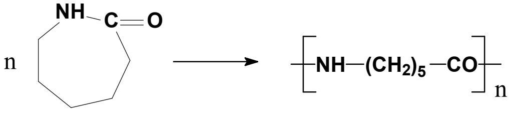


(3)

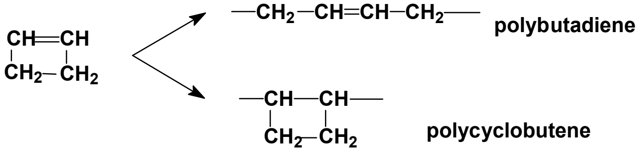


(4)

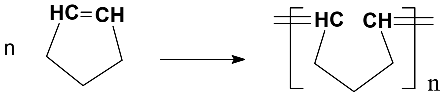
Lactones are polymerized to polyesters and lactams – to polyamides. From the last group the most important is ε-caprolactam which polymerization provides a valuable noncondensation route to the synthesis of aliphatic polyamide 6.



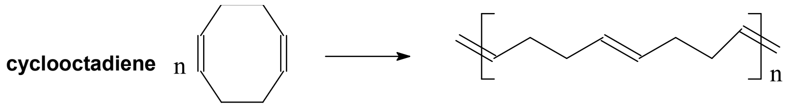
The coordination-type catalyst appeared to be very effective in polymerization of heterocyclic as well as cycloalkenes (cyclobuten, cyclopenten, norbornene).

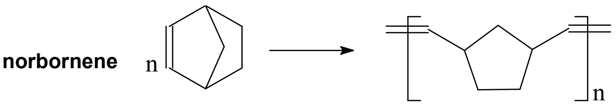


For the latter especially interesting was metathesis polymerization (ROMP – ***ring opening metathesis polymerization***) which resulted in polyunsaturated polymers called polyalkenamers:



The examples of monomers that can be polymerized by the metathesis polymerization are given below:





Copolymerization

The polymerization process in which more than one monomer (most often two) take part is named ***copolymerization*** and its product - ***copolymers***. To describe the molecule of a homopolymer, the number of units present in an average chain is sufficient. For a copolymer however also the composition and the sequence of monomers in the chain is necessary.

Copolymers can be obtained in all types of polymerization. The best known and described is free radical copolymerization.

Free radical copolymerization

The general scheme of copolymerization does not differ from that of homopolymerization - initiation, propagation, termination and transfer reactions. However the nature of the taken monomers plays a great role in copolymerization. The main difference between homopolymerization and copolymerization is the propagation stage. In the reaction medium there are two kinds of radicals ($M_1\cdot$ and $M_2\cdot$), which can react with two various monomers (M_1 and M_2), hence four propagation reactions are possible:

reaction	**rection rate**
$M_1\cdot + M_1 \Rightarrow M_1M_1\cdot$	$k_{11}[M_1\cdot][M_1]$
$M_1\cdot + M_2 \Rightarrow M_1M_2\cdot$	$k_{12}[M_1\cdot][M_2]$
$M_2\cdot + M_1 \Rightarrow M_2M_1\cdot$	$k_{21}[M_2\cdot][M_1]$
$M_2\cdot + M_2 \Rightarrow M_2M_2\cdot$	$k_{22}[M_2\cdot][M_2]$

$\mathbf{k_{11}}$ and $\mathbf{k_{22}}$ constants are the same as in homopolymerization but $\mathbf{k_{21}}$ and $\mathbf{k_{12}}$ constant of heteropolymerization strongly depend on monomers nature, radicals and monomers reactivity and polar influence among them.

Under steady-state conditions and by defining the ratio k_{11}/k_{12} as $\mathbf{r_1}$ a k_{22}/ k_{21} as $\mathbf{r_2}$ (***reactivity ratios***) one can withdraw the ***copolymer equation***. It gives the instantaneous composition of the copolymer formed γ as a function of the instantaneous composition of the comonomers mixture:

$$\gamma = \frac{1 + r_1([M_1]/[M_2])}{1 + r_2([M_2]/[M_1])}$$

Five different and typical situations can be considered, depending upon the values taken by r_1 and r_2 :

- **$r_1 < 1$ and $r_2 < 1$**

The growing chain 1 tends to incorporate preferently the monomer 2 and, conversely, chain 2 incorporates rather monomer 1 - both monomers easily undergo copolymerization and in the formed polymer the long sequences of one monomer are not observed.

- **$r_1 > 1$ and $r_2 < 1$** (or opposite)

The polymerization of the monomer 1 is favored and the formed copolymer contains less comonomer 2 than 1.

- **$r_1 > 1$ and $r_2 > 1$**

Each monomer tends to react with its own radicals. Instead of a copolymer, the mixture of homopolymers or a block copolymer could be obtained; such a system is not known in radical polymerization.

- **$r_1 \sim r_2 \sim 1$**

The composition of the copolymer is identical to a composition of comonomers mixture. Sometimes such a system is called "azeotropic copolymerization". The other situation where azeotropic copolymerization occurs is when

$$\left(\frac{[M_1]}{[M_2]}\right)_{azeotrop} = \frac{1-r_2}{1-r_1}$$

- **$r_1 \sim r_2 \sim 0$**

Each monomer reacts only with radical coming from the other monomer hence the perfect alternated copolymer is formed.

There is also one special case of copolymerization where $r_1 * r_2 = 1$. It is called "ideal copolymerization". Here two types of active centers have the same capacity to add M_1 or M_2. The sequence of both monomers in the chain is statistical and copolymerization equation takes the following form:

$$\gamma = r_1 [M_1] / [M_2]$$

Ionic copolymerization

The differences in the reactivity of growing species are more pronounced in ionic polymerization then in free radical polymerization. Only a few monomers give "statistical" copolymers. Among them the styrene-butadiene polymerized anionically is best known under the name of SBR (styrene-butadiene rubber). Anionic copolymerization is essentially utilized for the preparation of block copolymers (see this chapter "anionic polymerization").

The contrast among the three methods of polymerization is brought out clearly by the results of these processes. In Table 3.2.3 the compositions of styrene-methyl methacrylate copolymers are shown. It can be seen that monomers exhibit various reactivity with different initiators.

Table 3.2.3. Dependence of composition of styrene-methyl methacrylate copolymer on polymerization mechanism

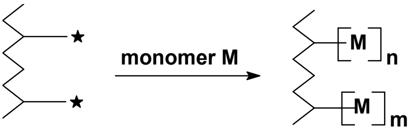
Catalyst	**Copolymerization mechanism**	**Styrene content in copolymer,%**
benzoil peroxide	**radical**	**51**
tin tetrachloride	**cationic**	**99**
metalic sodium	**anionic**	**1**

Copolymerization by coordination catalysts

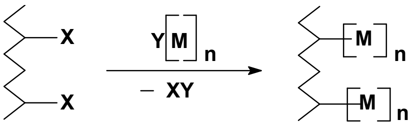
There are not many theoretical information on this type of copolymerization but some of such copolymers are commercially produced. The butadiene-isoprene copolymers, polypropylene-polyethylene rubbers, polyethylene copolymerized with small amounts of the α-olefins (LLDPE), are the examples.

Graft copolymers

Graft copolymerization results from the formation of an active site at a point on a polymer molecule other than its end and exposure to a second monomer. It is the so called "grafting from" method that utilizes most often the free radical processes. The other mechanisms of grafting (ionic, coordination) are however also possible.



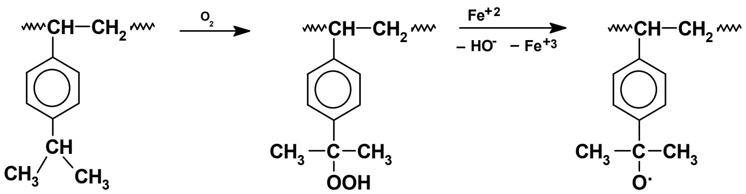
In the "grafting to" process the polymer chain is bonded to the other polymer with the help of functional groups or in the process of living polymerization.



Methods of synthesis:

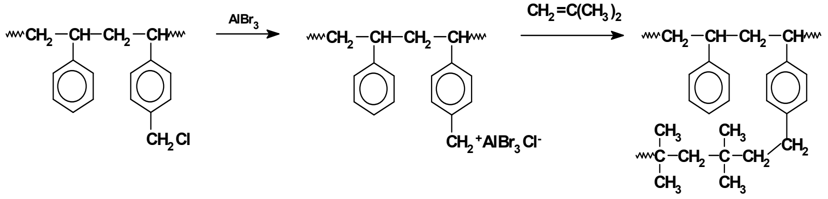
- The simplest way of grafting is heating the monomer-polymer mixture with a radical initiator. The transfer of growing radicals to a polymer will form the grafting polymer. The disadvantage of such a method is the large amount of formed homopolymer hence the isolation of the pure graft polymer is almost impossible.
- Introducing into the polymer chain groups that are able to initiate polymerization; below are the examples of generating the hydroperoxide groups :

$$\sim CH_2-CHR\sim + O_2 \longrightarrow \sim CH_2-\underset{OOH}{\underset{|}{C}}R\sim$$

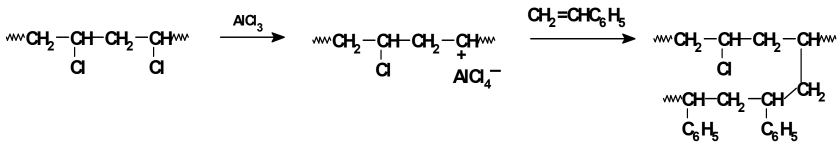


- Changing the functional groups present in a polymer into the initiating centra. Some examples are given below.

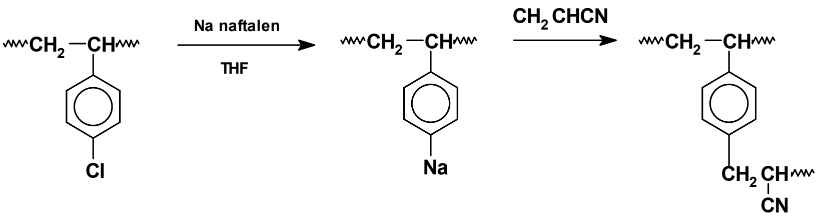
Chloromethylated polystyrene in the presence of $AlBr_3$ (cationic mechanism) reacts with 2-methylpropene, resulting in polystyrene grafted with poly(2-methylpropene):



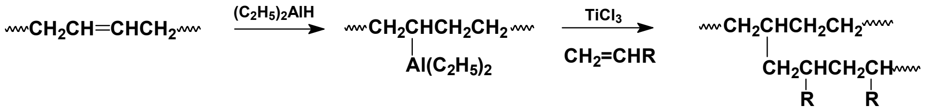
Poly(vinyl chloride) grafted with styrene also according to the cationic mechanism:



Acrylonitrile grafted anionically on poly(p-chlorostyrene) (THF, in the presence of sodium naftalene):



Unsaturated polymers can be grafted with Ziegler-Natta catalysts:



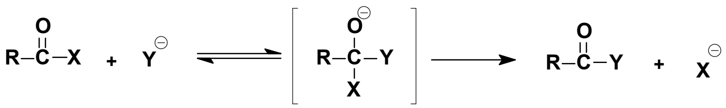
3.3. STEP-GROWTH POLYMERIZATION

Step-growth (sometimes called stepwise polymerization) involves reactions of a chemical compound carrying X and Y antagonist functional groups. There are two kinds of such polymerization - polycondensation, in which low molar mass species are generated, and polyaddition.

Reactions used in step-growth polymerization

- ***Nucleophilic substitution reactions on carbonyls***

It can be illustrated by the equation:

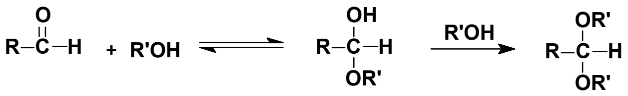


with **X = -OH, -OR', -NH$_2$, -NHR', -OCOR', -Cl**

Y = R'O$^-$, R'OH, R'NH$_2$, R'COO$^-$ R, R' = alkyl, aryl

This reaction can be catalyzed by acids (Lewis or protonic). According to this mechanism polycondensation of polyesters and polyamides undergoes.

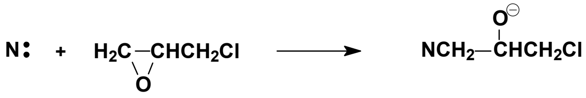
- ***Addition reactions on carbonyls***



Important polymers formed in this way include polyacetals, phenolic resins and amino resins.

- ***Nucleophilic substitution reactions***

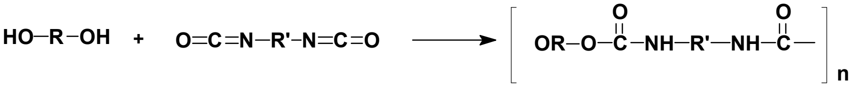
The most important among many polymerizations based on this type of reactions is that involving epoxides:



Typically, the nucleophile is a bifunctional hydroxy compoud such as bisphenol A.

- ***Double-bond addition reactions***

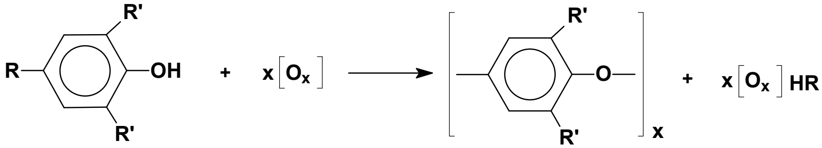
This reaction is often associated only with the chain polymerization but some important stepwise polymerizations are also based on it. Of major interest among these is the synthesis of polyurethanes and polyureas:



$$HO{-}R{-}OH \;+\; O{=}C{=}N{-}R'{-}N{=}C{=}O \longrightarrow \left[OR{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R'{-}NH{-}\overset{O}{\overset{\|}{C}}{-} \right]_n$$

- ***Free-radical coupling***

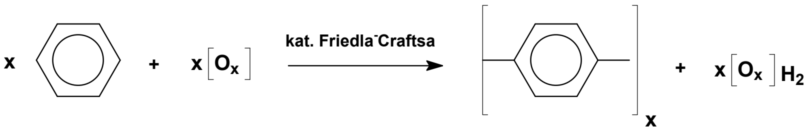
This reaction is used for the preparation of arylene ether polymers or arylene alkylidene polymers. The typical example of such polymerization is the production of poly(phenylene oxide):



where [Ox] is an oxidizing agent.

- ***Aromatic-electrophilic-substitution reactions***

A typical example of this type of reaction is the production of poly(p-phenylene).



Polycondensation

From all types of the step-growth polymerization the polycondensation is the best known. It is polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules. The classical theory of polycondensation is based on the statement that the reactivity of end groups is independent of the chain length. So all reactive species, including linear oligomers and polymers can react with each other at any time and the chain lengths increase with the conversion degree.

Requirements for high molecular weight

To obtain high-molecular-weight condensation reactions some conditions have to be fulfilled.

- *Both antagonist functional groups have to be present in exactly equal amounts*

If one of the groups exists in excess, it will remain unreacted at the chain ends and low- or medium-molecular-weight polymers are obtained. To assure an exact 1:1 ratio of the two functional groups three ways are possible:

- both reagents are carefully purified and mixed together in as close to a 1:1 ratio as it is experimentally feasible,
- taking a monomer which contains both of the functionalities, ie glycolic acid or amino acid,
- sometimes it is possible to use easy to purify 1:1 complex or salt of monomers bearing the antagonist group; as an example 1:1 salts of the dicarboxylic acid (i.e. adipic acid) with diamines (i.e. hexamethylenediamine) can be taken.

- *Very long polymerization time*

The dependence of an average degree of polymerization $\overline{DP}$ on reaction time (t) for the equivalent (1:1) system is given by the equation:

$$\overline{DP} = 1 + [Co]\, k_1\, t$$

where [Co] – concentration of functional groups.

From the equation it is clearly seen that molecular weight of polymer increases linearly with the reaction time.

- *Low molar mass species* generated during condensation reactions *should be removed.*

The condensation reactions are reversible hence such an action increases the conversion of functional groups hence the molecular weight of the product.

Molecular weight control

The dependence of an average degree of polymerization on the extent of the reaction p (defined as the fraction of the functional groups that have reacted at time t) is given by the Carother's equation:

$$\overline{DP}_n = 1/1\text{-}p \qquad \overline{DP}_w = (1+p)/(1-p) \qquad MWD = \overline{DP}_w / \overline{DP}_n = 1+p \approx 2$$

where $\overline{DP}_n$ and $\overline{DP}_w$ are the average number and weight polymerization degree, respectively and MWD – molecular weight distribution.

It is clearly seen that when the extent of reaction goes to 1, polymerization degree goes to the infinity (Fig.3.3.1).

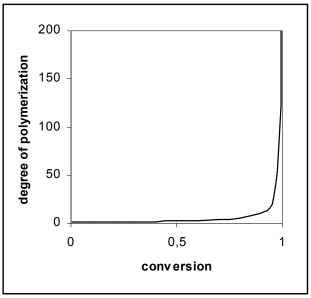


Fig. 3.3.1.
Dependence of polymer molecular weight on conversion in the polycondensation

What then, if the polymer of low or medium molecular weight is demanded? There are three ways to achieve this goal:

- Stopping the reaction at the desired point – the product however is not stable for subsequent heating and will cause further condensation what will change the polymer molecular weight.
- Adjusting the composition of the reaction mixture of two bifunctional reagents A and away from stoichiometric equivalence by adding a slight excess of one bifunctional reagent.

In this case the polymer molecular weight will be limited:

$$\overline{DP}_n = (1+r) / [2r\,(1-p) + 1 - r]$$

where: p – conversion of functional groups being in minority (A), r – ratio of N_A/N_B

(N_A, N_B – amount of moles of reagent A and B) and $r < 1$

When $p \longrightarrow 1$ $\overline{DP}_n = (1+r)/(1-r)$

This solution is not the best because polymers that contain active groups may undergo some degradation reactions and molecular weight change.

- Adjusting the composition of the reaction mixture of two bifunctional reagents A and B away from stoichiometric equivalence by adding a small amount of a monofunctional reagent C that has the same functional groups as B. The limiting value of polymerization degree for conversion p equal 1 is:

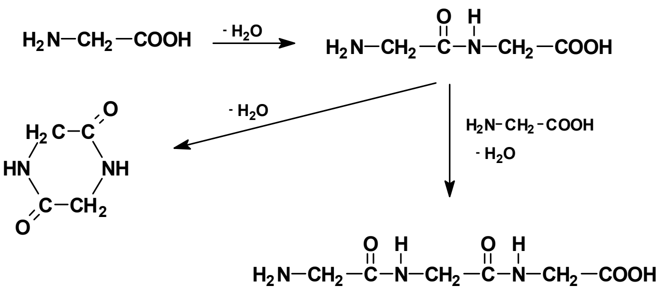
$$\overline{DP}_n = 4/s \qquad\qquad s = N_C/N_A$$

where N_C is the amount of moles of the monofunctional reagent C.

Side reactions during polycondensation

- *Ring formation versus polymerization*

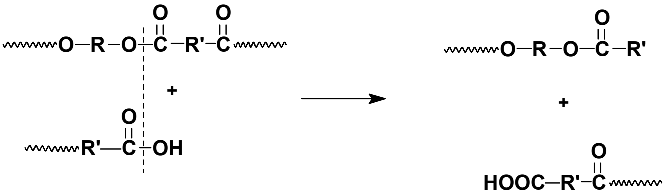
At every step in a polycondensation reaction the cyclization may occur at the expense of the linear chain growth. As an example the initial steps in the polymerization of glycine (amino acid) are shown:



The inclination to the cyclization depends on the skeletal bond angles, bond lengths, side-group steric effects, the torsional mobility of the bond, and the ring strain. Low temperature and high concentration of the reagents favor linear propagation.

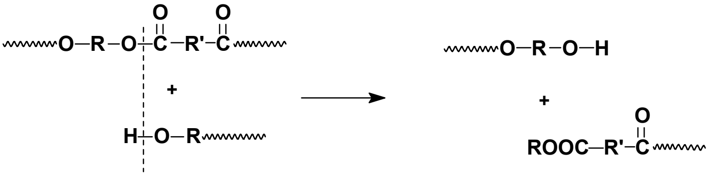
- *Scrambling reactions*

Condensation polymers that contain active end groups at the elevated temperature can undergo many degradation reactions. Depending on the kind of functional groups it can be

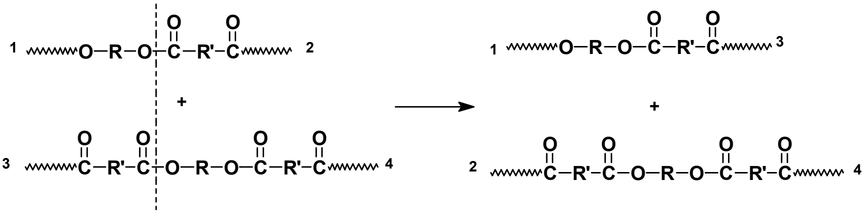


acidolysis:

alcoholysis:



transesterification:



and others like amidolysis or transamidation.

A total number of molecules remains the same but the average molecular weight may change. The same happens when two different polymer samples are mixed and heated; the system will scramble to achieve the most probable molecular weight distribution.

4. PROCESSING OF POLYMER MATERIALS

4.1. INTRODUCTION

Polymers are produced in the form of powders, beads, pellets, granulates, or melts and usually cannot be directly used or processed. They have to be washed, dried or degassed and then compounded – mixed with additives and modifiers to adjust the material properties to the technological requirements of the application.

Additives are used in low proportion (typically less than 5%) and do not affect the mechanical properties of the material. ***Modifiers*** are added in higher proportions.

Among additives one can find ***heat stabilizers*** (required for polymers that are thermally unstable), ***antioxidants*** (stabilize against the thermo - oxidizing degradation) ***chelating agents*** (trap the metal residues of catalyst), ***internal lubricants*** (improve the flow behavior), ***external lubricants*** (lower the forces of friction), ***thixotropic*** additives (for materials processed by compression molding or calendering), ***anti-static agents*** (to prevent electrostatic charging), ***adhesion promoters*** (to enhance the interaction between the polymer and the filler), ***flame retardants*** and many others.

Two most important groups of modifiers are ***plasticizers*** (lower the glass transition of the polymer by making it soft at room temperature) and ***fillers***. This last group of compounds is added to the polymer to lower its cost (extenders) or to improve its mechanical properties (reinforcing fillers). If reinforcing filler is in the form of fibers or films, such materials are called ***composities***.

The method of processing depends on the kind of polymer – thermosetting or thermoplastic. In general, plastics processes have three phases:

- **heating** - to soften or melt the plastic,
- **shaping/forming** - under some kind of constraint,
- **cooling/crosslinking** – to retain the shape.

4.2. MAIN TECHNIQUES OF POLYMER PROCESSING

- ***Compression molding***

It is used normally for the fabrication of thermosetting materials. The polymer is placed in the metal mold and heated. The mold is then closed and held shut until the resin has cured. After the opening the object is released or ejected. Below there is a scheme of the method (Fig.4.1).

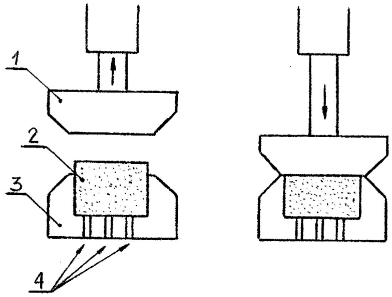


Fig. 4.1. Compression molding:
1–plunger
2–molding powder
3–cavity block
4–ejector pins

- ***Injection molding***

The method can be used for both thermoplastic and thermosetting polymers. The powdered polymer or resin is heated in the cylindrical chamber above the melting (softening) point (Fig. 4.2A) and then forced by a plunger into a two-piece mold (Fig.4.2B). After cooling (or curing) the solid product is ejected and the cycle is repeated.

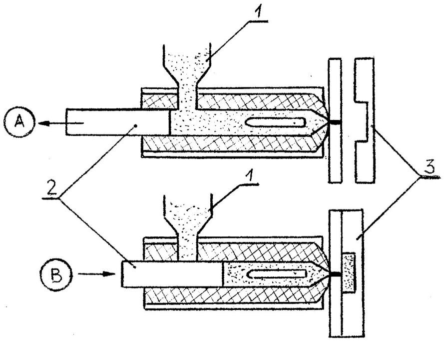


Fig.4.2. Injection-molding:

1 – hopper

2 – plunger

3 – movable part of mold

- ***Blow molding***

This technique is used for thermoplastics to make hollow objects such as bottles or tanks. A thermally softened tube from the extruder is directed into an opened, two-piece mold. The mold closes around the tube then compressed gas is injected into the tube which expands up to the inside wall of the mold (Fig.4.3). The thermoplastic hardens on cooling, the mold opens and the object is removed.

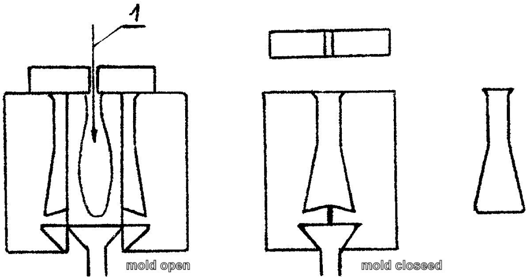


Fig.4.3. Blow-molding: 1 – inlet of compressed air

- ***Thermoforming***

A sheet of thermoplastic polymer is heated above the softening temperature, and then pressed into a mold by the application of pressure or vacuum (Fig.4.4). The technique is used to make shallow objects like trays.

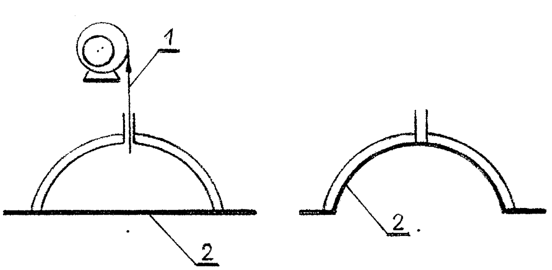


Fig.4.4.

Thermoforming of polymer sheets: 1 – vacuum,
2 – polymer sheet

- ***Rotational molding***

The solid material is melted inside a closed mold. The mold is then rotated in such a way that the polymer coats the inside surface uniformly as it cools. This techniques is used for the fabrication of hollow objects like water tanks, luggage or battery cases.

- ***Extrusion***

Extrusion applies mainly to thermoplastic materials to produce tubes, pipes, sheets, films and filaments. The polymer melt is extruded with the extremely high pressure through the nozzle of a die whose cross-sectional shape determines the shape of the obtained product (Fig.4.5).

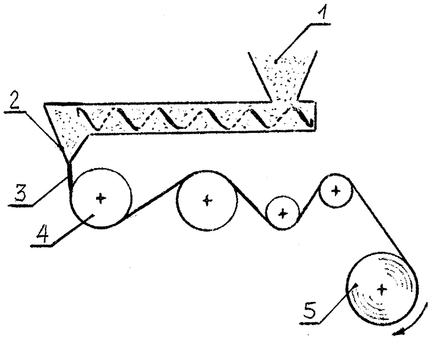


Fig.4.5. Melt extrusion of polymer film (or filament):

1 – polymer pellets
2 – die
3 – film
4 – cooling roller
5 – film (filament) wind-up

The extrusion process using a die in the form of thin slit, results in forming a polymer film. From extrusion the **extrusion-blowing** (bubble blown) process is derived (Fig.4.6.).

The air blown through the extruded tube produces a tubular film of large diameter, flattened then by the rolls. The majority of films are manufactured in this manner.

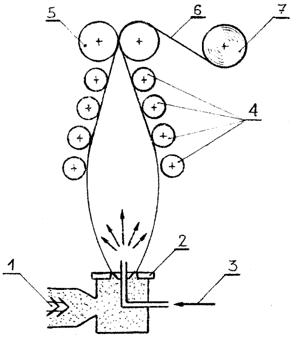


Fig. 4.6. Extrusion blowing of film:

1–screw extruder

2–annular die

3–compressed air

4 – flattening rollers

5 – “nip” rollers

6 – film

7 – wind-up roller

Except the extrusion there are a few other ways of the ***preparation of films:***

- ***Solution casting***

The solution of polymer is poured onto a flat, nonadhesive surface (the uniform thickness of the layer has to be ensured) and the solvent is allowed to evaporate. The dry film is peeled from the substrate. The method is most often used in the laboratories but industrial devices are also known (Fig.4.7).

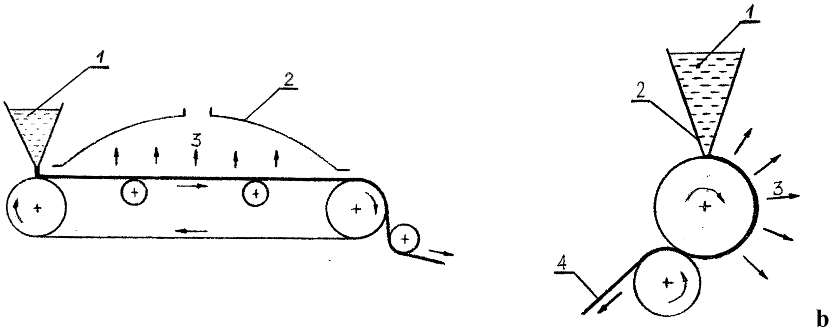


Fig. 4.7. Industrial casting film from a solution

a. use of **rotating drums**: 1 – polymer solution, 2 – hood for solvent removal, 3 – solvent vapor

b. use of a **moving-belt** system: 1 – polymer solution slit die,

- ***Melt pressing***

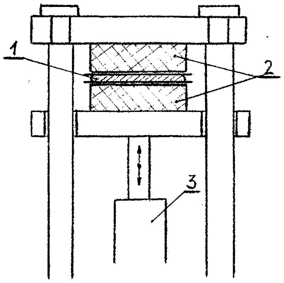


Fig.4.8. Melt pressing of polymer film in the hydraulic press:
1 – polymer between non-sticking foil
2 – heated platens
3 – hydraulic unit

This is a laboratory method of polymer films preparation. The polymer (between sheets of a nonadhesive film) is placed between the two heated platens of the hydraulic press (Fig.4.8). After melting pressure is applied, then the sample is cooled and the film is separated from the foil.

- ***Calendering***

This technique is used to produce sheets, films and plates of variable thickness and also to mix, formulate and homogenize polymers. The principle of the method is shown in Fig 4.9.

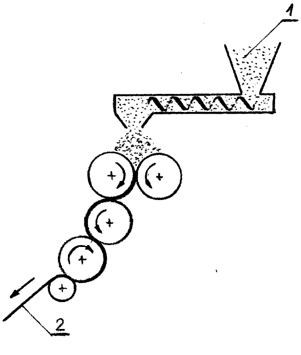


Fig.4.9. Film production by calendering:
1 – compounding
2 – stretching, annealing, and wind-up.

One of the most important branches of the polymer technology is the production of synthetic fibers. Fibers can be produced by two fundamental techniques: solution spinning and melt spinning.

- ***Melt spinning***

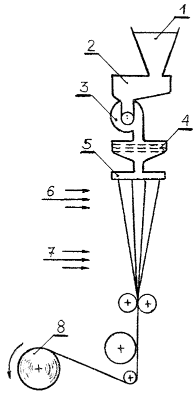


Fig.4.10. Melt spinning of fiber:

1 – polymer pellets
2 – heated melt-grid
3 – pump
4 – filter
5 – spinneret
6 – cold gas
7 – fiber conditioning (steam)
8 – wind-up

This process is the most widely used. The polymer melt is sent under pressure through a spinneret comprising a great number of narrow holes. The filaments are pulled off at high speed whereby they cool below the melting point and solidify while forming a yarn (Fig. 4.10). The latter is oriented by stretching up to 400-500%, to enhance its mechanical properties.

- ***Solution spinning***

In this method instead of melt (like in the previous method) the viscous solution of polymer is taken. After coming out of the spinneret the solvent can be removed from the solution or by drying (in the hot air stream) or by coagulation in a nonsolvent bath. The first of these two methods is known as ***dry spinning*** (Fig.4.11) while the other – ***wet spinning*** (Fig. 4.12).

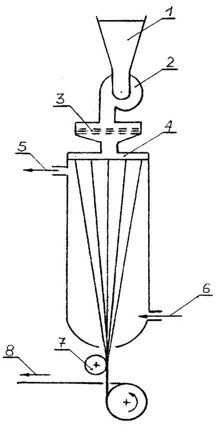


Fig.4.11. Dry spinning of fibers:

1 – polymer solution, 2 – pump,
3 – filter, 4 – spinneret,
5 – solvent, vapor outlet, 6 – hot gas,
7 – finishing,
8 – fiber going to orientation and wind-up

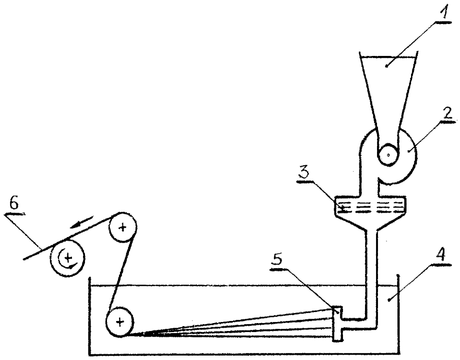


Fig. 4.12. Wet spinning of fiber:

1 – polymer solution
2 – pump
3 – filter
4 – coagulation bath
5 – spinneret
6 – fiber going to washing, orientation and wind-up.

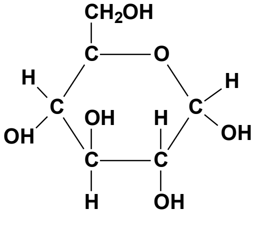
5. NATURAL POLYMERS

Polymers are widely found in nature. The human body contains many natural polymers, such as proteins and nucleic acids. Cellulose, another natural polymer, is the main structural component of plants. The number of natural polymers is huge but most of them can be classified as one of the four groups:

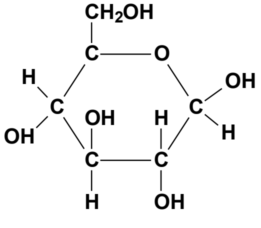
- polysaccharides,
- proteins,
- polynucleotides,
- hydrocarbons.

5.1. POLYSACCHARIDES

Polysaccharides are ***cyclolinear polyethers*** formed by the condensation reaction of sugars. From the large number of known polysaccharides the cellulose, starch, and glycogen are the most important. All the three mentioned polymers are homopolymers of glucose. There are two cyclic forms of glucose - α-D-glucose and β-D-glucose which differ in configuration of hemiacetal carbon.



α-D-glucose



β-D-glucose

In a solution these two forms are easily interchangeable. In polymers the hydroxyl group of that carbon makes the ether bond with the hydroxyl group of other molecules. This changes hemiacetal in stable acetal of α or β structure.

Cellulose is the poly(β-D-glucose). It is the most abundant structural material used by plants. Cotton or flax are nearly 100% cellulose and wood is roughly 50% cellulose. For in each glucose molecule there are three free hydroxy groups, cellulose chains are hydrogen bonded and are fully extended. That makes cellulose a highly crystalline polymer.

It is soluble in only a few highly specific solvents, as a complex of Cu with ammonia, complex of Cd with ethylenediamine, *N*-Methylmorpholine-*N*-oxide, and concentrated solutions of some Sn, Sb or Bi salts.

The cellulose is modified in industry in high quantities. It undergoes the reaction characteristic for hydroxyls but its crystalline structure limits the penetration of reagents. Many reactions are then preceded by ***mercerization***. Mercerization is a treatment of the crude cellulosic material with aqueous sodium hydroxide. In the presence of air the aging process takes place which results in lowering molecular weight and crystallinity, looser structure, more proper for dyes and other chemical agents.

Reaction of cellulose with the nitric acid gives ***cellulose nitrate***, incorrectly named *nitrocellulose*. The fully modified material has 13.8% of N instead of the theoretical 14.4 because part of hydroxyls react with catalyst - sulfuric acid. Cellulose nitrates that contain 12.5-13.4 nitrogen are explosive and are known as a "gun cotton". Cellulose nitrate plasticized with camphor was the first widely used plastic – ***celluloid.*** It was highly flammable material and for this reason is now withdrawn from the market.

The reaction of cellulose with acetic anhydride (also catalyzed by sulfuric acid) yields ***cellulose triacetate***. Its partial hydrolysis results in product that is soluble in acetone and finds many applications as textile fibers, photographic films and many others. There are known also mixed esters of cellulose like acetate-butyrate, or acetate-propionate.

Ethers of cellulose can be formed by the treatment of alkaline cellulose compositions with an alkyl halide. The reaction with methyl chloride, methyl iodide or dimethyl sulfate yields ***methylcellulose***, polymer soluble in water. ***Ethyl cellulose*** and ***carboxymethylcellulose*** are prepared by the reaction of alkaline cellulose with ethyl chloride chloroacetic acid respectively. Ethers of cellulose are widely applied in cosmetic, pharmaceutical and food industry. Cellulose can be also crosslinked (what gives the uncreasable textile) or grafted with such monomers as vinylidene chloride (resistance to abrasion) or styrene (good adherence to rubber).

Cellulose fibres

Cellulose fibres may be made of pure or modified cellulose. The former are known as ***Rayon*** or ***synthetic silk***, although these names are often extended on all fibres based on cellulose.

Three main ways of production of cellulose fibers can be distinguished:

- *Dissolution of cellulose, extrusion through spinnerettes into regeneration bath (usually water)*

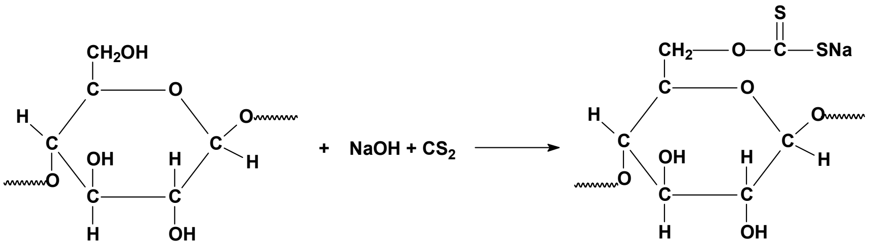
In the Schweizer (***cuprammonium***) process dissolution of cellulose material is made in complex of copper oxide and ammonium hydroxide. The obtained material is very high quality but cost of copper lost during processing made that this method is rarely used at the present time.

In the Lyocell process ***N-Methylmorpholine-N-oxide*** is used as a solvent for cellulose. The method is new and fullfils all ecological requirements. The fibers have improved physicomechanical properties, are easy to dye, resistant to fire and germicidal.

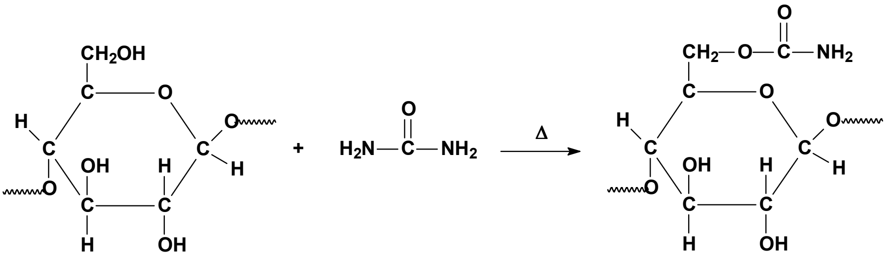
In the ***Celsol*** method celulose is treated with the ***specyfic enzyme mixture*** what makes material soluble in NaOH.

- *Modification of cellulose, dissolution of product, fiber formation and cellulose regeneration*

The most popular method of Rayon production (more than 90%) makes use of the reaction of ***alkaline cellulose with carbon disulfide***. Viscous solution of cellulose xanthate (hence called "***viscose***") is extruded in the form of fiber then regenerated with acid.



The reaction of cellulose with urea yields ***cellulose carbamate*** that is soluble in NaOH solution and from that solution formed in fibers and regenerated in acids.



- *Production of fibers from modified cellulose*

Two earlier mentioned products of cellulose modification namely nitrate and acetate are able to form fibers. However as the nitrate is highly explosive nowadays only the former is used for this purpose. Textile produced from cellulose acetate is commonly named as acetate silk and finds many applications. The properties of cellulose acetate fibers depend on the acetylation degree.

Starch is the principal energy-storage polysaccharide of the photosynthetic plants. It is mainly a homopolymer of α-D-glucose. Starch molecules include two types of glucose polymers, amylose and amylopectin, the latter being the major starch component in most plants, making up about three-fourths of the total starch in wheat flour. Amylose is a straight chain polymer with an average of about 200 glucose units per molecule.

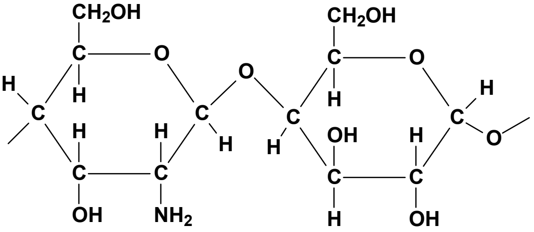
A typical amylopectin molecule has about 1,000 glucose molecules arranged into branched chains with a branch occurring every 24 to 30 glucose units. The complete hydrolysis of amylopectin yields glucose; the partial hydrolysis produces mixtures called dextrins, which are used as food additives and in mucilage, paste, and finishes for paper and fabrics. Nowadays a large quantities of starch are used for modification of other polymers to obtain biodegradable materials. From such materials wrapping foils and flower pots are produced.

Glycogen is a storage polysaccharide found in animal tissues. Its resembles starch in its composition but is higher branched than amylopectin component of starch.

Chitin, a polysaccharide similar to cellulose, is the Earth's second most abundant polysaccharide (after cellulose). It is present in the cell walls of fungi and is the fundamental substance in the exoskeletons of crustaceans, insects, and spiders.

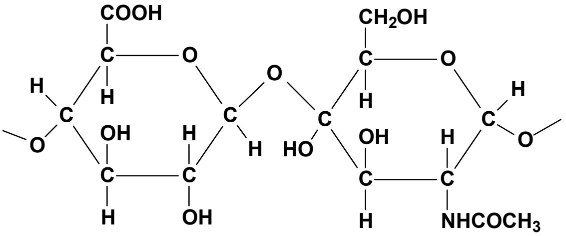
The structure of chitin is identical to that of cellulose, except for the replacement of the OH group on the C-2 carbon of each of the glucose units with an –$NHCOCH_3$ group. The principal source of chitin is the shellfish waste.

The partial deacetylation of chitin yield ***chitosan*** that is biodegradable, bioactive and biocompatible material. It has numerous applications covering various fields like medicine, biotechnology, wastewater treatment, and artificial membranes, including artificial skin, and many others.



chitosan

Hyaluronan (hyaluronic acid) is found in many tissues of the body, such as skin, cartilage, and the vitreous humour. Hyaluronan is a polymer of disaccharides, composed of D-glucoronic acid and D-N-acetylglucosamine, linked via alternating β-1,4 and β-1,3 glycosidic bonds. Polymers of hyaluronan can range in size from 5,000 to 20,000,000 Da *in vivo*.



hyaluronic acid

Hyaluronic acid is gaining great popularity in the cosmetic and medical industries.

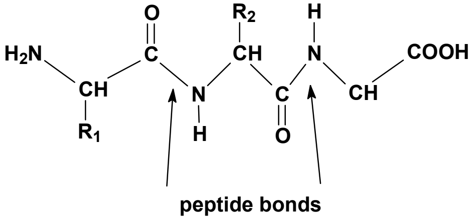
Alginic acid is a polysaccharide found in cell walls of many algae and seegrass . It is not soluble in water but swells significantly increasing its volume. It is used in cosmetic and food industry.

Polysaccharides find also a **biomedical application**. Textiles made of cellulose and its derivatives are used in protective **surgical gowns, operating room drapes, masks, shoe cover**. Hollow fibers' membranes made of cellulose acetate and membranes from regenerated cellulose are used in **artificial kidney device** (hemodialyzer) and the former also in **osmotic drug delivery systems**. **Medical gauze** is made of cottton fiber. Polysaccharides serve also as **pharmaceutical coatings**.

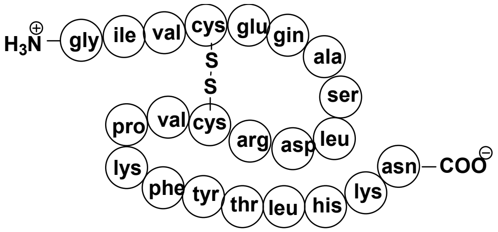
Combined cellulose esters as acetate-propionate or acetate-butyrate are used in articles such **as tubing and special trays for urological or spinal procedures, membranes in dialyzers, filters and IV buret housing**.

5.2. PEPTIDES AND PROTEINS

Peptides are short polymers of amino acids linked by ***peptide bonds***. They have the same chemical structure as ***proteins*** (sometimes called ***polypeptides***), but are shorter in length. In nature, there is much more proteins than peptides. Proteins exhibit an enormous variety of structures. The degree of polymerization of proteins range from about 50 to over 8 000.



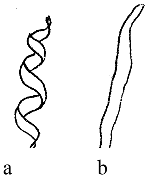
The ***primary structure*** of a protein is the amino-acid sequence of the polypeptide chain(s), without regard to the spatial arrangement. Very important is the location of any disulfide (-S-S-) bridges.



The sequence and properties of side chains determine all that is unique about a particular protein, including its biological function and its specific three-dimensional structure. Every protein has a specific sequence of amino acids and a well defined number. They are then monodispersive polymers.

There are only 20 commonly occuring amino acids, and each of them introduces some characteristic features to the protein.

The ***secondary structure*** of a segment of polypeptide chain is the local spatial arrangement of its main-chain atoms without the regard to the conformation of its side chains or to its relationship with other segments. Of all the regular secondary structures the ***alpha-helix*** (a) and ***beta-structure*** (b) conformations are the most thermodynamically stable.



The **tertiary structure** refers to the three-dimensional structure of the entire peptide chain. To be biologically active, proteins must adopt specific folded three-dimensional, tertiary structures. If this is disrupted, the protein is said to be **denatured**, and it loses its activity.

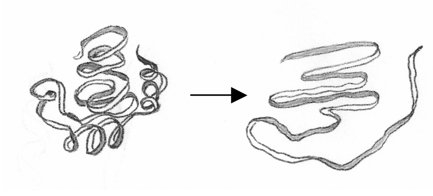


Fig. 5.2.1. Denaturation of protein

The denaturation process presumably involves an unfolding or at least an alteration in the nature of the folded structure and is the response of the native protein to heat, acid, alkali, and a variety of other chemical and physical agents.

Complexes of 2 or more polypeptide chains are held together by noncovalent forces (usually) but in precise ratios and with a precise 3-D configuration make the ***quaternary structure*** of a protein.

Proteins depending on the conformational characteristics can be divided into two classes: fibrous and globular. ***Fibrous proteins*** are tough, insoluble materials found in the protective and connective tissues of animals, birds, and reptiles. Among them are ***α-keratines*** (found in hair, wool, horn, nails, feathers, and leather*),* ***β-keratin*** (silk fibroin) and ***collagens*** (found in animal connective tissue and tendons).

Globular proteins are soluble in aqueous media. They are responsible for organizing the chemical reactions that take place in a living system. Enzymes, antibodies, hemoglobin, myoglobin, serum albumin and some hormones are all globular proteins.

Every function in the living cell depends on proteins:

- the motion and locomotion of cells and organisms - contractile proteins (muscles),
- the catalysis of all biochemical reactions (enzymes),
- the structure of cells, and the extracellular matrix in which they are embedded (collagens),
- the transport of materials in body fluids (blood),
- the receptors for hormones and other signaling molecules,
- an essential nutrient for heterotrophs,
- the transcription factors that turn genes on and off to guide the differentiation of the cell and its later responsiveness to signals reaching it.

Difficulties of traditional synthesis of peptides by condensation of amino acids was solved by ***solid phase peptide synthesis*** invented by Bruce Merrifield in 1959. The principle behind his idea is that if the peptide is bound to an insoluble support then any unreacted reagents left at the end of a synthetic step can be removed by a simple wash procedure, greatly decreasing the time required for synthesis makes able automation of the process.

Some proteins find application in biomedicine. Silk fibers serve as non-absorbable suture, collagen (also in composites) is a matrix for dermic growth (artificial skin), gelatine-modified phenolic resins and other fibrin proteins are used as biological tissue adhesives, gelatin, collagen albumin – in biodegradable drug carrier systems. Gelatin is also used as an ingredient in implantable medical devices, such as in some bone void filler.

5.3. POLYNUCLEOTIDES

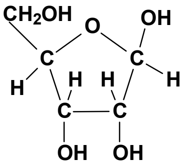
Polynucleotides, known also as a ***nucleic acids***, are the macromolecules found within living cells, that are responsible for the storage of genetic information, for its replication, and for providing templates that direct the synthesis of proteins. They are the macromolecular polyesters of phosphoric acid, a sequence of nucleotides. Each monomer unit - ***nucleotide*** - is composed of a phosphoric acid residue plus a sugar residue (polymer main chain) and a heterocyclic organic base (side group attached to the sugar).

Nucleic acids are of two types: deoxyribonucleic acid (**DNA**), the storehouse of genetic information, and ribonucleic acid (**RNA**), which transfers genetic information from cell DNA to cytoplasm, where protein synthesis takes place. The various forms of DNA contain only the sugar deoxyribose, and four bases: ***adenine, cytosine, guanine and tymine.***

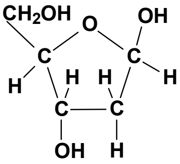
Each DNA supramolecular units consist of two polymeric strands that are bound together on the form of well known "double helix". RNA contains only the sugar ribose and adenine, cytosine, guanine and ***uracil.*** It is a single-strand polynucleotide.

RNA

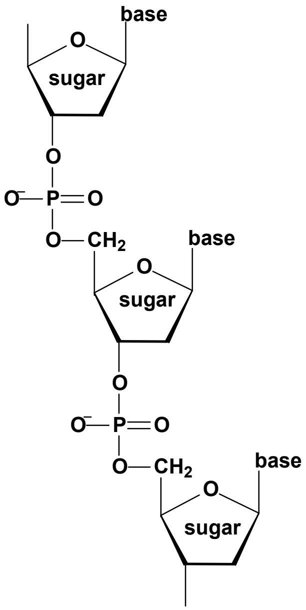
DNA

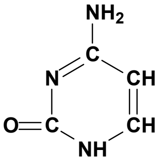


ribose

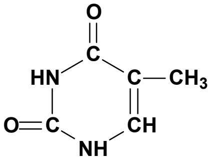


deoxyribose

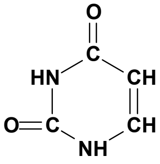




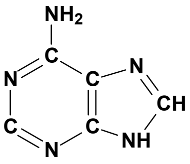
cytosine



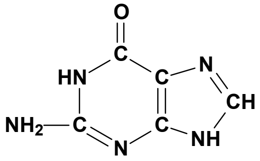
thymine



uracil



adenine

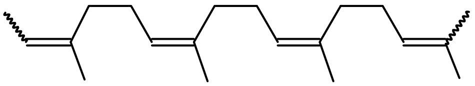


guanine

5.4. NATURAL HYDROCARBONS

In nature one can find many various hydrocarbon materials as natural rubber, gutta-percha, balata, asphalt, or bitum.

Natural rubber is obtained from the *Hevea brasiliensis* tree in the form of latex. ***Latex*** is a about 35% emulsion of ***cis-1,4-polyisoprene***,

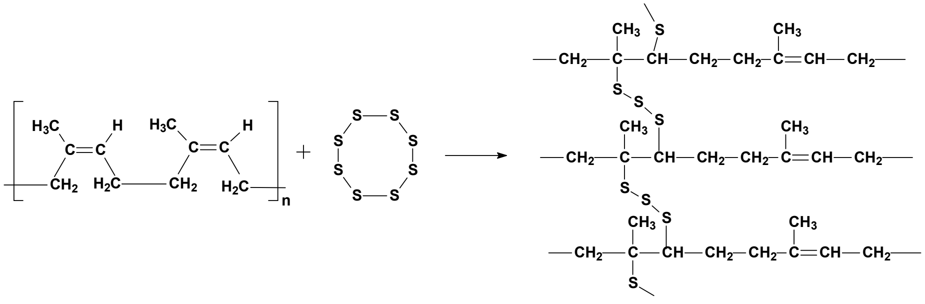


with a molecular weight of 100,000 to 1,000,000, in the water. Typically, a small percentage (up to 5% of dry mass) of other materials, such as proteins, fatty acid, resins, and inorganic materials (salts) are found in natural rubber.

Latex is generally processed into either latex concentrate for manufacture of *dipped goods* or it can be coagulated under controlled, clean conditions using weak acid (formic, acetic). Slabs of coagulum are milled in a successive pairs of rollers giving sheets of uniform thickness. The sheets can be dried by natural ventilation (*pale crepe*) or dried over open wood fire (*smoked crepe*).

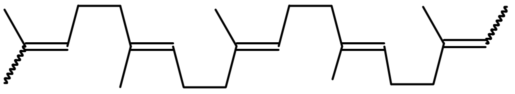
Natural rubber is an elastomer and a thermoplastic. Uncured natural rubber is sticky, easily deforms when warm, and is brittle when cold. Its chains can move independently relative to each other, which enables the material to change shape. Crosslinking introduced by ***vulcanization*** prevents the polymer chains from moving independently. As a result, when stress is applied the vulcanized rubber will deform, but upon the release of the stress, the article will revert to its original shape.

The vulcanized material is less sticky and has superior mechanical properties. It shows elasticity even in -80°C. A vast array of products are made with vulcanized rubber including tires, shoe soles, hoses, and hockey pucks. Hard vulcanized rubber is known as *ebonite* and is used to make hard articles such as bowling balls and clarinet mouth pieces. The sulphur and sulphur-containing derivatives are the most often vulcanizing agents. Some substances accelators and activators are also added. Vulcanization scheme is shown below:



There are other plants containing natural rubber latex. Interesting is *guayule* (*parthenium argentatum*), native to North America, being a useful, non-allergenic alternate source for Hevea derived rubber.

Chemically, ***gutta-percha*** and ***balata*** are also a polymer of isoprene, but composed of trans-1,4-polyisoprene:



These materials are bioinert, resilient, and are good electrical insulators. They have excellent adherence to the other materials and are better chemically resistant than natural rubber. It is used for production of golf balls, isolation under-sea cables, surgical articles, o-rings and other.

Asphalts are highly complex and not well-characterized materials containing saturated and unsaturated aliphatic and aromatic compounds with up to 150 carbon atoms. Their composition varies depending on the source of crude oil. Many of the compounds contain oxygen, nitrogen, sulfur, and other heteroatoms. Asphalt typically contains about 80% by weight of carbon; around 10% hydrogen; up to 6% sulfur; small amounts of oxygen and nitrogen; and trace amounts of metals such as iron, nickel, and vanadium. The molecular weights of the constituent compounds range from several hundred to many thousands. It is a thermoplastic material of remarkable waterproofing and binding properties. Asphalt-containing materials find application not only in paving and road construction, but also in roofing, coatings, adhesives, and batteries.

6. CHARACTERISTIC OF THE MAIN POLYMER GROUPS

The properties of a polymer depend on its skeleton (backbone) and also on the presence of side groups. The skeleton decides of the chain flexibility and polymer stability to chemical reagents and temperature. For most polymers the side groups determine solubility, crystallinity, or surface chemistry.

6.1. POLYMERS WITH ALIPHATIC CARBON-CARBON BOND IN THE MAIN CHAIN

The carbon-carbon single bond confers great flexibility to a polymer chain. This is the consequence of the inherently low barrier to torsion. The main weakness of such a chain unit is its sensitivity to the termooxidative cleavage. The side groups other than hydrogen atoms may protect the chain against degradation.

Polyolefins are polymers of olefins (alkenes); they do not possess polar group. The simplest polymer from this group is ***polyethylene (PE).***

$T_g \sim -80^oC$ $\quad$ $-CH_2\text{-}CH_2\text{-}$

It is the most important synthetic polymer. Free radical polymerization of ethylene in high temperature and pressure leads to ***low-density polyethylene (LDPE)***. It is highly branched due to transfer reactions taking place during polymerization. LDPE is translucent material of density from 0.915-0.925g/cm^3. Applied mainly in form of film sheets for packaging, also used as tubes, wire and cable insulators, houseware, toys, and in many other applications.

Polymerization of ethylene by coordination catalysis leads to polymers that are perfectly linear and highly crystallizable ***high-density polyethylene (HDPE).*** Its degree of crystallization is close to 70% and density reaches 0.97g/cm^3. HDPE is used for pipes, films, and large containers. The other types of PE include:

ULD PE – ultra-low-density PE

Its density ranges from 0.86 to 0.915g//cm^3. This polymer is used for production of transparent films resistant to tearing, for food wrapping.

LMW PE – low- molecular-weight polyethylene

It looks like wax and is used as coating for paper and other packaging materials, for production of printing dyes and wax crayons.

UHMW PE – ultra-high-molecular-weight PE

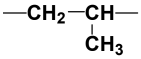
Molecular weight reaches 6 000 000 Da. It has exceptional abrasion and impact resistance compared to other polyethylenes. Its uses include bearings, gaskets, conveyor-belt parts and other high-wear-resistance applications.

PE can be also **crosslinked** by peroxides (used in wire and cable industry, also for pipes and hoses) or by irradiation with high-energy electrons (films of thermal stability and high tensile strength, also heat shrinkable).

All kinds of PE are widely used in **biomedical applications. LDPE** is used for **ultra clean packaging, stoppers, vials, syringe components, filters, medical tape (**with acrylate pressure-sensitive adhesive) and as **sealant layer** ensure **a hermetic package**. **UHMWPE** can be found in **catheter balloons, stent covers or vascular grafts, used also for medical sutures, endoprostheses and for hip and knee joint replacement.** Made of it **suture** is used **in cardiovascular and orthopedic surgery procedures. PE nonwovens** are used for production of **ostomy bags. Crosslinked PE** is used **for high-pressure catheter balloons.**

Alkyl side groups reinforce the hydrocarbon character of the skeleton providing hydrophobicity and solubility in organic solvents.

Polypropylene (PP) $T_g \sim -20^{\circ}C$

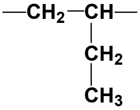


$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

PP can be made as isotactic, syndiotactic, or atactic form. Only the tactic form of PP has properties of commercial interest. Its high crystallinity imparts its high tensile strength, stiffness, and hardness. PP has excellent electrical properties and the chemical inertness and moisture resistance. Because of the presence of tertiary hydrogen it is less stable than PE to heat, light and oxidative attack and must be stabilized. Injection molded articles are widely used in the automotive and appliance fields. As filaments it is used for ropes, cordage, webbing and carpets production.

Disposable syringes, medical specimens (urine, stool) containers, self sealing sterilization pouch, packaging, sterilization wraps, pharmaceutical filter media, hernia meshes, endoprostheses, sutures, tubing and hubs of vessel dilators, and many others sterilizable medical devices are made of polypropylene**. Nonwoven PP fabric** can be used for **surgical and isolation gowns, face masks and fillers**.

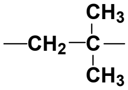
Poly(butene-1) $T_g \sim -24^{o}C$



$$-CH_2-\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{CH}}}-$$

Mechanical properties are like those of LDPE, but it has higher flexibility, resistance to creep, environmental stress cracking, chemicals, and abrasion. It is used for hot water containers, pipes, cable insulation, wrapping films, sealing tapes, shoe soles, floor covering and polyolefins modification. In a blend with PE it is used in **medical packaging**.

Polyisobutylene (PIB) –butyl rubber $T_g \sim -73^{o}C$

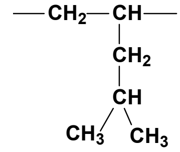


$$-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$$

It is properly a copolymer but the other monomer - isoprene - is used in a very low content (about 1%). The latter is used only to make possible the vulcanization of material. The polymer is amorphous and at room temperature exhibits elastomeric behavior. Its main property is its impermeability to gases, and resistance to most chemicals and water.

It has found an application in production of tubeless tires, sealing compounds, joints, various coatings and as an additive to gasoline increasing the motors power. It is used also as lubricating oil additive, hot-melt adhesives and chewing gum base. From biomedical applications the most important is using as **implant material for soft tissue replacement and reconstruction** and in **medical plasters**.

Poly(4-methyl-1 pentene) (PMP)



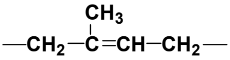
$$-CH_2-CH(CH_2CH(CH_3)_2)-$$

This polymer has the lowest density (0.83) from all olefins, it is transparent, flexible and chemicals resistant. It is used for production of household articles, **medical tools (sterilized)**, hoses and food wrapping.

Double C=C bond in the main chain

The aliphatic carbon-carbon double bonds are expected to generate chain stiffness. However such an effect is observed only for chains with alternating single and double bonds (polyacetylene). In other polymers the torsional mobility of the adjacent single bonds is enhanced. Double bonds in a hydrocarbon skeleton are sites that are sensitive to chemical attack, especially by ozone or by oxygen.

Polybutadiene (BR-butadiene rubber) $T_g \sim -110^{o}C$ $—CH_2—CH{=}CH—CH_2—$



$$—CH_2—\underset{}{\overset{CH_3}{\overset{|}{C}}}{=}CH—CH_2—$$

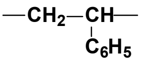
Polyisoprene (IR – isoprene rubber) $T_g \sim -72^{o}C$

Both polymers have similar properties. Double bonds in the chain make polymer vulcanization possible. Cis-isomers are used in tire industry along with natural rubber, also shoes soles, adhesives. Trans-isomer has a limited and specific application. Huge amounts of polybutadiene go for production of high-impact polystyrene. Various rubber products find an application in **medical industry** – the examples are **gloves, catheters, diaphragms, tubing, tube caps and stoppers, wheels and casters for hospital beds and trolleys**, and many others.

Aryl side groups

Phenyl rings are hydrophobic, rigid, and relatively bulky, so they impose stiffness and steric hindrance on to any chain to which they are attached. Aromatic rings adsorb UV energy thus undergo photolytic reactions that can lead to discoloration and decomposition of a polymer.

Polystyrene (PS) (poly(1-phenylethylene) $T_g \sim 100^{o}C$



$$—CH_2—\underset{C_6H_5}{\underset{|}{CH}}—$$

Commercial polymer is the amorphous, thermoplastic material, transparent, hard and brittle. Used for production of many small articles (toys, boxes, trays, disposable dishes and cases), optical components and others. In the form of rigid foams PS is utilized in the packaging industry and in the insulation buildings.

Numerous polystyrene products as diagnostic instruments and disposable labware, petri dishes, tissue culture components, flasks, pipettes, trays, syringes, they find an application in biomedical laboratories. Polystyrene derivative – sodium sulfonate – is used to treat a high level of potassium in blood and as an immune-modulation drug for the complement inhibition.

Chlorine as a side group unit

Chlorine connected directly to a carbon skeleton, increases chain stiffness and usually (except of benzyl chloride units) enhances its chemical resistance and reduces the solubility in hydrocarbon solvents or fuels. Carbon-chlorine bonds are prone to photochemical reactions in sunlight and the addition of stabilizers is necessary. The chlorine-containing polymers are not suitable for use as biomaterials but many products are used in medical industry.

The most important in this polymer group is

Poly(vinyl chloride) (PVC) $T_g \sim 80^oC$ $-CH_2-CHCl-$

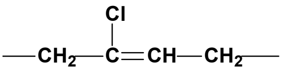
As thermoplastic polymer is utilized in two forms: rigid and plasticized. Pure polymer is very hard, stiff, used for example for production of pipes, house siding, doors and window frames, small electrical equipment. PVC fibers are used to manufacture fireproof furnishing fabrics. Plasticized PVC is elastic well extruded into film or tubes and used as a cable insulator, artificial leather, floor covering, shower curtains, gaskets.

PVC is used to manufacture **medical tubing for dialysis, blood transfusion and feeding, endotracheal, feeding and pressure monitoring, heart and lung bypass sets, hard valves in medical devices catheters, drip chambers and caps, suction tubing connectors, blood containers, urine continence and ostomy products, oxygen tents**, **inhalation masks, surgical and examination gloves, blister pack for pills and tablets** and others.

Poly(vinylidene chloride) (PVDC) $T_g \sim -17^oC$ $-CH_2-CCl_2-$

Its application is determined by two physicochemical characteristics – very low permeability to gases and liquids (films in food packaging, containers, coatings) and flame resistance (textile fibers for furnishing fabrics).

Polychloroprene (CR – chloroprene rubber, neoprene)



$$-CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2-$$

It is the oldest synthetic rubber, cured with metal oxides. It finds applications due to its durability, oil, fuel, and ozone resistance, good adhesive properties, and fireproof character. It is widely used for the manufacture of flexible tubes, sealing joints, adhesives, and paints.

Fluorine as a side-group unit

The presence of fluorine has a profound effect on nearly all the properties of the material. This is why “fluoropolymers” usually are treated as a separate class of polymers with the unique properties. The presence of C-F bonds causes extreme hydrophobicity and water insolubility and surface lubricity. It raises the thermal and oxidative stability and confers solvent, fuel, and oil resistance. They are biocompatible.

Poly(vinyl fluoride) (PVF $T_g \sim 50^oC$ $—CH_2—CHF—$

In the absence of molecular oxygen, PVF is thermally stable up to 450^oC. It is used for production of biaxially stretched films (tough but flexible) and coatings of excellent resistance to aging, used to cover roofs and metal particles.

Poly(vinylidene fluoride) (PVD $T_g \sim -35^oC$ $—CH_2—CF_2—$

It is a highly crystalline polymer with good mechanical properties, weatherability and chemical and solvent resistance. It is used as a coating, gasketing, in piping, molded and lined tanks, pumps, and valves in chemical and nuclear power industries. Due to its high permittivity and low dielectric losses PVDF is used for the insulation of electric and electronic devices. It is useful as an electret in the transducer technology. Its **piezoelectric properties are used** in microphones, loudspeakers, ultrasound devices, high quality electric violins, **respiration monitors** and **wide range of medical and biological imaging.** It is also used as a **coating for medical devices**. PVDC membranes are used in micro- and ultrafiltration.

The best known and the most important in this group of polymers is

Polytetrafluoroethylene (PTFE) $—CF_2—CF_2—$

The degree of crystallinity of PTFE reaches 90% and is the highest among the synthetic polymers. The polymer is insoluble in all solvents even at high temperatures. It is nonflammable and exhibits high chemical inertia – only alkali metals dissolved in liquid ammonia attack the polymer. PTFE has a particularly low friction coefficient that induces self-lubricating properties. As highly hydrophobic polymer it is a very effective electrical insulator.

PTFE cannot be processed by the method characteristic for polymers like injection molding or extrusion, because of a very high melting temperature (380^oC) in which its degradation begins. The PTFE powder is processed by sintering like metal powders.

The application of PTFE is very wide – from electrical (wire and cable insulator, insulation for motors, generators, transformers, coils), through chemical equipment (gaskets, pump and valves parts, laboratory equipment, reactors lining) to low-friction and antistatic applications (nonlubricated bearings, lining for food-processing equipment, mold-release devices). The PTFE fiber is used in gasketing, belting, filter clothes, pump and valves packing.

From the expanded PTFE (9 mln pores per inch^2) fabric (Gore-Tex) for water-resistant and wind-resistant, “breatheable” clothes are produced. The microporous structure of Gore can be engineered so its use as **blood vessels and patches for soft tissue regeneration, and surgical sutures for use in vascular, cardiac, general surgery and orthopedic procedures is possible.**

PTFE has **diverse medical applications** including the use in **annuloplasty rings, batteries for defibrillators and pacemakers, cardiac patches, vena caval clips, vascular grafts for repairing diseased arteries and tissues, implantable pumps, implants for impotence, implants for incontinence, prosthetic joints, bone replacements, artificial heart valves, tendon, ligament and cornea, pledgets, various types of sheeting, dialysis shunts, sutures, myringotomy tubes, valved conduits**, **wound closure and as fibres in blood purification devices.**

Polychlorotrifluoroethylene (PCTFE) $T_g \sim -55^oC$ $—CF_2—CFCl—$

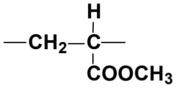
Its numerous properties like high density, chemical inertia, thermostability, flame-resistance are only a little worse than these of PTFE. Instead it exhibits good mechanical properties at very low temperatures and what is more important – it can be processed by techniques common for most polymers.

It is applied in machines part, gaskets and valves working at low temperatures, as barrier materials for gases, insulating materials for special cables (air force), anticorrosive coatings. Its **high barrier performance finds an application in the pharmaceutical and medical packing**. It thermoforms well on conventional **blister packaging** equipment and provides the highest barrier of any clear film.

Polar side groups – esters

The presence of an ester group favors solubility in organic solvents. If the ester group is small (methyl, ethyl) polymers are relatively polar and soluble in polar solvents. As the ester group becomes longer, the polymer is dissolved in nonpolar solvents. There are two groups of such polymers. One is derived from acrylic and methacrylic acid and other from poly(vinyl alcohol).

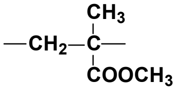
Poly(methyl acrylate) (PMA) $T_g \sim 9^oC$



$$-CH_2-\overset{H}{\underset{COOCH_3}{C}}-$$

Atactic, rubbery polymer of a relatively low glass temperature. Rarely used as a homopolymer (in paper industry, emulsion paints, adhesives, textile fiber processing), more often used as a component of copolymers.

Poly(methyl methacrylate) (PMMA) $T_g \sim 105^oC$



$$-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-$$

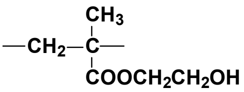
It is amorphous clear, colorless transparent plastic. It is the most transparent among the common polymers, its transmission coefficient is higher than that of mineral glass. Its application in the field of optical instrumentation however is limited by its low scratch resistance. It is used in glazing and in optics (automotive lenses, reflective devices, instruments covers). The roof over the Olympic Stadium in Munnich is made of PMMA sheets.

PMMA is also a highly appreciated material in biomedical engineering. It has a **good degree of compatibility with human issue**, and can be used **for replacement intraocular lenses in the eye** when the original lens have been removed in the treatment of cataracts. In orthopedic surgery, **PMMA bone cement is used to affix implants** (in arthroplastic procedures of the hip, knee and other joints for the fixation of polymer or metallic prosthetic implants to living bone), **to remodel lost bone and as a filler material for osteoporotic bone.**

The bone cement acts like a grout and not so much like a glue in arthroplasty. Although sticky, it does not bond to either the bone or the implant, it primarily fills the spaces between the prosthesis and the bone preventing motion. In **cosmetic surgery**, tiny PMMA microspheres suspended in some biological fluid are injected under the skin to reduce wrinkles or scars permanently. A large **majority of white dental filling materials (i.e. composites)** have PMMA as their main organic component.

A lot of equipment of medical laboratory as **diagnostic cuvettes, syringe components, filter housing, and test packs, crystalography trays, blood dialyzer and renal cassettes, optical sensors view ports, lightig diffusers, microfluid rotors** are made of PMMA.

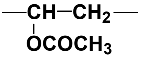
Poly(hydroxyethyl methacrylate) poly(HEMA)



$$-CH_2-\overset{CH_3}{\underset{COOCH_2CH_2OH}{C}}-$$

Weakly crosslinked gel swells in water, is elastic and strong. Poly(HEMA) is one of the most important hydrogels in the biomaterials world since it has many advantages over other hydrogels. These include water-content similar to living tissue, inertness to biological processes, resistance to degradation, permeability to metabolites, resistance to absorption by the body. It can be easily manufactured into many shapes and forms, and be easily sterilized. The most common example of poly(HEMA) is its use as **contact lenses**. It is also a potential **drug delivery device**.

Poly(vinyl acetate) (PVA or PVAc) T_g ~ 30°C



$$-\underset{OCOCH_3}{CH}-CH_2-$$

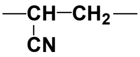
This polymer is atactic and hence amorphous. The glass transition close to the room temperature makes it sticky and undergoes cold flow at only slightly elevated temperatures. It is soluble in many organic solvents and is sensitive to hydrolysis in either acidic or basic medium. PVA adherence to many materials (cellulose, wood, glass, metal) is very good so it is widely used in adhesives, both of emulsion type and of the hot-melt type. The major use of PVA is the production of poly(vinyl alcohol) and in the production of water-based emulsion paints.

Polar side groups – cyano group

The cyano units are polar, hydrophilic groups that impose a special set of properties on carbon backbone polymers. They reduce the solubility in nonpolar organic media and increase the solubility in solvents such as dimethylformamide or dimethyl sulfoxide. The polarity of the side group imposes restrictions on the chain mobility (higher Tg).

The main representative of polymers with cyano-side groups is

Polyacrylonitrile (PAN) T_g ~ 85°C

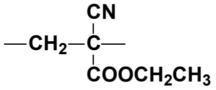


$$-\underset{CN}{CH}-CH_2-$$

It is a polar, semicrystalline polymer, used almost exclusively for the production of textile fibers. These usually contain a small proportion (below 5%) of another comonomer. PAN homopolymer fiber is a precursor of carbon fibers.

PAN has excellent stability to sunlight, chemical reagents, and microorganisms. PAN based membranes are utilized in the fields of the food industry, pharmaceutical industry, medical industry (**artificial kidney, medical packing)**) and the treatment of drinking water.

Poly(ethyl cyanoacrylate)

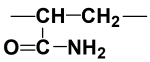


$$\text{—CH}_2\text{—}\overset{\text{CN}}{\underset{\text{COOCH}_2\text{CH}_3}{\text{C}}}\text{—}$$

Ethyl cyanoacrylate monomer is a main ingredient of “magic glue” for even traces of water catalyse its rapid anionic polymerization. It is used also as **tissue adhesive in medicine.**

Polar side groups – amide group

***Polyacrylamide* (PAAM)** T_g ~ 165°C



$$\text{—}\underset{\text{O=C—NH}_2}{\text{CH}}\text{—CH}_2\text{—}$$

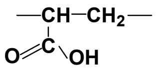
Acrylamide can be polymerized to very high molecular weights. The solid polymer is a brittle glass, hygroscopic, easy undergoing the alkaline hydrolysis. It is very soluble in water and all applications of PAAM are related to this feature.

It is used as a flocculating agent for the treatment of waste water and ores. It can be applied to disturbed oils at construction sites to reduce erosion and improve settling of the suspended sediment. PAAM increases the soil’s available pore volume, thus increasing infiltration and reducing the quantity of stormwater runoff that can cause erosion. Coating PAAM on paper gives a barrier effect and hydrophilic character that are required for printing. High molecular weight polymer can be used as a viscosifying agent to facilitate oil recovery and as industrial thickeners. PAAM gel electrophoresis is used to **medical microbiology**. Lightly crosslinked PAAM gives hydrogel that is used as a **wound dressing and for controlled drag release.**

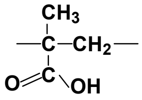
Polar side groups – carboxylic group

The properties of such polymers are closely related to the presence of carboxylic acid functional groups: sensitivity to pH, hydrosolubility, cross-linking by dehydration or in the presence of divalent ions, strong interactions with polar surfaces. In solution they show typical polyelectrolyte behavior, including abnormally high viscosities.

Poly(acrylic) acid $T_g \sim 106^oC$ ***poly(methacrylic acid)***



$$-\underset{\substack{| \\ O=C-OH}}{CH}-CH_2-$$



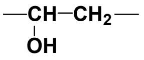
$$-\overset{\substack{CH_3 \\ |}}{\underset{\substack{| \\ O=C-OH}}{C}}-CH_2-$$

The most of their applications are related to water solubility – thickening agents of aqueous solutions, flocculating agent, ion-exchange resins, ingredient of certain adhesive formulations. Slightly crosslinked they become ***superabsorbents (hydrogels***) that can absorb much more water then their weight. These can be applied in baby pampers, in wrappings for meat, in agriculture to retain water in soil, as **active wound dressings and in the tissue engineering**.

Polar side groups –hydroxy group

Hydroxy groups are hydrophilic and water-solubilizing substituents. They form strong hydrogen bonds. Such intramolecular bonding serves to restrict skeletal torsion motions what increases its glass temperature.

Poly(vinyl alcohol) (PVAL) $T_g \sim 99^oC$



$$-\underset{\substack{| \\ OH}}{CH}-CH_2-$$

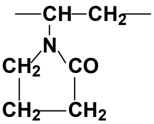
This polymer is obtained only by hydrolysis of poly(vinyl acetate) and always some acetate groups are left, influencing the properties of that polymer. PVAL is a crystalline polymer what makes that it dissolves in water and other polar solvents only at elevated temperatures. It degrades easily in higher temperatures; it is also biodegradable.

PVAL is used in adhesive formulations, for final coating of textile fibers and papers, as a thickening agent (for example in suspension polymerization), as a packaging film. It is also used for production of fibers but those have to be insolubilized by the reaction with formaldehyde. PVAL fibers have high water absorption and can replace cotton.

As a hydrogel it is used for biomedical applications, for example as an **active wound dressing** and **soft implants**, as a **matrix for tissue regeneration and cells proliferation**. Used also in **eye drops (artificial tears)** and **hard contact lenses solutions** as a lubricant, as an **embolization agent** in medical procedures and as **coating in medical packing**.

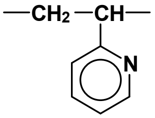
Other important vinyl polymers

Polyvinylpyrrolidone (PVP) $T_g \sim 175^oC$



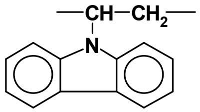
This polymer is a highly hygroscopic solid of high glass transition temperature. Polymer is soluble in water and in many fairly polar organic solvents. PVP is utilized only as solutions because is easily degraded in temperatures used for the classical polymer processing. Many of its applications are related to the chelating properties of this polymer. It forms complexes with molecular iodine and is used as a reservoir of this disinfecting agent. Its strong interaction with dyes facilitates their anchoring on textile fibers by complexation with the corresponding polymers. It is used also in cosmetics, adhesives, binders, thickeners and as a **diluting agent for blood plasma**. In form of hydrogel it is used in **wound dressing** and in **systems of slow release of active substances**.

Poly(vinylpyridine)



It is soluble in aqueous acid or in ethanol but insoluble in neutral or basic aqueous media. It is polyelectrolyte and ion exchanger of high capacity and chemical, mechanical and thermal stability. It is also used as an adhesive and binding agent for rubbers.

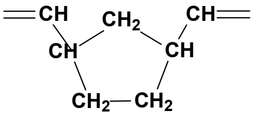
Polyvinylcarbazole $T_g \sim 200^oC$



It is a hydrophobic polymer of high glass transition temperature and a high crystallinity degree. Its main features are high thermal resistance, chemical resistance and good dielectric properties. It is used for manufacturing chemical equipment (acid-, base-, and fluorine resistant), electric insulators used in high temperatures, as a substitute of asbestos and mica. As a photoconducting material it is used in xerography, for production of termistores, photoresist, elements of thin-layer electronics and photo-memory.

6.2. POLYMERS WITH ALIPHATIC RINGS IN THE MAIN CHAIN

These polymers should show improved mechanical and thermal properties. However there is only one such polymer used commercially – ***polynorbornene***:

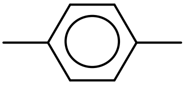


It has additionally a double bond in each monomer unit of the chain. It is used mainly in the rubber industry for anti-vibration (rail, building, industry), anti-impact (personal protective equipment, shoe parts, bumpers) and grip improvement (toy tires, racing tires, transmission systems, transports systems for copiers, feeders, etc.). It has also high absorbance of oils hence it is used in ecological catastrophes with its participation.

6.3. POLYMERS WITH AROMATIC RINGS IN THE MAIN CHAIN

Aromatic rings in a polymer backbone confer rigidity and extended chain character to the macromolecule. Such polymers are generally much stronger and of better thermooxidative resistance than these with the aliphatic chain. So many polymers designed for high temperature use contain aromatic units in the main chain. Some of them can show main-chain liquid crystallinity. Polymers with conjugated aromatic rings can function as electronic conductors. The polymers of aromatic ladder structures show extremally rigid rod character and thermooxidative stability but these properties are achieved at expense of processibility.

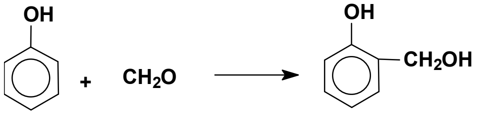
Poly-p-phenylene



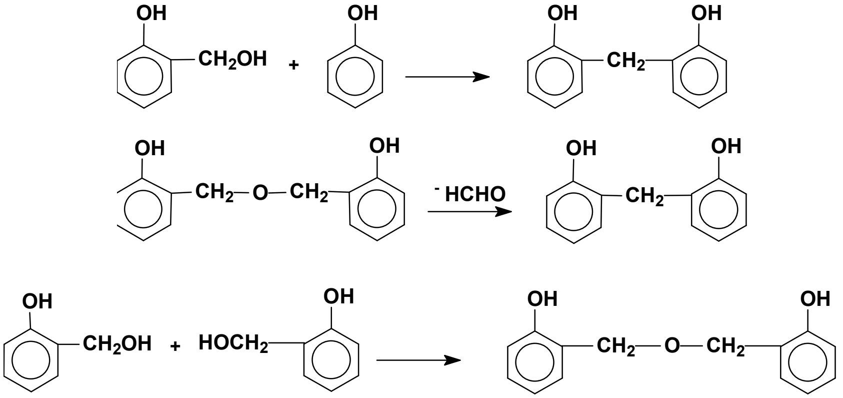
This polymer is insoluble, of high thermal resistivity and when doped, of electrical conductivity. Up to now however it has not found a practical application.

Phenolic resins

Phenolic resins are products of reaction between the phenols and aldehydes (mainly formaldehyde). The first step in the reaction is the formation of addition compounds known as methylolol derivatives:



The subsequent condensation reactions can be as follows:



Depending on the used parameters (catalyst, formaldehyde/phenol ratio) these reactions can lead to **novolacs** (acid, ratio<1) or **resoles** (base, ratio>1). The first are thermoplastics and for curing they need more formaldehyde (usually in form of urotropine). The resols are thermosets and become cured under the influence of temperature. Both as a result give infusible, crosslinked materials of the same structure – net of alternating (aromatic ring – CH_2 group) units.

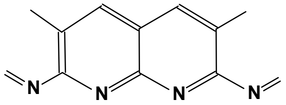
Phenolic resins have good chemical and thermal resistance, dielectric strength, and dimensional stability. Their flammability and moisture absorption are low.

The largest use of the phenolic resins are in heat-setting adhesives for plywood. As alcoholic solutions they are used for impregnating paper, wood and other fillers applied in decorative laminates for counter tops and wall covering and industrial laminates for electrical parts including printed circuits. The excellent adhesive properties and bonding strength made possible using them as brake lining, abrasive wheels and sandpaper.

Shaped products as cutlery handles or toilet seats are also manufactured. Phenolic resins with various functional groups introduced, are used in the production of ion-exchange resins.

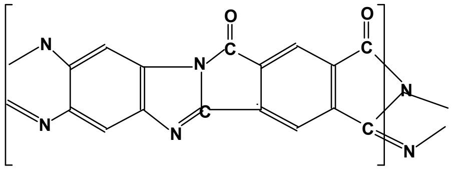
Almost all classes of polymers (***polyethers, polyesters, polyamides and so on***) consist also of macromolecules with aromatic rings in the backbone. These will be described later.

Polymers consisting of an uninterrupted series of rings are called **"ladder" polymers**. They have far greater thermal stability than other polymers, for two adjacent bonds in the backbone have to break before the polymer degrades in molecular weight. The ladder polymers usually are obtained by the modification of existing polymers. The good example is that obtained by cyclization and oxidation of polyacrylonitryle:



This material is the precursor of the carbon fibers.

The other example is ***poliimidazopirrolon***



The ladder polymers are not soluble or meltable, so processing is difficult. Because of this, at present there are no commercial uses for true ladder polymers.

6.4. POLYMERS WITH HETEROATOMS IN THE MAIN CHAIN

Oxygen

- ***The etheric carbon-oxygen bond C-O-C (polyethers)***

Oxygen bonds in a hydrocarbon chain usually behave as “swivel groups” that provide the torsional mobility of skeletal and flexibility of material. This is a consequence of:

- the absence of side group attached to the oxygen atom,

- possibility of changes of bond angles at oxygen in response to conformational changes.

Ether linkages are generally stable to hydrolysis and to thermooxidation. In the case when nearby side groups are small, the polymers are hydrophilic or even water soluble.

Polyoxymethylene (POM, polyformaldehyde, acetal) $T_g = -30^oC$ $—O—CH_2—$

This polymer of formaldehyde or of trioxane belongs to the so called ***acetal resins*** – polyethers, in which group R in the main chain is a methylene group. To be useful, polymer has to be stabilized that is usually done by acetylation of the hydroxyl end group of the polymer using acetyl anhydride.

POM is the polymer in which crystallinity degree can exceed 80%. Due to its strong cohesive energy POM is a technical polymer exhibiting high mechanical characteristics – the impact strength, stiffness and yield stress are greater than those of other crystalline polymers. Major uses for the acetal resins are direct replacements for metals in automobile part, pump housing and mechanism, laser printer engine, gears, springs, clips, gaskets in fuel system components, toys (kids watches), washing machines, electric toothbrushes and shavers, faucets, safety belt buckles and a variety of machine and instrument parts.

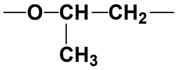
POM’s medical grades are excellent candidates for dry powder inhalers, insulin injection pens, medication dosing systems, joint replacement components and other medical devices.

Poly(ethylene oxide) (PEO, poly(ethylene glycol)) $—O—CH_2—CH_2—$

Polymer obtained by ring-opening polymerization of ethylene oxide, is highly crystalline, hygroscopic and soluble in water at elevated temperatures. It is widely used in the biomedical field (low toxicity) and in the industry as a viscosifying agent of aqueous media, as a flocculating agent, and in a number of adhesive formulations.

It is used also in the standard method of conservation of articles that spent some time in water (even in a Tudor's war ship that spent in water 450 years). Slightly crosslinked poly(ethylene oxide) (***superabsorbent***) is used in agriculture and **in medicine as a matrix for tissue regeneration**.

Poly(propylene oxide) - PprO (polypropylene glycol)

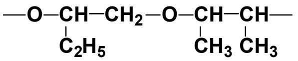


$-O-\underset{CH_3}{CH}-CH_2-$

This polymer is amorphous and more hydrophobic than PEO. It is used mainly as a precursor for polyurethanes.

The other important polyethers are:

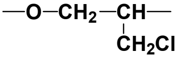
Poly(butylene oxide)



$-O-\underset{C_2H_5}{CH}-CH_2-O-\underset{CH_3}{CH}-\underset{CH_3}{CH}-$

that is used as an additive to fuels, oils, greases, as a detergent and an antifoaming agent,

Polyepichlorohydrin



$-O-CH_2-\underset{CH_2Cl}{CH}-$

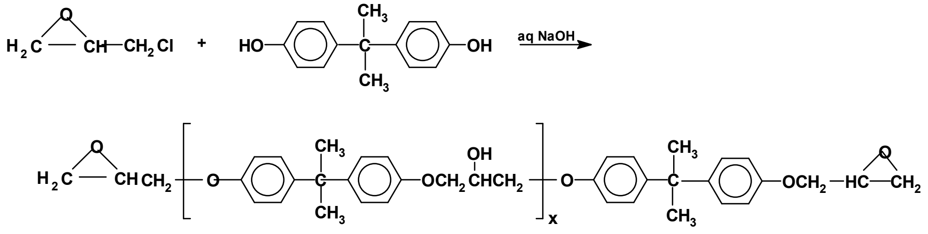
elastomer, water and oil resistant; used as coating, also for production membranes in fuel pump, hoses for oil and fuel, as a special rubber, and

Polytetrahydrofurane - (poly(tetramethylene ether) glycol $-O-CH_2-CH_2-CH_2-CH_2-$

used as a precursor for production of elastomeric polyurethanes and polyester thermoplastic elastomers.

Epoxy resins (EP)

These polymers belong to polyethers but because they contain one or more epoxy groups the name "epoxy resin" is commonly used. They are the products of reaction of epichlorhydrin with difunctional hydroxy or amine compounds such as bisphenol A, aminophenol, novolacs.



These materials are oligomers, prepolymers, which to be useful have to be hardened. All systems that contain a hydrogen atom are able to react with the oxirane group. The following compounds can be used: primary and secondary amines, phenols, acids or their anhydrides, and so on.

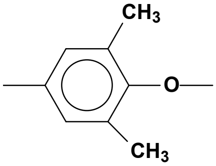
There are three main domains of the epoxy polymers application:

- Coatings and encapsulation, industrial flooring – related to the good adherence, hardness, resistance to chemicals and easy processing of these materials. The example of using them is **sealing to protect microchips** in miniature electronic circuits mainly **for medical technology**.
- Matrices of composite materials with aramide, carbon fibers, or with glass fiber (mechanical strength, chemical resistance, electrical insulating properties)
- Rigid adhesives (adherence and strong cohesion) processable also at ambient temperature; they are used in the construction of aircraft, automobiles, bicycles, golf clubs, skis, snow boards, and other applications and are exceptional adhesives for wood, metal, glass, stone, and some plastics.

Aromatic polyethers

All polymers of this group have a high thermal and chemical stability as well as excellent mechanical characteristics. The most important is poly(2,6 dimethylphenylene oxide), the polymer named ***poly(phenylene oxide)*** (PPO) obtained by the oxidizing polycondensation of 2,6-dimethylphenol.

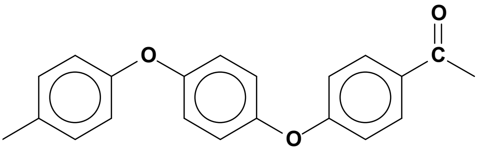
$T_g \sim 210^oC$



It is most widely used from all high-temperature polymers. PPO oligomers are high quality oils that could be used up to 200^oC. It is totally miscible with polystyrene and such blends are used for structural parts, electronic and electric devices, household and automotive items. **In biomedical applications PPO can be used for sterilizable instruments and many parts for sanitary and medical engineering.** The membranes made of PPO are used ultrafiltration, nanofiltration, pervaporation and gas separation.

There are known aromatic polyethers that have an additional ketone group. The most popular from this group is:

Polyetheretherketone (PEEK) $T_g = 143^oC$



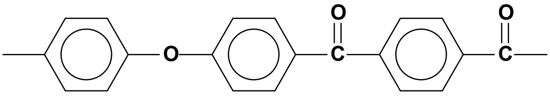
PEEK is a semicrystalline thermoplastic with excellent mechanical and chemical resistance properties that are retained to high temperatures. It is highly resistant to thermal degradation as well as an attack by both organic and aqueous environments. The high mechanical properties, very low smoke emission and self extinguishing characteristics bring PEEK in to numerous demanding applications in the aerospace, automotive, teletronic, and chemical process industries as automotive engine parts, aerospace components, bearings, piston parts, pumps, compressor plate valves, circuit boards, and audio speakers, printers, copiers, and connectors.

It is one of the few plastics compatible with ultra-high vacuum applications. It is a real light-weight, high performance metal replacement. A superior combination of high strength, stiffness and toughness, together with its proven biocompatibility, make PEEK ideally suited for demanding medical applications. PEEK is considered an advanced **biomaterial used in medical implants** with strength and durability characteristics that outperform other implantable polymers. Inherently radiolucent, PEEK does not generate image artifacts that interfere with the assessment of the healing site via X-ray, CT or MRI imaging modalities.

Its medical application is then very wide and includes **spinal, orthopedic and cardiovascular implantation, surgical instruments, endoscoper, analytical equipment, medical dosing, application in the vivo diagnostic**. In dentistry it is used for crowns, bridges, implants, healing caps, gingival formers and temporary abutments.

The other polymer possessing both the - ether and ketone - groups (in other proportions) is :

Polyetherketoneketone (PEKK)



This polymer is better than metal in many applications because it is a non-corroding, chemically inert material of reduced weight, excellent abrasion resistance, better process flexibility, and tailored formulation. Its density and stiffness is similar to human bone. **It is biocompatible and can be sterilized by all known methods.**

Biomedical application of PEKK include anesthesia equipment, catheters, drug delivery, sterilization and analytical equipment, short and long term implantable devices.

- ***The carbon-oxygen bonds in polyesters***

This bond in polyesters as in polyethers provides chain flexibility. However, the properties of many polyesters are determined by their crystallinity. Their chemical stability strongly depends on the other chain units present. Low ratio of hydrocarbon to ester unit makes these polymers chemically unstable while the presence of the aromatic group provides some steric and hydrophobic protection against hydrolysis.

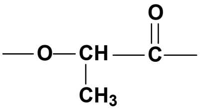
Polyesters can be obtained in a few ways:

- polycondensation of diacids (also their anhydrides or chlorides) with glycols,
- ester interchange (crossestrification between dimethyl terephthalate and glycol –method used for the most widely used PET),
- homopolycondensation of hydroxyacids,
- ring-opening polymerization of lactones,
- some special methods like the reaction of terephthalic acid with ethylene oxide for PET production.

Linear aliphatic polyesters

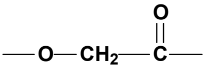
They usually have too low melting (softening) temperature to be used for engineering applications. Those with hydroxylic end groups are prepolymers for manufacturing of polyurethanes. Many of aliphatic polyesters are biodegradable and bioabsorbable. As examples can serve:

Poly(glycolic acid) (PGA) $T_g \sim 36^oC$



$$-O-\underset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-$$

Poly(lactic acid) (PLA) $T_g \sim 57^oC$



$$-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-$$

They are widely used **in biomedicine** because **the ester linkage is hydrolyzed at pH 7.5 at body temperature.** These polymers (or GA-LA copolymers) find application as **suture materials (in the fixation of bone fractures, closure of a soft tissue wound), as scaffolds in tissue engineering, as matrix for dermis growth (artificial skin) and in controlled drug delivery (delivery of steriods, an anticancer agent). PGA** is used in manufacturing of **implantable medical devices including anastomosis rings, pins, rods, plates and screws.** PLA is also employed in the preparation of bioplastic (biodegradable plastics) useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses as upholstery, disposable garments, and nappies.

Linear aliphatic-aromatic polyesters

Undoubtedly, the most important from all polyesters belongs to this group:

Poly(ethylene terephthalate) (PET) $T_g \sim 69^oC$ $-O-CH_2-CH_2-O-CO-C_6H_4-CO-$

Due to the regularity of its molecular structure PET is a highly crystallizable polymer but its degree of crystallinity can be modulated according to the desired characteristics required for its application.

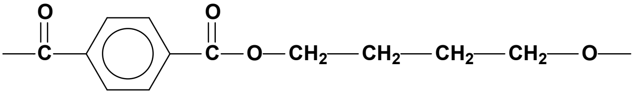
The major part of the production of PET is utilized for the manufacturing of textile fibers. It makes two-thirds of the production of all synthetic textile fibers. Textiles are very resistant to wrinkling. Felts made of polyester fibers have good resistance to temperature, to abrasion, and to further felting. The fibers are used either alone or mixed with cotton or wool. It is also popular as a tire cord.

PET films have better properties (resistance to failure on repeated flexing, tear strength, impact strength, toughness) than any other plastic films. PET film is often used in tape applications, such as the carrier for magnetic tape or baking for pressure sensitive adhesive tapes. PET is used also as a technical polymer for production of bottles for soft-drink use, trays for frozen dinners (they withstand both freezing and baking temperatures), automotive parts and machine parts.

This polyester has a very wide **medical application.** It is used for the production of **artificial tendon and ligament, large diameter blood vessel prosthesis, medical and pharmaceutical packaging and non-absorbable suture. PET fabric is used in fixation of implants and hernia repair, and as reinforcing material for tissue reconstruction and for other surgical applications**.

Poly(butylene terephthalate) (PBT)

Two additional, in comparison with PET, methylene groups incorporated in the chain increases the mobility of the chains and their crystallizability. The high mobility and lower than in PET melting point make this polymer easier to process than PET.

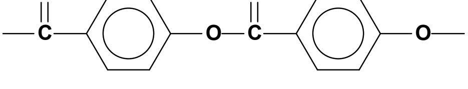


PBT has relatively low moisture absorption, extremely good self-lubrication, fatigue and solvent resistance and good maintainance of mechanical properties at elevated temperatures. Key markets include “under the hood” automotive application such as ignition systems and carburetion. The other applications include electrical and electronic applications, power tools, small and large appliance components, gearwheels, bearings and other sliding elements, fluid handling pumps, spray gun, paper holder for copier. PBT excellent dimensional stability and mechanical strength, even with extremely low wall thickness made it suitable for production of a **powder inhaler.** It can be processed into **nonwoven media for blood filtration and solids separations.**

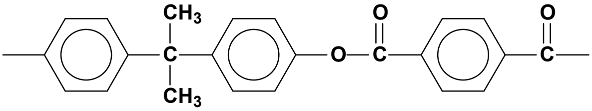
Linear aromatic polyesters (polyarylates**)**

These polyesters consist of aromatic rings linked by ester groups. Two representative polyarylates are:

poly–4–hydroxybenzoate



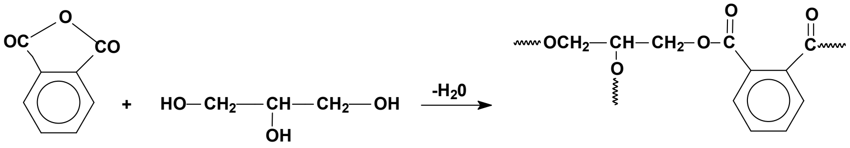
and ***poly(bisphenol-A-terephthalate)***:



Polyarylates are considered tough, resistant to UV radiation, resistant to heat and, in the amorphous form, transparent. They are engineering thermoplastic resins that can be used for automotive, appliance and electrical applications requiring outstanding heat resistance. They find application in solar panels, outdoor lighting, fire helmets and electrical connectors.

Three-dimensional saturated polyesters (alkyd resins)

They are condensation polymers obtained from the reaction of polyols (glycerol, pentaerythritol) with carboxylic polyacids (or their esters, anhydrides).

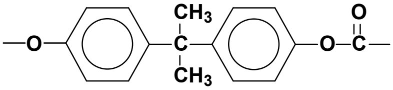


First, the condensation reaction is conducted without crossing the gel point. The obtained prepolymer is hardened by heating in the mold at about 250°C. The most important applications of alkyd resins are the field of paints and varnishes.

Unsaturated polyesters (UP)

The unsaturated polyesters that are the precursors of the polyester network are obtained by copolycondensation of diols with various anhydrides as maleic anhydride and ortho- and iso-phtalic anhydrides. These prepolymers are dissolved in styrene and “copolymerization” between styrene and unsaturated polyester is initiated by radical initiators. Due to the brittleness of this material UP are almost exclusively used as matrices of composities with glass fibers as fillers. They are utilized in the fields of mechanical engineering.

Polycarbonates (PC) $T_g \sim 150^oC$



This is a class of polyesters based on carbonic acid. They are made from bisphenol A (4,4'-dihydroxydiphenyl-2,2'-propane) and phosgene or by ester exchange between bisphenol A and diphenyl carbonate.

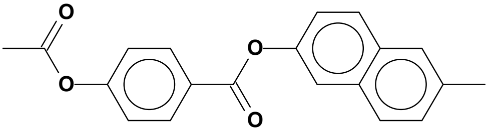
This polymer is a thermoplastic of very good mechanical properties. It has unusually high impact strength, even in low temperatures. It has low moisture absorption, good heat resistance and good thermal and oxidative stability in the melt. It is transparent (it is unable to crystallize spontaneously and used in an amorphous state) and self extinguishing.

Typical applications include telephone parts, business machine housing, high-quality household appliances, machinery housing, unbreakable glazing applications, laboratory equipment (stopcocs, syringes, centrifugal force separator, cleanroom assembly), protective helmet, sunglasses, chips, chip carriers, hard-disk drivers, CD's, and DVD's.

Because it is expensive, its use in medical industry is limited to special applications, for **example equipment for blood oxygenator, dialysis or infusion, a surgery drill guide (**PC is very stiff and dimensionally accurate to facilitate the delicate surgery), **insulin management system or a breath analyzer.**

From many known **copolyesters** these of:

p-hydroxybenzoic acid/2,6-hydroxynaphthoic acid (known under the trade name **Vectra**)



seems to be the most important.

They are highly crystalline liquid crystal polymers (LCP's), thermotropic (melt-orienting) thermoplastics that can deliver exceptionally precise and stable dimensions, high temperature performance and chemical resistance in very thin–walled applications. They can operate up to 240°C, and are characterized by very high tensile strength and very high elastic module, high impact-resistance, inherent flame retardancy, very good chemical and oxidation resistance, and very low water absorption.

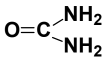
These properties have led to the use of Vectra LCP's in many electrical and electronic applications (sockets, bobbins, switches, connectors, chip carriers, sensors), for the manufacturing of connecting parts in fiber optics, of telecommunication devices, of chemical processing machines, in the automobile and machine construction industries, as well as the field of the air- and spacecraft technology.

Vectra LCP's have replaced stainless steel in many medical applications. They are resistant to the most sterilization methods. Vectra LCP's are specified in numerous medical applications such as surgical instruments, dental tools, sterilizable trays and equipment, drug delivery systems and diagnostics.

Nitrogen

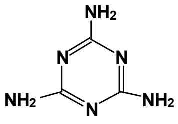
- ***The carbon-nitrogen bonds in amino resins***

The two important groups of amino resins are the condensation products of urea (1) and melamine (2) with formaldehyde.



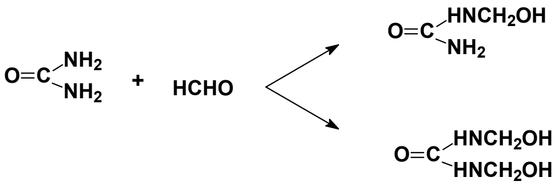
$O{=}C\begin{matrix}NH_2\\NH_2\end{matrix}$

urea

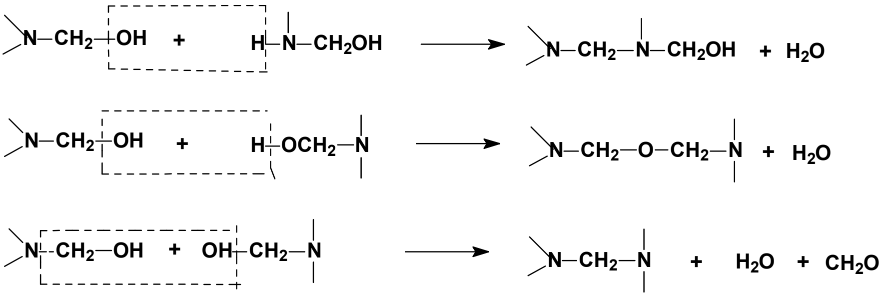


melamine

The first reaction is the addition of formaldehyde to amine groups forming methylolo-compounds.



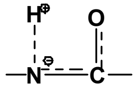
These products undergo condensation giving at the beginning a partially dehydrated product, still soluble in water and at this stage are used to impregnate the filler (usually cellulose). Further condensation leads to the crosslinked material.



The amino resins are clear and colorless, what differs them from very similar phenolic resins. The melamine-formaldehyde resins have better properties than urea-formaldehyde ones but they are also more expensive.

The major application of amino resins is in the field of adhesives in the industry of wood (plywood, furniture). They are also used as textile treatment and coating resins, protective coatings, molding coatings, and paper treatment and coating resins. The urea resins are widely used for cosmetic container closures, appliance housing, and stove hardware. From cellulose filled melamine resins the high-quality dinnerware are produced.

- ***The carbon-nitrogen bonds in polyamides***



Generally speaking the amide linkage is a “chain-stiffening” unit because of the partial double-bond character of the N-C bond and the possibilities for internal and external hydrogen bonding that exist in polyamides. However, the final properties of a specific polyamide will depend on the kind and amount of other groups present in the chain.

Inclination to hydrolysis will strongly depend on the material and surface effects. Highly crystalline polyamides are inaccessible to water and other reagents, while others, like globular proteins, each individual repeating unit is accessible to water, acids and enzymes.

High-molecular weight polyamides can be obtained in a few ways:

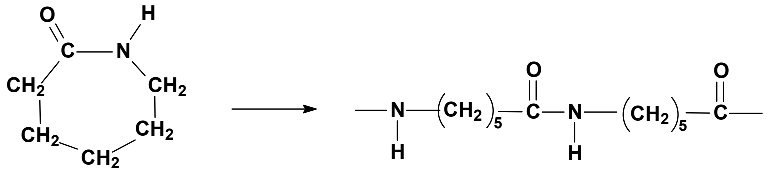
- Polycondensation of diacids with diamines; often it is polymerization of 1:1 salt, which is easy formed and purified. Instead of acids their chlorides can be used. In this case reaction is much faster and molecular weight higher than in other processes and equimolar ratio of both reagents is not necessary.
- Homopolycondensation of amino acids.
- Ring-opening polymerization of lactams.

Aliphatic polyamides

Aliphatic polyamides are sometimes (especially in US) called "nylons". In their name one or two numbers are present. If one – polyamide results from polycondensation of amino acid or polymerization of the corresponding lactam, and is the number of carbon atoms in the "monomer" molecule $PA_{(n+1)}$.
For example:

$$-NH-(CH_2)_n-CO-$$

As an example can serve ***polyamide 6*** that is synthesized from ε-caprolactam:

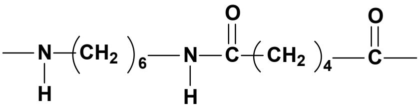


If the polyamide is a product of polycondensation of diamine with diacid, its name consists of two numbers – first is the number of carbon atoms in the amine, second – in the acid.

$PA_{(a,b+2)}$

$$-NH-(R)_a-NH-CO-(R)_b-CO-$$

As an example – ***polyamid 6,6*** $T_g \sim 45^oC$



$$-\underset{H}{N}-(CH_2)_6-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$$

Contrary to their ester analogs aliphatic polyamides exhibit excellent thermomechanical properties. They are characterized by a combination of high strength, elasticity, toughness, and abrasion resistance and good mechanical properties are maintained up to 150°C. The solvent resistance of aliphatic polyamides is good; only phenols, fluorinated alcohols, and formic acid dissolve the polymer at room temperature. Their outdoor weathering properties are not the best and these polyamides should be stabilized or pigmented with carbon black.

The three quarters of the production are used for the manufacturing of textile fibers (mainly for carpets, apparels and tire cords but also for parachutes, powder bags, tents, ropes), the rest is utilized as a thermoplastic technical polymer.

As an engineering material it is a substitute of metal in bearings, gears, cams, and good material for rollers, slides, and door latches, bearings and thread guides in textile machinery, also jackets for electrical wires. PA films are used as packaging, e.g. meat wrappings and sausage sheaths, also in cleanroom packaging and waste can liners.

In medicine polyamids 6 and 6,6 are used as **non-absorbable suture for the use in general soft tissue approximation and/or ligation including use in cardiovascular, neurological and ophthalmic procedures, medical tubing, high-pressure catheter balloons** and some applications in dentistry (composites with glass as **partial dental prostheses**). **Blood glucose meter** is made of PA 6,6 lubricated with PTFE.

Polyamides can be used as the matrix material in composite materials, with reinforcing fibres like glass or carbon fiber. These are frequently used in car components next to the engine, such as intake manifolds, where the good heat resistance of such materials makes them feasible competitors to metals.

Many polyamides and copolyamides can be synthesized, but over 85% of total market belong to PA 6 and PA 6,6. The other polyamides of industrial significance are:

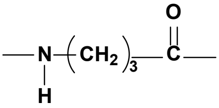
Polyamide 6,10 $—NH—(CH_2)_6—NH—CO—(CH_2)_8—CO—$

Lower brittle temperature and lower water absorption than polyamide 6 or 6,6. Retains room temperature toughness at low temperatures. It is applied for zip fasteners, electrical insulators, precision parts, and filaments for brushes.

Polyamide 4,6 $-NH-(CH_2)_4-NH-CO-(CH_2)_4-CO-$

This polyamide provides an amazingly broad range of applications that derive from its unique set of properties as the highest mechanical property retention at high temperatures (better than heat-stabilized polyamide 6,6-), excellent resistance to wear and friction, and outstanding flow for easy processing and design freedom, what results in reduced processing cycle time (faster crystallization rates).

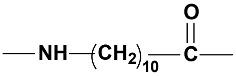
Polyamide 4



$$-\underset{\displaystyle H}{\underset{|}{N}}-(CH_2)_3-\overset{\displaystyle O}{\overset{\|}{C}}-$$

Unlike other polyamides, it can be biodegraded in an activated sludge. Used in the **slow-release pharmaceutical compositions** shows high bioavailability and stability. Useful also as a tackifier for water-thinned coatings, adhesives, detergents, etc.

Polyamide 11 (Poly(11-amino-undecanoic-amide)



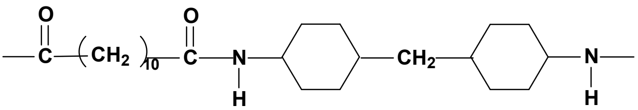
$$-NH-(CH_2)_{10}-\overset{\displaystyle O}{\overset{\|}{C}}-$$

It is weaker but more resilient than the most common types of polyamides (6 and 6,6). It is used in high-performance applications such as automotive fuel lines, pneumatic airbrake tubing, electrical anti-termite cable sheathing, oil and gas flexible pipes and control fluid umbilicals, sports shoes, and electronic device components.

This polymer is very important **in medical industry for manufacturing of balloon angioplasty catheters, urological catheters, nutritional bags, dental floss, tubing hubs, sterile bottles** and others. Very similar ***polyamide 12*** is used as **sterylizable coatings of orthopedic instruments and knee-joint supports, also for manufacturing hospital furniture and permanent installations.**

Aliphatic - cycloaliphatic polyamides

Such polyamides as **Trogamid CX** (trade name) series are synthesized from aliphatic diacids (dodecanoic acid) and cycloaliphatic amines (bis-para-aminocyclohexyl methane).

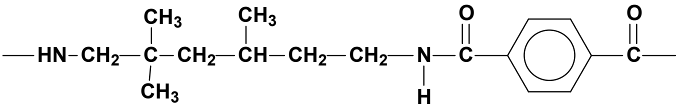


They are glass-clear, UV-resistant compounds with excellent resistance to chemicals and stress cracking. The material is licensed under USP, Class VI, the highest class in the United States Pharmacopeia that even allows exposure to blood. Therefore they are suitable **for manufacturing structural components that come into direct contact with drugs or bodily fluids. These include infusion and transfusion components such as connectors, adapters, and multiple stopcocks and the housings of devices**.

The other areas of application include water management, filter technology, laboratory and medical technology, the **manufacturing frame and lenses of eyeglasses** (light transmission 92%!), or bottles for the cosmetics industry and luxury dress apparel.

Aliphatic –aromatic polyamides

The example of that group of polyamides is **Trogamid T** (trade name):

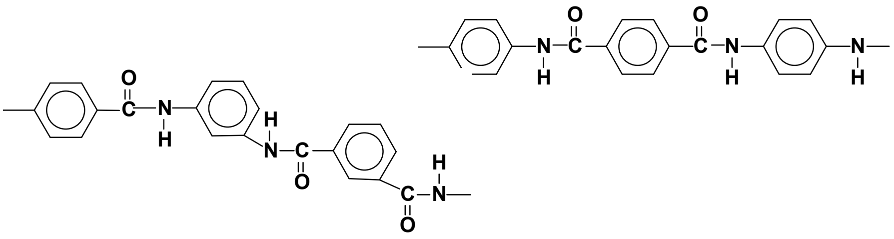


These polymers have irregular structure so they are amorphous (or semicrystalline, the crystallites of which polymers are so small that they do not scatter visible light) hence are as clear as glass. They possess high resistance to chemicals and stress cracking. The other outstanding properties of it are: a high level of UV resistance, low water absorption, which leaves the mechanical properties virtually unaffected, high dimensional stability, high impact resistance, even at low temperatures, high glass transition temperature, abrasion and scratch resistance, easy processing.

Thanks to this special combination of properties, these kinds of polymers are used in many branches of industry: for example, in electrical engineering for high-voltage switch casings, battery seals and relay casings, in filter technology for filter cups, pump casings and inspection glasses, and in machinery and engineering for flow meters, liquid-level indicators, and valve blocks and common control blocks for dispensing and metering equipment **and for medical equipment**.

Aromatic polyamides

Aromatic polyamides are named aramids. Two of them under the Du Pont trade names **Kevlar** and **Nomex** are very well known:



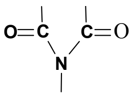
Nomex Kevlar

They are used for production of fibers that have excellent mechanical properties. Kevlar cable can match the strength of steel at the same diameter and 20% of the weight. They preserve their properties up to temperatures higher than 200^oC and are practically inflamable. They resist very well most of chemicals except strong acids.

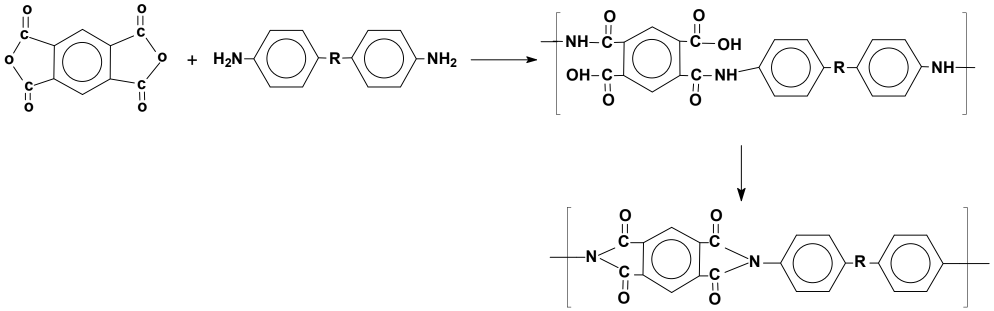
Today, aramids are used in everything from airplane parts to reinforced suspension bridge structures, to suspension bridge cables, to fiber optic cables, not to mention a variety of consumer goods. Lightweight, bullet-resistant body armor, protection vests, and military helmets, heat resistant gloves are common army equipment. Textiles used as high-temperature filters, in fire and flame resistant clothing, protective equipment such as vests and helmets for firefighters, hot air filtration, reinforcement of rubber goods such as tires, ropes and cables, sailcloth and astronaut space suits.

The main application is in the field of composite materials with, for example epoxy resins. They help improve the safety, performance and durability of automotive components for a wide variety of vehicles. They are used to build wind turbines, boats, yachts, aircrafts, to strengthen concrete structures.

- ***The carbon-nitrogen bonds in polyimides***

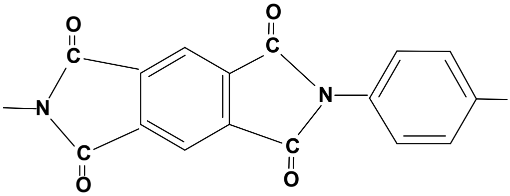


The polyimides are made by the polycondensation of aromatic dianhydrides and aromatic amines (scheme below):



Their synthesis is not simple. In the first stage the polyamic acid is produced. It is soluble and processable material from which desired forms of material (films, fabricated solid parts) are obtained. The further condensation converts them to the polyimide.

The one of most popular polyimides is known under the DuPont's trade name **Kapton**:



The aromatic/heterocyclic structure of polyimides accounts for their high-level performances:

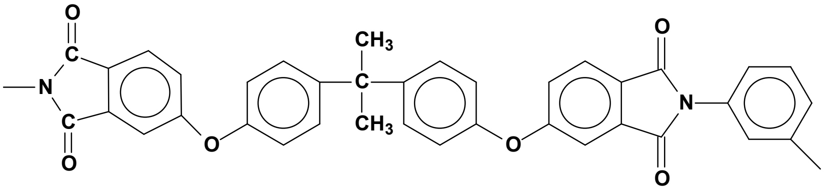
- excellent mechanical characteristics preserved over a wide range of temperatures (from -240 to +370 ^{o}C),
- strong resistance to degradation by thermooxidation,
- insensitivity to hydrolysis and many chemicals (except strong acids and bases) and ionizing radiation,
- very low flammability- dense polyimide fabric flame penetrates more than for 15 min.

Polyimides are widely used as films, utilized as membranes working at high temperatures, for flexible circuits and for photovolataic substrates. They are used also in automotive (air-bag systems) and aerospace (non-flammable, lightweight material for aircraft insulation), as electrical insulations and coatings for electronic systems.

Polyimide-based circuitry for heaters are used in blood analyzers, dialysis instrumentation, DNA analysis, genetic testing systems, invasive probes, life support fluid warmers, sterilizers, tissue processors, transportable incubators, thermal cyclers, and hybridization ovens. Various PI tapes (high-temperature, low-static; masking..) are used for electronic, optics, auto- and **medical manufacturing.** Polyimide fibers are used in hot gas filtration, as protective clothes and sealing.

There are also known polyimides that contain additionally other functional groups.

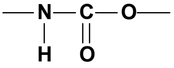
Polyetherimide $T_g \sim 220^{o}C$



is an amorphous, high-performance thermoplastic. This material is characterized by high strength and rigidity at elevated temperatures, long-term heat resistance, highly dimensional stability, good electrical properties, broad chemical resistance and is injection moldable. Also, it exhibits an inherent flame resistance and a low smoke generation without the need for incorporating additives. Unmodified polyetherimide material is amber transparent in color.

It has found an application in transportation, electrical/electronic appliances, industrial uses, packaging, appliances and jet engine components. A number of **medical equipment components (as medical instruments trays, pumps, IV sets, pharmaceutical containers and accessories, medical, surgical and dental instruments)** are made from PEI taking advantage of its **excellent resistance to repeated sterylization** (all kinds). Polyetherimide also seems to be an interesting **material for the production of membranes for the application in biohybrid organ systems.**

- ***The carbon-nitrogen bonds in polyurethanes***

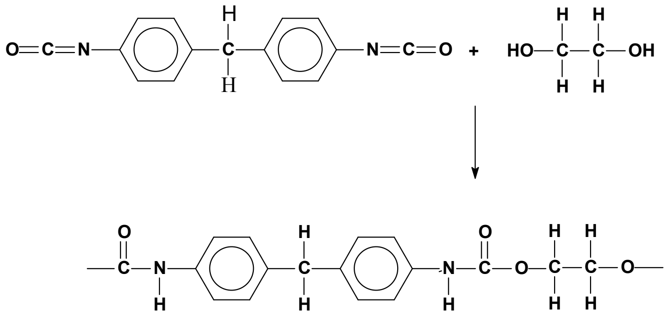


$$-\underset{\displaystyle H}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-O-$$

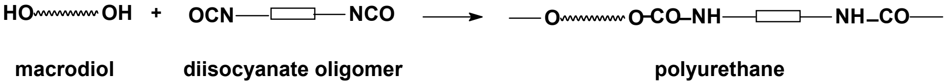
Molecular structure of polyurethane suggests that it combines the inherent properties of amide and ether functional groups. The former induce a high density of cohesive energy through possibility of H-bonds, whereas the latter favor the free rotation around the bond, what is a source of molecular flexibility.

However great influence on the material properties have also flanking segments of polyurethanes that impose their own characteristics on the polymer.

Polyurethanes are reaction products synthesized from diisocyanates and diols:



The characteristics of each polyurethane can be attributed to its structure. Generally, thermoplastic polyurethanes consist of segmented copolymers (with multiple and short blocks) with alternation of rigid (hard) and flexible (soft) sequences. Rigid aromatic or cycloaliphatic diisocyanate and short diol (ethylene glycol, propylene glycol, etc.) make up the hard domains (prepolymer syntesized with the excess of diizocyanate, to assure isocyanate end groups) and the chain extender (macrodiol as PEO, that reacts with isocyanate prepolymer) makes up the soft domain. The structure of such polyurethanes is schematically shown below:



Varying the ratios of these two domains allows polyurethanes to be formulated from very soft to very hard materials.

Depending then on the reagents used (their functionality and ratio), the kind and amount of a catalyst, synthesis parameters and modifiers used one can produce the whole range of various products:

- Linear thermoplastic polyurethanes used mainly for production of elastic fibers
- Flexible and rigid foams.

In this process the use is made of reaction of the excess isocyanate groups in the polymer with water:

$$R{-}N{=}C{=}O + H_2O \longrightarrow RNH_2 + CO_2$$

CO_2 involved in this reaction blows the foam, at the same time that crosslinking is effected.

Flexible urethane foams are used for cushions for furniture and automobiles, while rigid ones are valuable for sandwich structures used in prefabrication in the building industry, for thermal insulation in refrigerators, acoustic insulation, portable insulated chests and many others.

- Rubber-like elastomers – used for example in tubeless tires and footwear.

- Adhesives - for metals, plastics, wood, porcelain…

- Coatings – anticorrosive and protective , appret for textiles and paper.

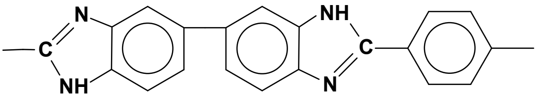
- Artificial leather- microporous, elastic, impermeable for water but permeable for air.

Polyurethanes have properties that make them outstanding materials for use in medical devices: high tensile strength, high ultimate elongation, **good biocompatibility**, **very low cytoxicity and mutagenicity**, high abrasion resistance, good hydrolytic stability, can be **sterilized with ethylene oxide and gamma irradiation,** retention of elastomeric properties at low temperature, good melt processing characteristics for extrusion, injection molding, etc.

Polyurethanes have become increasingly the material of choice in the design of medical grade components **like artificial heart and kidney components, surgical prostheses, several types of catheters and artificial blood vessels, in axiofacial surgery, heart assisting devices, tubing for haemodialysis, endotracheal tubes, gas therapy tubing, and containers for intravenous solution feeding kits.** Further applications include their use in **formulating haemostatic coating and biomedical adhesive systems. Flexible PU foams** are being used in the **construction of bandaging materials, surgical dressing and absorbent materials in general medical practice.**

- ***The other polymers with carbon-nitrogen bonds***

Polybenzimidazole ***(PBI)*** $T_g \sim 143^oC$



PBI is prepared by step-growth polymerization from 3,3',4,4'-tetraaminobiphenyl and diphenyl isophthalate.

It is an infusible, high performance polymer with a wholly aromatic molecule of high thermal stability. Its decomposition starts at 540°C. Products made from it are non-flammable and demonstrate high strength properties, chemical resistance, and have low wear and friction coefficients. It offers the highest heat resistance and mechanical property retention over 205°C of any unfilled plastic.

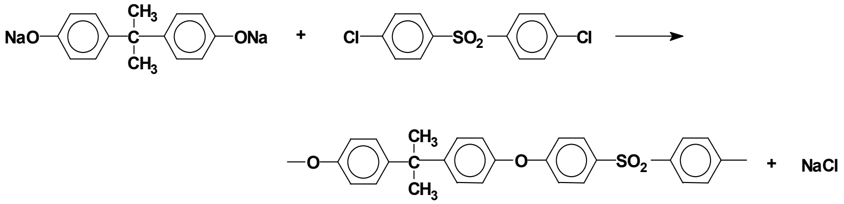
PBI is used to make fibres, component parts, composite materials and films. Fibres are used to fabricate high-performance protective apparel such as firefighter turnout coats and suits, astronaut space suits, high temperature protective gloves, welders' apparel, race driver suits, braided packings, and aircraft wall fabrics. The other application include composites, membranes, fuel cells, printed circuit boards and seals. PBI has excellent ultrasonic transparency which makes it an ideal choice for parts such as probe tip lenses in the ultrasonic measuring equipment.

Sulfur

Sulfur can be present in the polymers as sulfur-sulfur, sulfur-carbon and sulfur-nitrogen bonds. The sulfur-sulfur bond is flexible but it is thermally labile and sensitive to the thermooxidative attack. Sulfur-nitrogen linkage is also oxygen sensitive and is interested mainly because of its high electrical conductivity. Sulfur-carbon bonds, especially in sulfone structure are resistant to oxidation hence aromatic polysulfones belong to the high-temperature polymer systems.

- ***The carbon-sulfur bonds in polysulfones***

The synthesis of ***polysulfones*** (PSU) can be shown on the example of that under the trade name **Udel** ($T_g \sim 190^\circ C$):



Polysulfones are rigid, high-strength, semi-tough, transparent plastics that offer high heat resistance and very good hydrolytic stability. They retain their good mechanical properties when exposed to steam and other sterilization techniques. Polysulfone's properties remain relatively consistent over a broad temperature range from -100°C to 100°C.

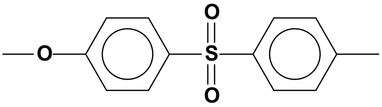
Polysulfones offer high chemical resistance to acidic and salt solutions, and good resistance to detergents, hot water and steam. In addition, polysulfones have excellent radiation stability, they are practically inflammable and are good insulators.

Polysulfones excel in many fluid-handling applications and have successfully replaced brass in pressurized hot water applications. They exhibit low creep under a sustained load at elevated temperatures and can withstand continuous exposure to hot chlorinated water.

They are commonly used for analytical instrumentation, **medical devices (heart valve holders, trocar handles, dental instruments, sterylization tray lids..)** and semiconductor process equipment components, faucet components, plumbing manifolds and in aircraft interiors. **The polysulfone membranes are widely used in hemodialysis an bacteriophags cleaning**, water treatment, bioprocessing, food and beverage industry.

Polyethersulfones (PES) are heat-resistant, transparent, amber, non-crystalline engineering plastics having the molecular structure as in the scheme below:

$T_g \sim 230^oC$

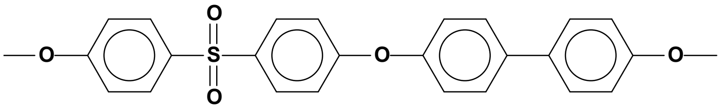


PES is a tough and rigid polymer. It has by far better high-temperature properties than conventional engineering plastics. PES remains in a satisfactory condition in the long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200ºC.

This material is compatible with **ethylene oxide, gamma irradiation, and autoclave methods of sterilization and passes all tests for biosafety, cytotoxicity, and hemolysis** and can be used in biomedical applications**.** It is known for its application in a cordless battery (used for sternum saws or bone drills), **sterylization case**, in fabrication of food service bases for hospitals (glass fiber reinforced PES), for **surgical tool for heart valve repair, and a kidney dialysis connector.**

Polyethersulfone is like polysulfone a very good material for manufacturing membranes. The strength and durability of such membrane filters are especially advantageous during procedures that require aggressive handling or automated equipment. Polyethersulfone membranes for aqueous solutions provide the **removal of fine particles, bacteria, viruses, and fungi** making it a versatile membrane for applications such as sample preparation, **sterile filtration (sterilization of buffers, culture media, additives, and pharmaceutical filtration) and infusion therapy**. PES membrane is also an extremely low protein binding minimizing the likelihood of the target analyte binding. They are used also in the **microbial analysis**.

Poly(phenyl sulfones) (PPSU) have no aliphatic groups in their structure; their representative is a polymer of the trade name **Radel R:**



The high heat resistance and excellent hydrolytic stability of PPSU make it excellent choice for hot water fitting and **medical devices requiring repeated steam sterilization**. It can be used in aircraft interiors for it fulfills requirements for low heat release, low smoke generation and low toxic gas emissions. Its typical application include **sterilization cases and trays, dental and surgical instruments, medical devices,** aircraft interiors, airline catering trolleys.

- ***The carbon-sulfur bonds in polysulfides***

Polysulfide elastomers (tiokols) are the reaction products of ethylene dihalides and alkali sulfides:

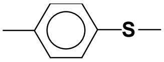
$$x\,RCl_2 + y\,Na_2S_y \longrightarrow \left(R - S_y \right)_x + 2x\,NaCl$$

The physical properties of the material depend on the length of the aliphatic chain and the number of sulfur atoms present.

The polysulfide elastomers are outstanding in oil and solvent resistance and in gas permeability. They are resistant also to aging and ozone. Their disadvantages are: disagreeable odors, poor heat resistance, low tensile strength.

Their applications include gasoline hoses and tanks, diaphragms and gaskets, baloon fabrics, variety of sealing and impregnations. They are the basis of solid-fuel rocket propellants.

Aromatic polysulfides as ***polyphenylene sulfide*** (PPS, $T_g \sim 85^oC$)



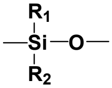
are practically inflammable, solvents resistant and of good dielectric properties. They are used as antiadhesive layers, anticorrosive coatings, containers or pipes, fuel system components, blower and pump parts, and power tools. The articles made of this polymer reinforced by carbon fibers or glass fibers can be used continuously at 150-200°C and find application in aerospace technology, liquid chemicals pump systems, electronic and electric equipment, appliances and automotive vehicles and machines. Fibers made of PPS find application as filter fabric for hot gas filtration, gaskets, and packaging.

PPS is used in medical devices requiring repeated sterilization, i.e., handles for sterile tools, sterilizable boxes.

6.5 POLYMERS WITHOUT CARBON IN THE MAIN CHAIN

Silicon polymers

The silicon atoms in polymer backbones can be present as Si-Si (polysilanes), Si-N (polysilazanes), and Si-O (polysiloxanes, silicone polymers). From all of these only the ***polysiloxanes***

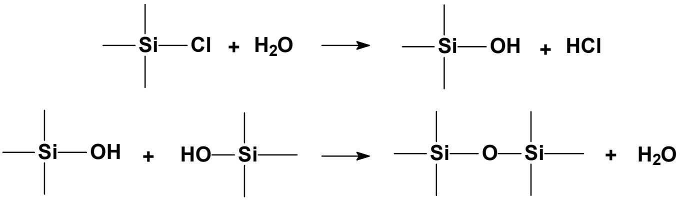


$$-\overset{R_1}{\underset{R_2}{Si}}-O-$$

have found commercial applications.

The silicon-oxygen bond has one of the highest torsional mobilities in any polymer backbone. Hence, when the side groups are small the polysiloxanes will have very low glass temperatures (-130°C for poly(dimethylsiloxane)) and the elastomeric character. Chemical stability of polysiloxanes is an effect of their hydrophobicity; in solution they are sensitive to a variety of reagents. Polysiloxanes have an unusual ability to absorb and transmit oxygen, what makes them suitable as membrane materials.

Silicone polymers are produced by intermolecular condensation of silanols, which are formed from halide or alkoxy intermediates by hydrolysis:



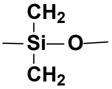
$$-Si-Cl + H_2O \longrightarrow -Si-OH + HCl$$

$$-Si-OH + HO-Si- \longrightarrow -Si-O-Si- + H_2O$$

The number of hydrolyzable –Si-Cl groups determines the structure of obtained siloxane. Dichloro- monomer gives linear polymer, monochloro generates units located at the chain end, trichloro - gives the crosslinked network.

The most important of these polymers is:

poly(dimethylsiloxane) PDMS T_g ~130°C



$$-\overset{CH_2}{\underset{CH_2}{Si}}-O-$$

Polysiloxanes have found application in many areas:

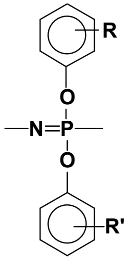
- Low molecular weight polymers (or even oligomers) are used as cooling and dielectric fluids, as oils and greases, as release and antifoam agents, in polishes and waxes, and for paper and textile treatment. **In medicine they are used to hydrophobize walls of bottles for blood or ampules for antibiotics, as an ingredient of protective ointments and oil for the scald treatment.**
- High molecular weight linear polymers, usually polydimethylsiloxanes, are used as elastomers. Depending on their formulation and their application they can be crosslinked by free radicals or by condensation of reactive end-groups such as silanols. They usually are reinforced by a finely divided material as silica, chalk, soot. Silicone elastomers have outstanding low-temperature flexibility (to –80°C), stability at high temperatures (to 250°C), and resistance to weathering and to lubricating oils. They are used as gaskets and seals, wire and cable insulation, coatings, and hot gas and liquid conduits, for manufacturing flexible molds. Due to the **bio-tolerance** they find wide **applications in the biomedical field** for example**: in plastic and reconstructive surgery (reconstruction of a nose, chin, ear, breast, fingers, elbow, feet), in maxillofacial prosthesis, the correction of a detached retina, the construction of an artificial heart and heart assisting devices as heart valves or bypasses.** The room temperature vulcanizing elastomers are very convenient for caulking, sealing, and encapsulating.
- The third group of silicone polymers applications are silicone resins. They contain Si atoms with no or only one organic substituent hence they are crosslinkable to harder and stiffer compounds than elastomers. The silicone resins are used primarily as insulating varnishes, impregnating and encapsulating agents, and in industrial paints.

Phosphorus polymers

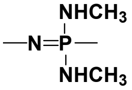
Phosphazene polymers contain P=N double bond in each repeating unit. Contrary to what might be expected, its backbone is characterized by high skeletal flexibility. The polymers possess a high chemical, photolytic and thermooxidative stability and is especially resistant to ozone and free-radical reagents.

Polyphosphazenes consist then of an inorganic phosphorous-nitrogen backbone and reactive pendant side groups that may be organic, organometallic or inorganic in nature. These side groups decide of specific properties of the polymer. Because of the endless number of permutations of these substituents it is possible to tailor polyphosphazenes to any performance demanded.

Some examples showing how the side groups change the polymer properties are shown below:

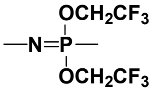


1



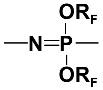
$$-N=\overset{NHCH_3}{\underset{NHCH_3}{P}}-$$

2



$$-N=\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}-$$

3



$$-N=\overset{OR_F}{\underset{OR_F}{P}}-$$

4

1-elastomer, inflammable,

2 - soluble in water,

3-hydrophobic, inflammable polymer used for films and fibers,

4-low-temperature, solvents and oil resistant, elastomer, inflammable,

Polyphosphazenes generally are **biocompatible** and their medical applications include **controlled drug delivery, biological membranes, coatings, various medical devices and components such as prosthetic and implants.** They are **potential materials for scaffolds for bone regeneration and artificial muscles.**

Polyphosphazene is currently the highest performing membrane material for methanol based proton-exchange membrane fuel cells. They are used also as ion conductive membranes for rechargeable polymer lithium batteries, advanced elastomers for applications in the aerospace engineering, photonic materials, fire-resistant polymers, adhesives, paints, membranes in electrodialysis, microfiltration, ultrafiltration, and reverse osmosis applications.

6.6 THE MOST IMPORTANT COMMERCIAL COPOLYMERS.

- ***ethylene-propylene rubbers***

Copolymerization of propylene with ethylene yields noncrystalline, rubbery products, chemically inert (lack of unsaturation) applied after crosslinking with organic peroxides. Sometimes a diene monomer (for example 1,4-hexadiene or dicyclopentadiene) is added to make crosslinking easier ; the resulting terpolymer is named as EPDM (ethylene-propylene-diene monomer) rubber. These polymers are resistant to weathering and heat.

Typical applications include gasket materials, o-rings, automotive weather-stripping materials, roofing membrane, belts, electrical insulation, hoses and tubes, garden and appliance hoses, rubber mechanical goods, plastic impact modification. **Medical bottle**s carrying solutions with high pH-value and some aerosols have **plugs** made of this material.

- ***ethylene-vinyl acetate** (EVA)*

The main function of vinyl acetate in this copolymer is to reduce crystallinity and introduce polarity, leading to more flexible and tougher product. Applied for production of **medical hoses (pipes) and syringes**, toys, cable isolation, multilayer packaging, wrapping films (i.e. for meat), glue. EVA is also used in **biomedical engineering applications as a drug delivery device**. The polymer is dissolved in an organic solvent, next a powdered drug and filler (typically an inert sugar) are added to the liquid solution and rapidly mixed to obtain a homogeneous mixture. The drug-filler-polymer mixture is then freezed, dried until solid. These devices slowly release a compound over time. While the polymer is not biodegradable within the body, it is quite inert and causes little or no reaction following the implantation.

- ***ethylene –α-olefin***

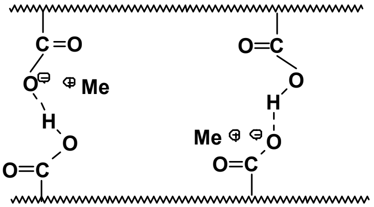
Addition of α-olefin such as butene, hexene, or octene generates the short-chain branching. Their presence assures excellent melt-flow and physical properties of a polymer. A major use are plastic trash bags.

- ***ethylene-norbornene***

This is a cyclic olefin polymer known under the trade name Topas. This materials exhibits a unique combination of properties which can be customized by varying the chemical structure of the copolymer. Performance benefits include: low density, high transparency, extremely low water absorption, excellent water vapor barrier properties, high rigidity, strength and hardness, **excellent biocompatibility**, very good resistance to acids and alkalis, very good electrical insulating properties and very good melt processability. It is suitable for the production of transparent moldings for the use in optical data storage, optics, e.g. **lenses**, sensors, **packaging of pharmaceuticals, medical devices and diagnostic disposables**. Films made from Topas offer opportunities in **blister packaging**, shrink sleeves, and shrink films.

- ***ethylene-carboxylic compound*** (methacrylic acid, sodium acrylate)

These copolymers are ionomers – class of thermoplastics containing ionizable carboxyl groups which can create ionic crosslinks between chains. Crosslinking occurs through metal “bridges” and is reversible.



It means that ionomers can be processed in a conventional way. Their most important features are high transparency, toughness, flexibility, adhesion, and oil resistance. The main application: sealants and tie-layers in food packaging, wrapping films for food (films are resistant to piercing), **medical packaging**, shoe soles, helmets, insulators, **syringes**, the outer layer of golf balls and impact modifiers for polyamides.

- ***butyl rubber***

Butyl rubbers are copolymers of isobutylene isoprene. The latter is added in small quantity to make the material vulcanizable. The very low residual unsaturation makes the crosslinked rubber chemically inert and less sensitive to oxidative aging than are most other elastomers. Its chains are very closely packed what results in unusually low permeability to gases. It is biocompatible and good dielectric. Most of the butyl rubber produced is used for inner tubes for tires, also for bottle stoppers (also as **special bottle plugs in medicine packaging**), tank and pond liners and **joint replacement**.

- ***styrene-divinylbenzene***

A suspension polymerization of styrene with several per cent of divinylbenzene results in uniform spheres of a crosslinked polymer. It can be relatively easy modified by introducing acidic or basic functionalities hence giving ion-exchange resins.

- ***styrene-acrylonitrile***

The product of major commercial interest contain, typically, 76% styrene and 24% acrylonitrile. This combination provides higher strength, rigidity, thermal and chemical resistance than polystyrene, but it is not quite as clear as crystal polystyrene. The application is very wide and includes food containers, kitchenware, computer products, packaging material, battery cases and various containers, electrical parts, plastic optical fibers, automotive interior parts, household goods, **various medical appliances (urine meters, diagnostic components, fluid handling devices, flat plate dialyzers)**, toys and many others.

- ***styrene-maleic anhydride***

Maleic anhydride does not homopolymerize but easily undergo copolymerization with styrene giving the alternating copolymer. This product is very well processable (flows very easily in the elevated temperatures), has better than PS heat resistance and may be used for the contact with food. Is then used as packing for hot dishes, oil, and milk products and for manufacture of microwave cookware. Its applications include binders, adhesives, paper sizing, coatings, production of automotive parts, covers and shielding of electric devices, compatilizing of polymer mixtures and modification poly(vinyl chloride). In India it is used as a **male contraceptive**.

- ***styrene-butadiene rubber** (SBR)*

The most important from all styrene copolymers. It is synthesized by two methods - radical polymerization in emulsion (cold rubber) and anionic in solution (solution SBR). Processing is as for natural rubber - carbon black as a filler and vulcanization with sulphur. They are compatible with other elastomers and can be used in blends. "Cold" SBR is superior to the other products for it contains less low-molecular weight rubber, less chain branching and crosslinking, and a higher proportions (70%) of the trans-1,4 configuration around the double bond. Generally the application of SBR is similar to natural rubber - tires, belting, hose, flooring, shoe soles, electrical insulation and others. **Thermoplastic styrenic elastomer (triblock SBS) has got acceptance as a compounded polymer and hot melt adhesives in a wide variety of medical device and packaging applications.**

- ***acrylonitrile-butadiene-styrene*** *(ABS)*

ABS resins are a two-phase system consisting of inclusions of rubber (styrene-butadiene copolymer) in a continuous glassy matrix (styrene-acrylonitrile). It is produced by the grafting of polystyrene or styrene-acrylonitrile copolymer onto butadiene or acrylonitrile-butadiene copolymer. The ABS resins have good temperature resistance and solvent resistance. This is engineering plastics, particularly suitable for high-abuse applications.

The examples of applications include automotive bumpers, battery cases, various containers, machine parts, housing for domestic appliances (e.g. vacuum chamber), safety helmets, pressure pipes, printer components, cosmetic packaging or soap dispenser, credit and phone cards, toys (Lego). The Typical applications of medical grade ABS include **components of intravenous (IV) systems, diagnostic test kits and surgical instruments, for example trays and kits, surgical staples, home test kits, roller clamps, asthma inhaler chamber, obstetic vacuum pump and a remote heart monitor**.

- ***nitrile rubber***

This material is a copolymer of butadiene and acrylonitrile. For oil-resistance (for that is primarily used) the content of the AN should be in the range 18-40%. Nitrile rubber is used for gasoline hoses, fuel tanks, automotive transmission belts, o-rings, gaskets, oil seals, belts, synthetic leather, printer's rollers, and cable jacketing.

In the form of latex it is used for impregnating paper, textiles and leather, in the preparation of adhesives and as a pigment binder. **In medicine** the uses of nitrile rubber include **disposable non-latex gloves, rubber parts in metering valves for aerosol pumps and oil-resistant bottle plugs for animal medicines, and other medical devices ranging from components for blood analysis machines to surgical instruments.**

- ***ethyl acrylate-methyl methacrylate***

Lower acrylate monomers are soft and rubbery. The addition of methyl methacrylate provides hardness and strength. Additionally small amounts of hydroxyl, carboxyl, amine or amide comonomers are used to provide adhesion and thermosetting ability. Such materials are used to produce high-quality latex paints for wood or wallboard, also for automotive and appliance coating, baked enamels and variety of finishes, polishes, and adhesives.

- ***ethyl acrylate-2-chloroethyl vinyl ether***

This copolymer has elastomeric properties and can be vulcanized. The most important features of it are heat resistance (can be used up to 180^{o}C) and the excellent oxidation resistance.

- ***vinyl chloride-vinyl acetate***

The addition of comonomer lowers glass temperature and increases solubility of a polymer in organic solvents. It also improves the stability and polymer processing. The application includes adhesives (for PVC, wood, leather, paper, glass), industrial coatings (for metal, wood, paper, cement and brick constructions), inks and overlacquers, marine and maintenance. It is approved for food-contact applications.

- ***vinyl chloride-acrylonitrile***

It is a useful fibre material with low flammability. Used for non-clothing applications as for blankets, carpets and filter cloths.

- ***vinylidene chloride-acrylonitrile***

This copolymer is used for coating cellophane, paper, PE in manufacture of multi-layer food packaging systems.

- ***vinyl chloride-vinylidene chloride***

It is self-extinguishing material of good resistance to a wide range of chemicals. This material is used in manufacturing of pipes and fittings for chemical industry. Films made of copolymer with a small (up to 15%) amount of vinylidene chloride are clear with good stretching resistance. Copolymer is used also as a bonding agent for non-woven fabrics and in medicine, as a **dural substitute in repairs of dural defects produced by surgery, trauma, or tumor, as bone lining, in the prevention of bone reunion in craniostenosis, and nerve wrap after neurolysis in cicatrization.** Copolymers containing more than 80% of vinylidene have very low permeability to water vapor, flavor, oxygen when compared to other plastics.

As a thin, clingy plastic wrap ("Saran Wrap") it is used primarily for wrapping food. Saran fiber is a heavy fiber (deck chair fabric, car upholstery, doll's hair, filter fabric). It is a remarkable barrier against water, oxygen and aromas, has superior chemical resistance to alkalis and acids, is insoluble in oil and organic solvents, has very low moisture regain and is impervious to mold, bacteria, and insects. Saran fiber has a high elastic recovery and resists wrinkling and creasing.

- ***hexafluoropropylene-tetrafluoroethylene***

This copolymer retains most of the properties of polytetrafluoroethylene (PTFE), but has melt viscosity that allows fabrication by conventional techniques. It retains mechanical strength for the continuous service up to 200^{o}C, is chemically inert and has zero water absorption. What is more, it has excellent weatherability, nonstick and low friction properties. It finds application similar to those of PTFE, as wire jacketing, films, tubes, rod and encapsulatng resins, in printed circuits, condensators, form lining, electric insulation, moulded parts for electric and electronic components, conveyor belts and roll covers, solar-collector windows and others.

- ***ethylene-tetrafluoroethylene, ethylene-chlorotrifluoroethylene***

These copolymers have 1:1 alternating structures. They retain much of the superior properties of fully fluorinated materials at the same time being engineering termoplastics with good strength, toughness and wear resistance. They find electrical applications for heat resistant insulations and jackets, for wiring in chemical plants, in chemical industry for valve components, packing, pumps impellers and laboratory ware.

- ***chlorotrifluoroethylene-vinylidene fluoride***

Depending on the composition these copolymers range from tough, flexible materials to elastomers. They are extremely resistant to powerful oxidizing agents. They are used as valves, ring seals, caulking compounds, also in automobile transmission and brake systems as gaskets and seals.

- ***hexafluoropropylene-vinylidene fluoride***

These materials are elastomers with good mechanical properties as well as high resistance to chemicals (oil-resistant). They are cured with amine compounds. They can be used in temperature even up to 300^{o}C (for short time) and 200^{o}C is the normal temperature of their work. Application includes wire and cable coatings, flexible and corrosion-resistant tubes, and liners for pipes and tubes.

- ***acrylic fibers***

The acrylic fibers are copolymers containing at least 85% of acrylonitrile. The rest is the other monomers such as vinyl acetate, acrylic esters, or vinyl pirrolidone that make possible fiber dyeing with conventional textile dyes. *Modacrylic* fibers are made of copolymer of acrylonitrile with vinyl chloride or vinylidene chloride (more than 20%).

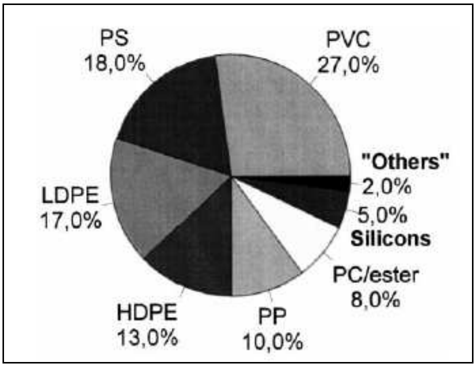
II. SELECTED APPLICATIONS OF POLYMERS IN MEDICINE

1. INTRODUCTION

During the last few decades there has been observed an increasing development of the search for new materials useful in biomedical technology. Among these were the first artificial heart valves, pacemakers, artificial liver of and kidney dialytic systems. It was possible also to construct some effective orthopaedic devices as knee or hip joints replacements. However, the selection of suitable material for a particular use was more or less based on a trial and error approach.

At the beginning of the 80's biomaterials were defined as *any substance, other than a drug, or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ or function of the body*. There are three mail categories of biomaterials: metals and their alloys, ceramics and polymers. Among them polymers took the largest group. They can be used for artificial replacements, sutures, vascular grafts, blood contact devices, tubes and bags, intraocular lenses, dental implants or soft tissue replacements.

The importance of biomaterials has increased lately thanks to significant development in material science related to the synthesis of new materials, blending and/or modification of tailor-made polymers. These activities are relatively simple in comparison to the sophisticated structure of replaced organs/tissue. Most polymer implants are produced from standard polymers, for example. On the world market 85% of implants are made from vinyl polymers, 13% are prepared from polycarbonate, silicone or polyester. It means almost all implants have a plastic origin. The graph below shows the distribution of polymers for biomedical applications:



The abbreviations' meanings are the following: PS - polystyrene, PVC – poly(vinyl chloride), PC – polycarbonate, PP – polypropylene, HDPE and LDPE – high density and low density polyethylene, respectively.

The used biomaterials should be characterized by two most important properties: they should have biofunctional character and should show biocompatibility. When the first feature is satisfied mostly by selection of a suitable material that is able to withstand the attack of aggressive environment without irritating the surrounding tissue the second feature has to be selected carefully. The term biocompatibility passed evolution for the last decades. At the beginning the material inertia was taken as the best criterion for selection of the biomaterials. It was demanded that these materials should not affect the surrounding tissue, irritate it and show neither carcinogenic, allergenic nor toxic effects. Now, a new approach has been developed. Biocompatible materials should show the tolerance effect towards their hosting body. This definition requests better recognition on the nature of processes that took place on the surface layer between an implant and a living tissue. To complete this topic we can consider a possible chain of interaction on the above mentioned border.

At first, the living body deposits proteins soluble in liquid on the surface of the implant. This process starts after a few seconds when the biomaterial is placed into the host body. The character of deposited proteins and their surface is depended on the nature of the implant surface. **At the next stage**, the stimuli of the artificial implant starts to generate the inflammation phenomenon: A granulated tissue is formed around the implant and its surface is covered by collagen fibrils and blood vessels. The body sees the implant as an injure and tries to plug it. During the prolonged exposition to the body fluids, some oxidative and hydrolytic processes appear. It is the **third stage** of the body response to the presence of the implant. Degradation processes of biomaterials start and mechanical property of the implant deteriorates gradually. At the **forth stage**, some freeing particles or degradation products are transported by lymph and by vessel systems to other parts of the body and can interact with other tissues. This short description shows how important is the selection of proper implant material and how complex processes appear in the system to be worked on.

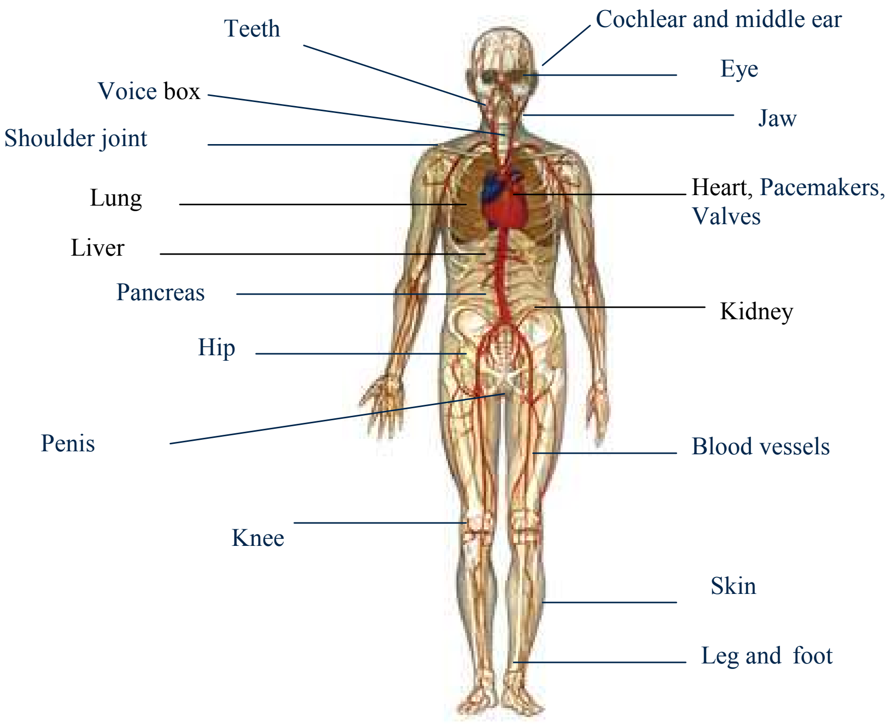
The most spectacular use of polymers in medicine is seen in their application in construction of artificial organs. However, before we come deeper to discuss this subject, a short introduction is needed. It is related to biomedical engineering, a new branch of medical efforts related to improvement of our health. At the simplest description, biomedical engineering is a discipline that advances knowledge and engineering, biology and medicine to improve human health through cross-disciplinary activities. It integrates engineering and biomedical sciences with clinical practices. Hence, any design of a medical device or an analytical tool should be preceded by an advanced analysis of the physiological system. What is important to add here, the analysis cannot focus on the particular organ or case only but should be extended to the whole living system as discussed above.

Now, the question on the replacement of some malfunctioning or damaged organs becomes the hot topic. What are the positive and what are the negative sides of such activity describes the chart below.

Advantages	No damage to the host sites
	No immune-rejection issue
	Rapid surgical procedures
	Reduction of number of patients on the waiting list
	Reduction of money spent on health service
Disadvantages	Limited compromise in function for artificial organs
	Problems with organs' adaptation to change in the local environment

The problem to introduce artificial organs is related to the following general thesis: our organs are very complex and perform many functions simultaneously, hence it is difficult to mimic them by the use of simple artificial organs. In such a situation we should consider artificial organs as the bridge to transplantation of natural organs, the bridge that keeps patients alive when they are waiting for natural organs.

The next graph presents some parts of our body that can be replaced by artificial organs. The cartoon is not shown to frighten the reader but to make her/him familiar with the extent of use of the artificial materials in the organ replacements.



The next chapters show applications of polymers in construction of an artificial kidney, liver, bones or lenses. Additionally, the problems related to the use of polymers for production of scaffolds are presented. To supplement the general insight into the role of polymers in medicine, the use of polymers in designing of the drug delivery system is discussed. However, polymers are not applied in the direct use in medicine. A lot of efforts are related to the separation and purification of the same chemicals that are used as bioactive components.

2. ARTIFICIAL KIDNEY

2.1. INTRODUCTION

At the beginning, according to the biomedical engineering scenario, we have to look at the functions of a kidney among the living mammalians. There are four general functions done by a kidney:

1) to clean blood and remove extra fluid,
2) to filter out wastes,
3) to keep chemical components in balance,
4) to control blood pressure and content of red cells.

Hence, the normal renal functions are related to keeping the proper homeostasis of salt and water, controlling electrolyte and acid-base balances, elimination of toxins, hydroxylation of vitamin D and to synthesis of erythroproteins. However, most of us point at excretion as the dominant function of a kidney. If so, the question is what molecules are removed from blood. The average amounts of excreted component is given below:

Urea –	30 g per day,
Creatinine –	2 g per day,
Salt	15 g per day,
Uric acid	0.7 g per day,
Water	1500 mL per day.

The process of blood purification took place in the nephron cells. The filtration process takes place in glomerulus where 1800 L of blood is pumped per day. It results in filtration of 160 L of liquid per day. However, our removal of urine is about 1.5-2.0 liters per day. It means that 158 L of fluid is absorbed in tubules and returned back to blood.

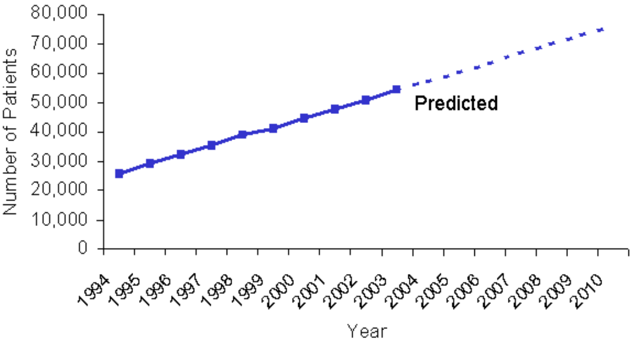
There are some symptoms of renal malfunctioning system. They include: the increase of urea concentration in blood, fluid retention, anemia, electrolyte imbalance and toxins accumulation. However, there is the high tolerance rate for renal failure – when more than 95% of kidney function is lost, the intervention is required.

In the case of an artificial kidney, it is possible to follow the idea of organ bridging. Let us have a look at the statistics from California. It was prepared in 2005 but still it shows the general trends in this branch of biomedical engineering. The table shows the average extended life-time for people treated with dialysis or transplantation. The right column shows the average time for healthy people.

Age	Dialysis		Transplant		Healthy people
	Male	Female	Male	Female	
15-19	16	15	39	40	62
20-24	14	13	35	36	57
25-29	11	10	31	32	53
30-34	9	9	27	28	48
35-39	8	8	23	25	43
40-44	7	6.9	20	22	38
45-49	6	6	17	19	34
50-54	5	5	14	16	29
55-59	4	4.5	12	14	25
60-64	3	3.8	10	12	21
65-69	3	3.2	8.5	10	17
70-74	2	2.7	6.8	8	14
75-79	2	2.4	6.9	7	11
80-84	2	2	6	6.4	9

[after Alex Wiseman, M.D., University of Colorado, Health Sciences Center, 1996]

The presented data explain directly how important is the use of an artificial device in waiting time for kidney transplantation. To strengthen the above impression one more graph is presented. It is demanded for a donor kidney in the USA.



Source: *2004 OPTN/SRTR Annual Report*, **Table 5.1. Predicted values for 2004-2010 based on slope of the line from 1994-2003.**

Growth in the waiting list for donor kidneys, USA 1994-2003

The figure clearly shows that the problem with kidney transplantation swells year by year and the use of an artificial substitute is the only one reasonable way.

2.2. HISTORY OF ARTIFICIAL KIDNEY

Despite some information on the artificial kidney discovery at the beginning of 20 century, Prof. Kolff is considered to be the father of dialytical treatment of patients with renal problems. The best way to understand origin of his work is to read his interview printed in the New York Times. Prof. Kolff described there: *Professor Brinkman at Groningen was the man who first told me about cellophane and dialysis. Brinkman was a wonderful man, and he knew cellophane. Cellophane tubing looks like ribbon, but it's hollow. It's artificial sausage skin, and it's an excellent membrane for dialysis. If you have blood inside here, small molecules will go through the pores of the membrane to the outside where you have the dialyzing fluid. So urea and other products that the kidneys normally excrete will go out*. As one can see, one of the kidney function can be mimicked by a sausage skin. Prof. Kolff was able to mimic the second function – keeping the proper salt balance. He explained as follows: *And another thing happens. Sodium chloride and other electrolytes will also go out. So, you add them to the dialyzing fluid on the outside, and they go out and in, and you get an equilibration through this membrane. If the sodium is too low, it goes higher; if it's too high,* *it goes lower. This normalizes the electrolytes in the blood plasma. The treatment with the artificial kidney is relatively simple.*

The device he constructed is shown in next picture (Prof. Kollf in the white jacket).

The artificial kidney device was built of a rotating drum with wooden bars wrapped with a cellophane tube. Blood was placed into the tube and the whole drum was rotated in a water bath. Then blood was injected back to the patient.

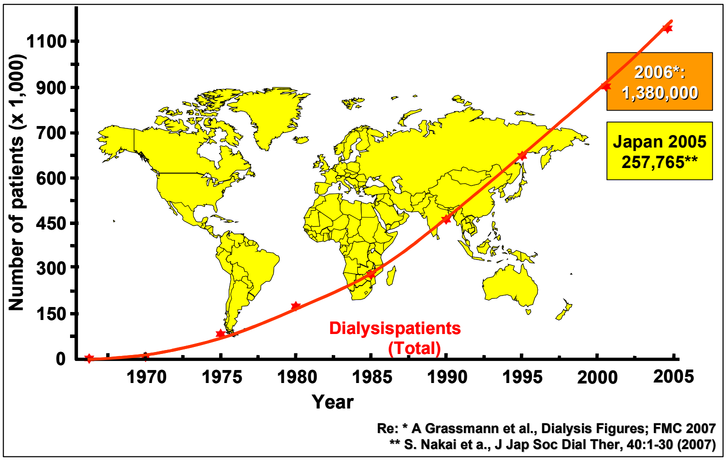
The first experiments gave not too positive results. Prof. Kolff noted: *Of the first 15 patients I treated with dialysis [...] only one survived. And that one might have survived if I had used another sequence of treatment, without the artificial kidney.* To give an insight into the atmosphere of that time Kolff admitted: *By the way [...] if the institutional review committee for research on human patients had existed at that time [...] the artificial kidney would never have been made. Never. My consciences was only my only brake. Otherwise, I could do what I wanted.* Finally, he came to the reflection: *But I had to explain to the patient what I was going to do, and I always did.*

As one can note the beginning is difficult. Always.

2.3. HEMODIALYSIS TODAY

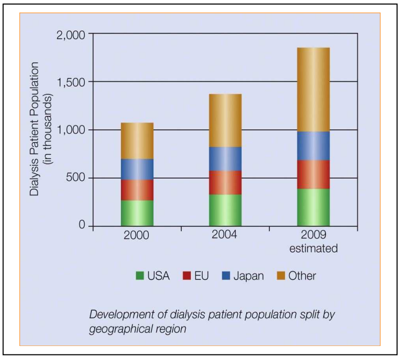
This part of the text is based on the presentation of Jörg Vienken, Fresenius Medical Care, Bad Homburg who kindly agreed to its distribution. This chapter is based mostly on his presentation during the Spring School of Membrane Processes – Warsaw University of Technology, 2007.

The best way to show the market of an artificial kidney is to check the annual sell rate of the devices. The picture below shows this value:

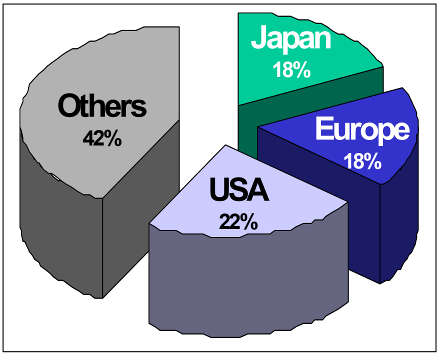


Re: * A Grassmann et al., Dialysis Figures; FMC 2007
** S. Nakai et a., J Jap Soc Dial Ther, 40:1-30 (2007)

The picture shows the monotonically growing number of patients that have to be dialyzed. However, the world distribution gives much deeper insight into the problem. Japan with a population round 80 mil. people need almost the same number of treatments as Europe does.



Development of dialysis patient population split by geographical region



The reason is related to Japanese customs where transplantation of organs is still not too popular. So, the number of dialyzed people is large enough.

There are two ways of blood detoxification today: dialysis and filtration. Both of them differ in properties of used membranes – when the first deals with a membrane having small pores and diffusion process the second applies larger pores and convective flow. However, the difference is not so large when someone considers the pore diameter: diffusive membrane – pores 1.3 nm, convective membranes – 3.1 nm. To see the problem, the reader is asked to look at the pore structure of a porous membrane.

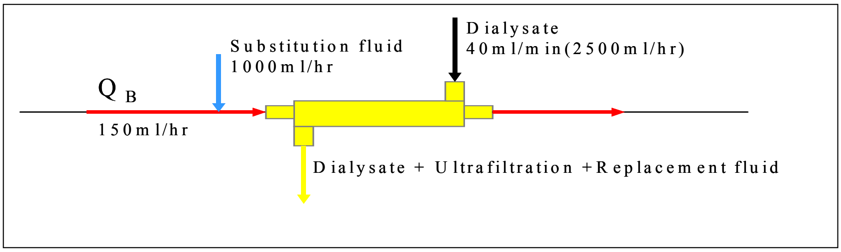
There is a set of pores with their own size distribution. Hence, it is a great challenge for membrane scientists to prepare membranes where pores of 1.3 and 3.1 nm do not belong to the same population. Anyway, such materials are available today on the market and dialysis wards can select the type of polymers as well as the module character of flow.

Today, four different polymers are used to prepare dialytical membranes. They are as follows: **cellulose, cellulose acetate, polysulfone and polyacrylonitrile**. However, the kind of polymers subjected to exposure to blood is not limited to these four. The picture below shows the modern construction of a dialytical module with millions of capillary membranes. The shell of device is built of polycarbonate. Capillaries are potter with polyurethane resin, the caps are made of **polyamides** and they are sealed with **silicone**. Hence several more polymers are used in the preparation of an artificial kidney and all of them should show the biocompatibility character. It is really a great challenge for the biomedical engineers to develop such a construction.

Coming back to the dialysis process one should memorize that **cellulose** and its **derivatives** are used for hemodialysis mostly when **polyacrylonitrle** and **polysulfone** for hemofiltration.

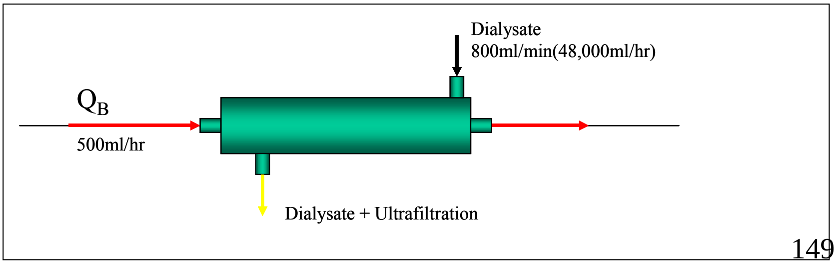
The difference between dialysis and filtration is shown in the figure below.

Hemofiltration



Here, dialytic fluid is added to blood and this mixture is filtrated. Toxic substances are removed with the convective flow to dialysate flushing membranes from the shell side. The method is fast and effective and over the last years has become more popular than a typical hemodialysis.

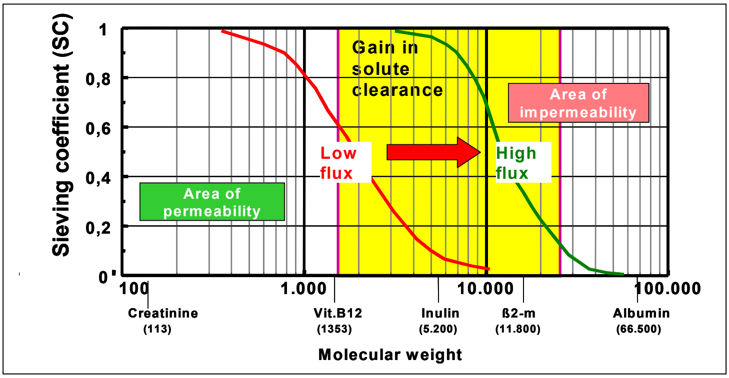
Hemodialysis



This method is based on the diffusion of toxic species through a dense membrane. For this reason it is much slower than hemofiltration.

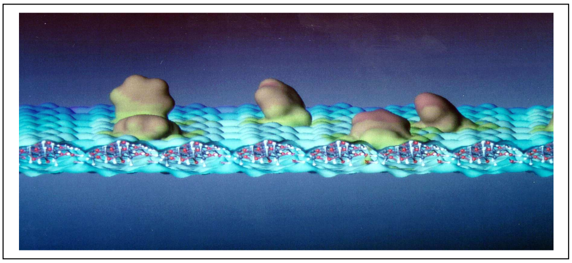
Question to be still open – what procedure is more effective in removal of toxic metabolites: dialysis or filtration?

The following chart may help in the understanding of the selection problem of the low or high flux membrane.



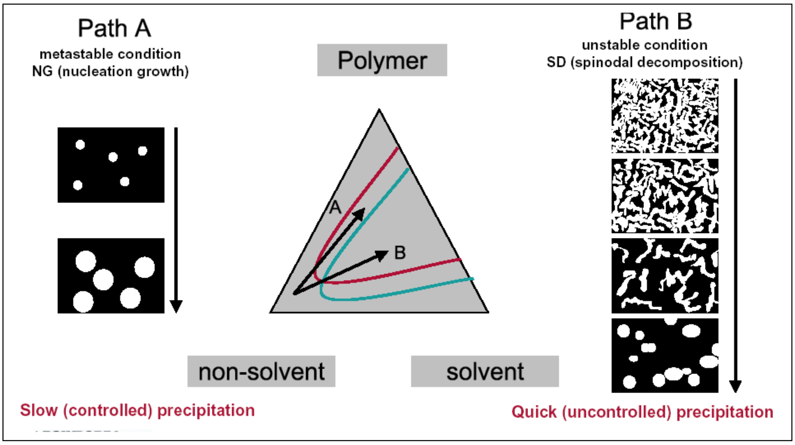
Now it is the best time to consider materials to be used in the construction of modern artificial kidneys. For many years, the belief that only natural materials can be used for construction of dialyzers has persisted. However, the last experiences in running such devices have shown that semi-synthetic as well as synthetic materials can be applied. Now, membranes are prepared from: **cellulose, modified cellulose, cellulose acetate, polycarbonate**, **polyacrylonitrile, polyamide, polysulfone** and **polyethersulfone.** Hence, the whole bunch of polymer materials is used – hydrophilic, hydrophobic or moderately hydrophilic.

How the character of material is important to what was discussed at the beginning of this chapter. The best membrane, it means with the best hemocompatibility, should be moderately hydrophilic. In the case of various materials, their surface is modified by the deposition of heparin or ‘grafting’ of some chemical functionalities (see the image of aromatic rings on cellulose surface).



2.4. TECHNOLOGY FOR CAPILLARY MEMBRANE PREPARATION

In most cases, membranes for hemodialysis and hemofiltration are prepared by the phase inversion technique. The schematic process presentation is shown in the Gibbs triangle:

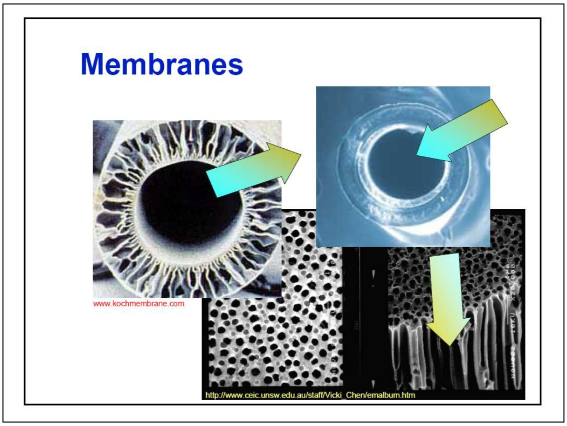


[figure courtesy of W.Ansorg, Membrane GmbH]

Membrane preparation scheme for solvent induced phase separation

After the addition of the non-solvent to the polymer solution, a phase inversion process starts. Depending on the concentration of polymer, two modes of separation may appear: the nucleation and growth or spinodal decomposition. Finally, the different structures of the membrane are obtained.

Today several technologies are used to prepare various kind of membranes. Some structures of them are shown below.



Membranes

www.kochmembrane.com

http://www.ceic.unsw.edu.au/staff/Vicki_Chen/emalbum.htm

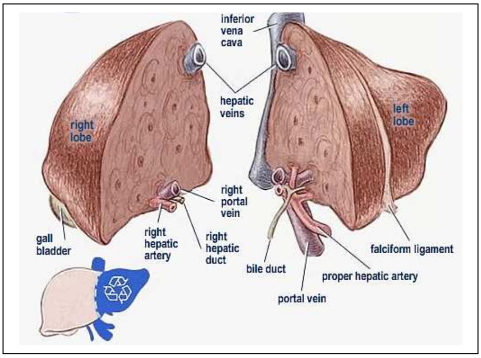
Finger-like pores on the left side and sponge-like structure on the right

2.5. SHORT SUMMARY

There are several types of artificial devices on the market today. There are observed some changes in their use for patients treatment. Low-fluxes kidney are more and more often replaced by the high-flux modules. More frequently are used synthetic than natural polymers. It seems that such a trend will be in progress within the next years. The presented material does not describe all problems related to studies on the artificial kidney. We discussed above a simple case – how to mimic nature, how to follow the function of a nephron. However, there are a lot of elements in the device used for hemodialysis. Some of them are prepared from polymers. There is another issue relevant to the treatment of renal patients – the production of water to be used as dialysate. It is done by reverse osmosis, the membrane process where polymer membranes play a key role.

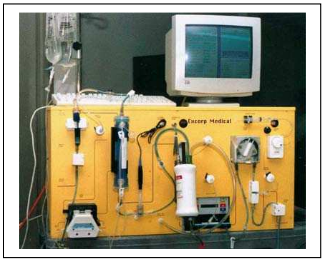
3. ARTIFICIAL LIVER

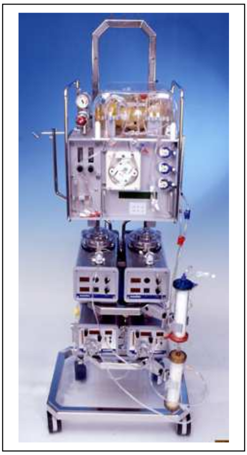
As usually, the beginning of an artificial liver construction belongs to biomedical engineers who have to evaluate the functions of a natural liver. Roughly calculating, a liver has more than 900 jobs to do. It stores energy, stops cuts from bleeding, kills germs, helps digest food, breaks down proteins, fats and carbohydrate, builds proteins, makes and secretes bile, maintains the immune system, removes wastes and filters' pollutants or toxins. All these jobs and much more are done by a liver.

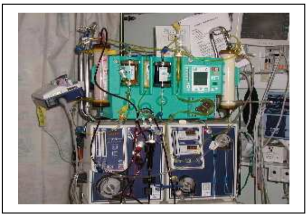


Hence, the selection of a function that should be mimicked is not such an easy task. So far, blood detoxification is frequently taken into consideration.

There have been several attempts to construct liver assisting devices (LAD). Some of them apply mechanical principles like diffusion and sorption while others mechanical separation with the biochemical action of hepatocytes –liver cells. In most cases, the extracorporeal artificial liver support devices are built. Some examples of such devices are shown below:





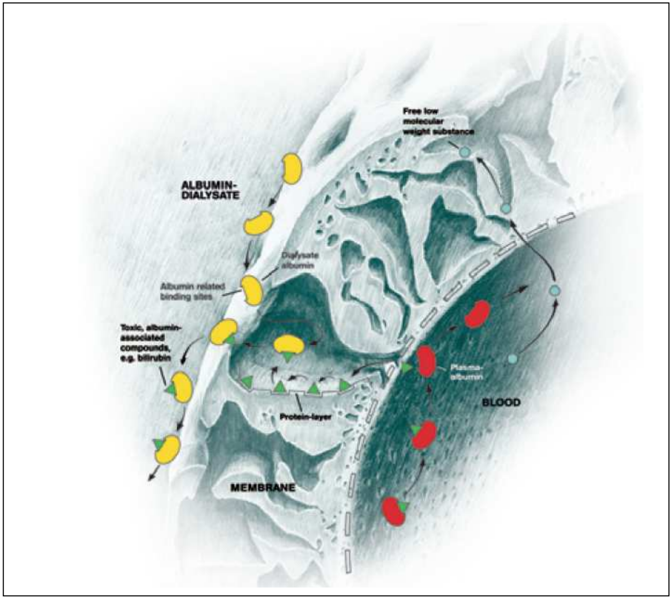


What is characteristic for all these devices is the presence of hemofiltration unit. Blood is filtrated and plasma is usually put into the contact with adsorbent. As sorbent activated carbon is commonly used.

The above idea has been finalized in the construction of MARS (molecular adsorbent recycling system) – one of the commercialized artificial liver. Its picture is shown below:

MARS device

Artificial plasma (BSA solution) is circulating in the loop. It contacts with blood through a membrane and is pumped through carbon (the black column) and ion-exchange resin (the white column) to remove toxins. Some parts of components are removed by dialysis in the module on the right side. The critical point of MARS construction was to find the way of toxins transportation through the first dialyzer. It was achieved by the immobilization of serum albumin into pores of the membranes.



Toxins, entrapped by albumin in patient's blood are delivered to the membrane where they are taken by albumin immobilized to pore walls. On the opposite side of the membrane, toxins are caught by albumin molecules circulating in the MARS loop.

Some others LAD's use living hepatocytes. This extra-corporeal liver assisting device consists of a hemofiltration unit that delivers plasma to close contact with hepatocytes grooving in incubators. The cells are kept alive by delivering feed and oxygen to them. The treated plasma is circulated back to patient. At this stage of LAD evaluation, the same materials as for an artificial kidney are used. They show the proper biocompatibility property and suitable geometry.

The chapter shows that materials and methodology invented for an artificial kidney can be applied for LAD with some minor modifications. As a matter of fact, the most important challenge for a material scientist is to find such a material that cannot initiate the deposition of cells on its surface and hence limit the fibrosis process. The experiences gained in the construction of an artificial kidney are welcome in the artificial liver manufacturing.

4. ARTIFICIAL SKIN

The functions of skin should be divided into biological and mechanical ones. The biological functions comprise: the facilitation of fibroblasts and microvascular cells migration to allow neoderma synthesis, protection inflammatory reaction and reaction with foreign bodies, prevention of infection, prevention of scar formation and so on. The mechanical functions are as follows: creating a mechanical barrier against permeation of bacteria, controlling of fluid flux, improving tear strength, bending rigidity and elasticity, controlling surface energy and peel strength, and so on.

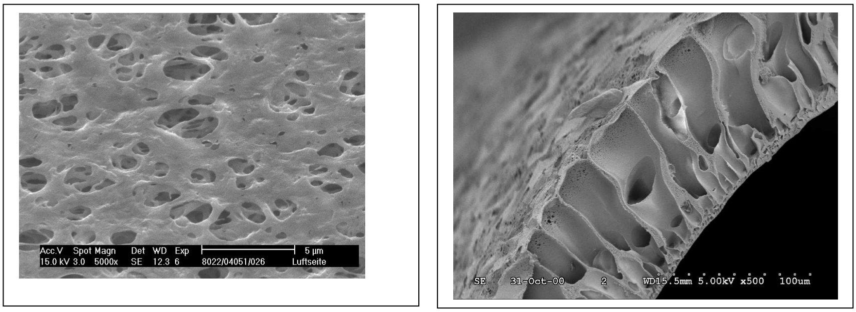
From the anatomical point of view skin is a very complicated organ. It is composed of three layers: epidermis, dermis and hypodermis. The first one provides protection, keeps pigmentation, helps immune system and sensing various stimuli. The second one forms the main body of skin and allows the whole system to live. The third one anchors skin to other tissues, works as a shock absorber and a thermal insulator.

Taking into account these functions, skin is an extremely difficult organ for mimicking. The common work of medical researchers and polymer engineers has resulted in launching the production of artificial skin that was constructed from biodegradable scaffold on which skin cells can grow. To obtain the proper matrix, the extracted fibroblasts are mixed with collagen that is used for the preparation of scaffolds. After several weeks of curing the wounded places, keratinocytes - extracted from donated foreskins, are seeded onto the new dermal tissue and create an epidermis.

Grafting of artificial skin offers more advantages over the techniques that graft natural skin. It eliminates the need for tissue typing. Artificial skin is prepared in large quantities, stored and used when it is needed. It does not contain immunogenic cells and for this reason is not rejected by the body. In consequence, time of treatment is significantly reduced. Some manufacturers used the artificial epidermis that is removed from skin just before grafting. It is composed of **silicon** or **Teflon**. However, the most important part of artificial skin is the porous structure composed of **collagen** and **polycarbonates** that allow growing skin cells into its structure. That part is called the scaffold.

Polymer scaffolds

Such a porous structure is commonly used in tissue engineering approaches. For the different purposes it is prepared from various materials and by means of various techniques. There are several methods of polymer processing that are applied for scaffolds manufacturing. One of it is the phase inversion that results in the preparation of porous structures with wide distribution of the pore diameter. The origin of this method was discussed in the general part of this book in chapter related to the phase separation.



Porous structure of polymers used as scaffolds. Top view – left side, cut –right side

The next methods are based on the selective removal of one component from the polymer blend or composite or on the freeze drying and use of supercritical CO_2 under a high pressure. The foaming of polymers is applied sometimes also. Polymers are processed with the foam precursor (porogen) that creates the pore structure under specific conditions. Styrofoam is the best example of it.

However, the described scaffolds form the porous matrix only. The next problem to be resolved by biomedicine engineers is to make these matrices friendly for growing cells and to use them in tissue engineering. How to reduce the immune response of the living bodies when they are put into contact with artificial matter and how to make them biocompatible.

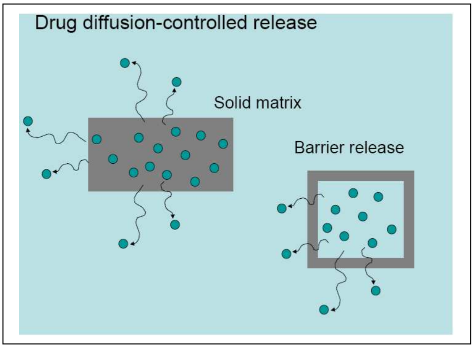
5. DRUG DELIVERY SYSTEMS

5.1. INTRODUCTION

The main problems associated with systemic drug administration are as follows:

1. the correct distribution of pharmaceuticals throughout the body,
2. the lack of drug specific affinity toward a pathological site,
3. the necessity to use a large total dose of a drug,
4. non-specific toxicity and other adverse side-effects.

The following points should be considered also before drug marketing: the method of administration (orally, injection, patches, implants and so on), inconvenience for injection, limited stability in solution of polymeric drugs and possibility of a patient's harm by medical errors. The following points shift the attention to the controlled drug delivery systems and new generation of such bodies – targeted drugs. When drug molecules are dispersed in polymer matrix they can move slowly to the vehicle border and are freed to the surroundings. It is the simplest method for building controlled drug delivery systems. The idea of it is shown in the picture below:



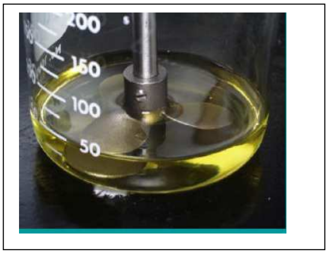
Sometimes, drug molecules are entrapped in a reservoir and have to pass an outer barrier to be released. These two systems deliver molecules in a diffusion controlled way. Hence, the idea of the zero-order drug delivery is granted.

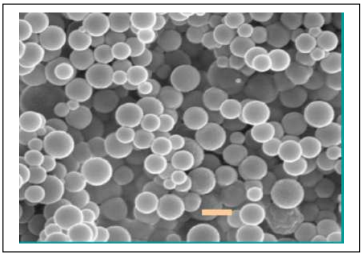
There are several types to control drug release. Some of them are described below.

5.2. DIFFUSION CONTROLLED RELEASE

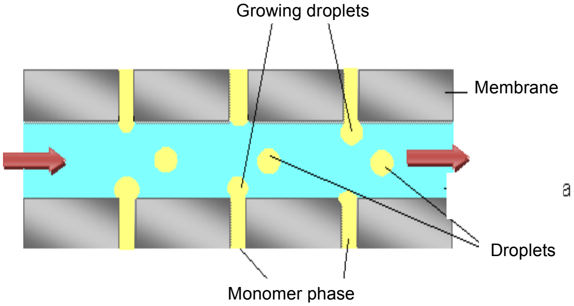
The representatives of them are shown below. They are easily modeled by the Fick equation and have well-defined release kinetics. The problems appear when large molecules (polymers) are intended for the delivery by such systems. Their diffusion is not sufficient and drugs concentration does not take the minimum effective level. Capsules or matrices for the diffusion controlled release are prepared from various materials: polymer spheres, liposomes, dendrimers, carbon nanostructures or inorganic particles.

The most popular way is by the rotor suspension of materials or by membrane emulsification. Both of them are shown below:





Suspension

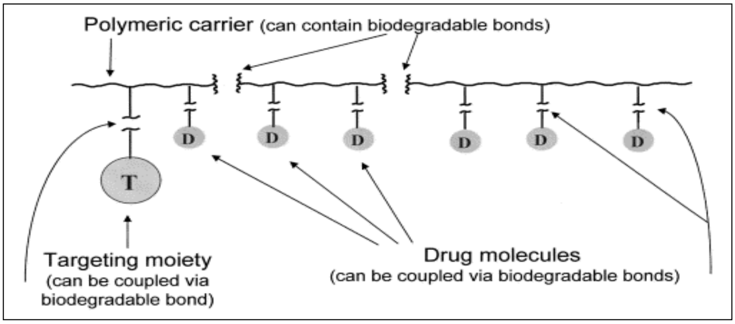


Membrane emulsification

5.3. CHEMICALLY ACTIVATED RELEASE

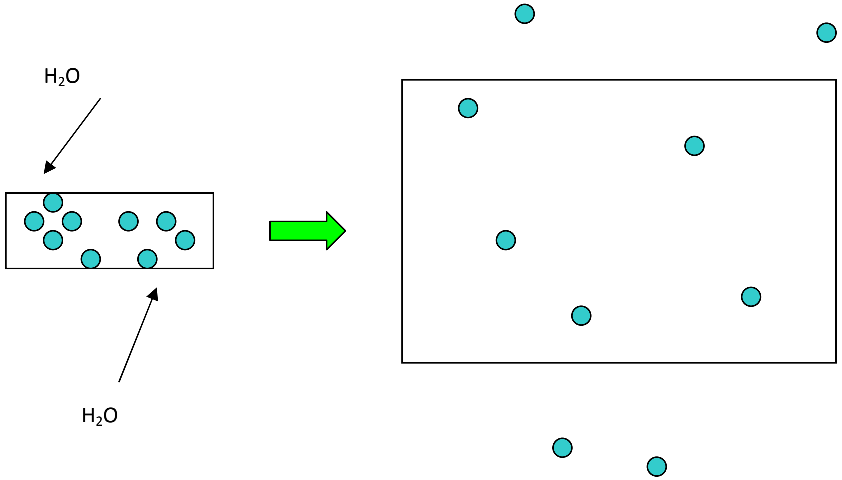
Several types of chemically activated materials can be classified as this group. The simplest is the eroding polymer matrix. There are two types of erosion, the surface one and the bulk one, but both are related to polymer degradation and freeing the drug molecules.

There is one more method for drug release related to the chemical reaction. It is shown schematically below. Usually, the hydrolysis of bonds bridging polymer with drugs allows them to move to surroundings.

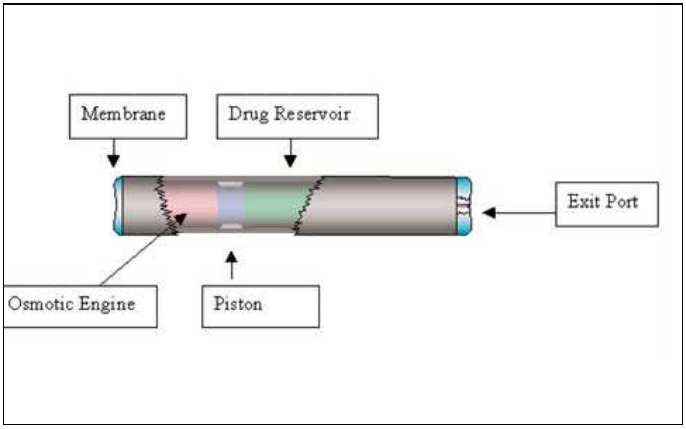


5.4. SOLVENT ACTIVATED SYSTEMS

This group includes swellable gels and osmotic systems. When the first swells, the distance among polymer chains gets larger and drug molecules do not meet the steric hindrances and can diffuse easily.



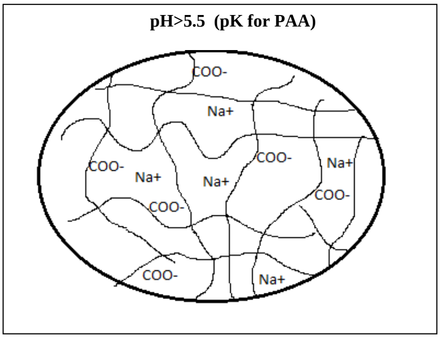
The second system is more complicated. It looks like an osmotic engine – a capsule containing hydrophilic polymer (usually poly(ethylene glycol)) that by adsorbing water swells and pushes out of the capsule the drug molecules. There are various configurations of such a system but in all cases the idea is the same: the drug is squeezed out of the capsule by the swelling gel. The example of DUROS system is shown below:



DUROS system

5.5. SMART SYSTEMS

This group includes these systems that can free drugs according to the specific stimuli: pH, temperature, ionic strength and so on. For example – **crosslinked poly(acrylic acid)** can swell and shrink at various pH levels. So, it can be used for the oral drug delivery to duodenum. The shrunk particles are moving thorough stomach (pH~2) and swell in the duodenum delivering drugs.



pH sensitive particles are usually prepared from polyelectrolytes.

When the drug delivering particles are armed with elements recognizing the ill-tissue, the whole system turns to drug targeting one. It is a ‘magic bullet’ that delivers the drug to the place where it is needed. There are many recognizing species among them, the most popular are: antibodies, hormones, lectins or other proteins, polysaccharides and low-molecular weight ligands. They are usually immobilized to the surface of a particle that is loaded with a drug.

In some cases, polymer particles carry nanomagnets and are located in the requested place by a strong magnetic field. Delivered by blood particles with nanomagnets (usually hydrated iron oxide) are stopped in an organ by the magnetic field and drug molecules are freed from them. Finally, when the magnetic filed is turned off, particles can go with blood stream.

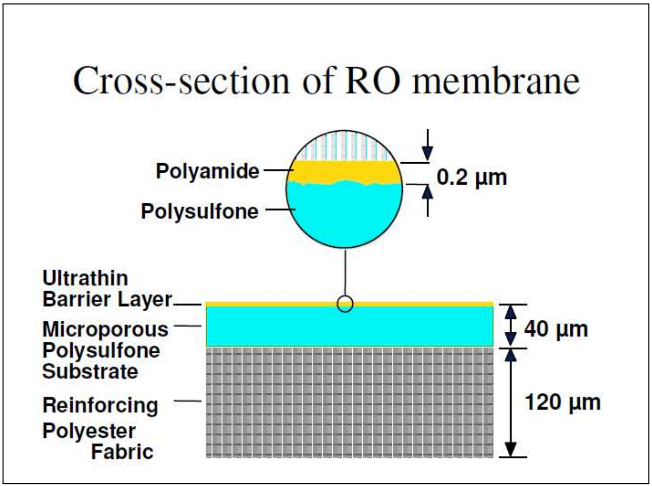
5.6. POLYMERS IN DRUG PREPARATION TECHNOLOGIES

In medicine, polymers are not used solely as construction materials. Sometimes, they participate in drug production. One of the best examples gives us the preparation of penicillin G. When the *Penicillium chrysogenum* cells are disintegrated to better extract penicillin G, the broth is filtrated. Permeate, it means the liquid passing through the microfiltration filter, is subjected to other purification protocols. One of them is the sorption in the chromatographic column. Of course, both the microfilter and the column packing are made of polymers.

The filtration membranes are made from various materials. Among them **polysulfone** and **polyethersulfone** are the most commonly used materials. Sometimes **polypropylene** or **polyamide** microfilters are applied. There are various materials used for chromatographic separation. However, in the separation of drugs a dominant place take **natural polymers**. It is the common belief that they do not contaminate the final product with dangerous species. In the next step of the antibiotic production, penicillin G is transferred to semi-synthetic penicillin. This step is also carried out on a polymer substrate. The hydrolysis of penicillin G and the synthesis of a new antibiotic are conducted in an enzymatic process by the immobilized penicillin acylase. In this case, a polymeric support should be selected carefully to allow using the enzyme for a long time. **Polyacrylamides** or modified **polyacrylates** are used as the enzyme supports. Sometimes, natural polymers: **polycarbohydrates,** like **cellulose**, **sepharose,** are applied to the high extent .

However, the most spectacular use of polymeric materials is their application in water purification. The phase of Samuel Taylor Coleridge, the English poet, is still valid. He said: ‘Water, water, every where, nor any drop to drink’. Really, the registered problem of water shortage will get deeper with the time. One of the reasonable ways to by-pass it is the use of sea water, the almost inexhaustible resource for water. However, that water should be treated before usage. Processes of membrane filtration combined with the reverse osmosis offer today water of high quality for a reasonable price. In the case of seawater desalination, the total cost is estimated from 0.50 to 0.80 USD per cubic meter.

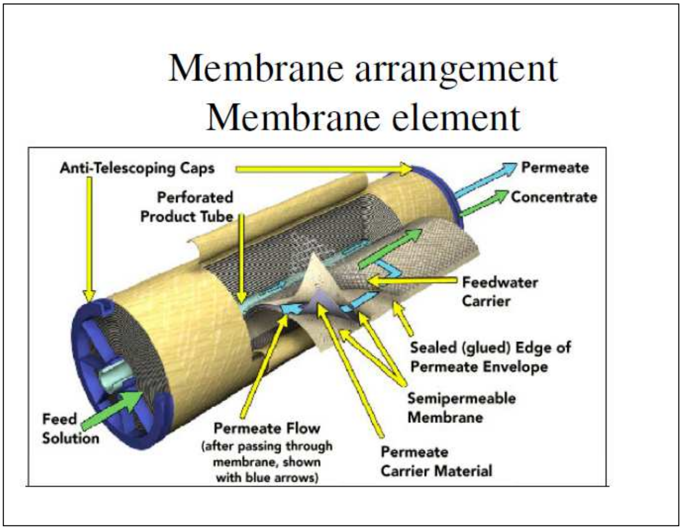
High quality water is needed for production of medicines, cleaning the production lines and as a medium for the dialysate preparation in the case of an artificial kidney or liver use. Today, membranes for the reverse osmosis processes are prepared from synthetic polymers. They are arranged in three layers systems with unwoven fabric as the basic support. The fabric (usually **polyesters**) is coated by a porous membrane (usually **polysulfone**) while the very thick separation layer is made of **polyamides**. The scheme of the composite membrane is shown below. The construction allows to apply 50-80 bar overpressure without damaging the RO membrane.



[courtesy of M.Busch, Dow chem.]

Scheme of RO membrane construction

Such a membrane is used in the spiral wound modules which construction is shown here:



Membrane arrangement
Membrane element

[courtesy of M. Busch, Dow chem.]

Scheme of RO module construction.

It is seen in the picture that the RO module consists of various pieces of ‘plastics’. Except the permeable membranes the following elements are used: spacers, seals, tubes, shells and connectors. All of them are in contact with water and all of them should show suitable properties towards this medium.

The presented pages give a short insight into the use of polymers in medicines only. It is not possible to prepare the more completed description as there are too many places where polymers can be applied. We are open for any ideas given by students about the more sophisticated use of polymer in biology and medicine.