Environmental management

Laboratory: Utilization of pollution and waste

Theory for experiment 25

Depolymerization of natural and synthetic polymers

dr Hanna Wilczura-Wachnik

University of Warsaw
Faculty of Chemistry
Division of Chemical Technology

Theoretical background

The word *polymer* means a large molecule (macromolecule) composed of repeating structural units called mers. These subunits are typically connected by covalent chemical bonds. Although the term polymer is sometimes taken to refer to plastics, it actually encompasses a large class comprising both natural and synthetic materials with a wide variety of properties.

Commonly the macromolecule is defined as the molecule with at least 2000 atoms. The number of repeating units (mers) in a given macromolecule is called a degree of polymerization. Degree of polymerization can be calculated according to the following relation:

$$\bar{P} = \frac{\bar{M}}{M_m}$$

where: $\bar{M}$ is polymer molecular weight and M_m is monomer molecular weight. The numerical value of degree of polymerization is considering as the limit dividing molecules on oligomers ($\bar{P} \leq 1000$) and polymers with $\bar{P} > 1000$.

Basically there are two types of macromolecules: synthetic polymers and biological polymers. As a synthetic polymers are classified those that do not exists in nature; they are man-made molecules. Biological polymers do exists in nature, but they can also be synthesized in the laboratory.

Polymers are studied mainly in the fields of the following polymer sciences: polymer chemistry and polymer physics.

Polymers play an essential and ubiquitous role in everyday human life because of the extraordinary range of properties. From familiar synthetic plastics and elastomers to natural biopolymers such as nucleic acids and proteins that are essential for life. As a natural polymeric materials are classified also shellac, amber, cotton and natural rubber which have been used for centuries. To natural polymers belong polysaccharides and cellulose which is the main constituent of wood and paper. The list of synthetic polymers is longer. It contains the following: synthetic rubber, neoprene, nylon, PVC, polystyrene, polyethylene, PVB, silicone, polypropylene, polyacrylonitrile and other.

Synthetic polymer chains commonly consist mainly of carbon atoms. The simple example of this macromolecule is polyethylene obtaining in ethylene polymerization (Figure 1). A repeating unit in polyethylene is based on ethylene monomer.
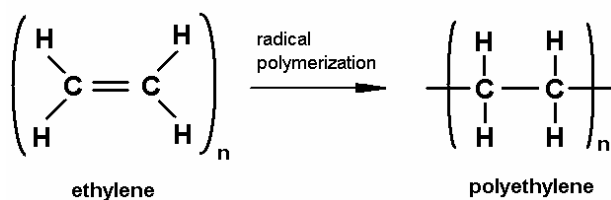

Figure 1. The polymerization of ethylene in to poly(ethylene).

Examples of repeating unit s of other polymer chains are shown in Figure 2.

ethylene $\quad nCH_2=CH_2 \longrightarrow -[CH_2-CH_2]_n^-$

propylene $\quad nCH_2=CH \longrightarrow -[CH_2-CH]_n^-$
$\qquad\qquad\qquad\quad |\qquad\qquad\quad |$
$\qquad\qquad\qquad CH_3 \qquad\qquad CH_3$

iso-butene $\qquad\quad CH_3 \qquad\qquad CH_3$
$\qquad\qquad\qquad\quad |\qquad\qquad\quad |$
$\qquad\qquad nCH_2=C \longrightarrow -[CH_2-C]_n^-$
$\qquad\qquad\qquad\quad |\qquad\qquad\quad |$
$\qquad\qquad\qquad CH_3 \qquad\qquad CH_3$

styrene $\quad nCH_2=CH \longrightarrow -[CH_2-CH]_n^-$
$\qquad\qquad\qquad\quad |\qquad\qquad\quad |$
$\qquad\qquad\qquad C_6H_5 \qquad\qquad C_6H_5$

butadiene $\quad nCH_2=CH-CH=CH_2 \longrightarrow -[CH_2-CH=CH-CH_2]_n^-$

isoprene $\quad nCH_2=CH-C=CH_2 \longrightarrow -[CH_2-CH=C-CH_2]_n^-$
$\qquad\qquad\qquad\qquad |\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\quad CH_3 \qquad\qquad\qquad CH_3$

vinyl chloride $\quad nCH_2=CH \longrightarrow -[CH_2-CH]_n^-$
$\qquad\qquad\qquad\qquad |\qquad\qquad\quad |$
$\qquad\qquad\qquad\quad Cl \qquad\qquad\quad Cl$

tetrafluoroethylene $\quad nCF_2=CF_2 \longrightarrow -[CF_2-CF_2]_n^-$

acrylic acid esters $\quad nCH_2=CH \longrightarrow -[CH_2-CH]_n^-$
$\qquad\qquad\qquad\qquad\quad |\qquad\qquad\quad |$
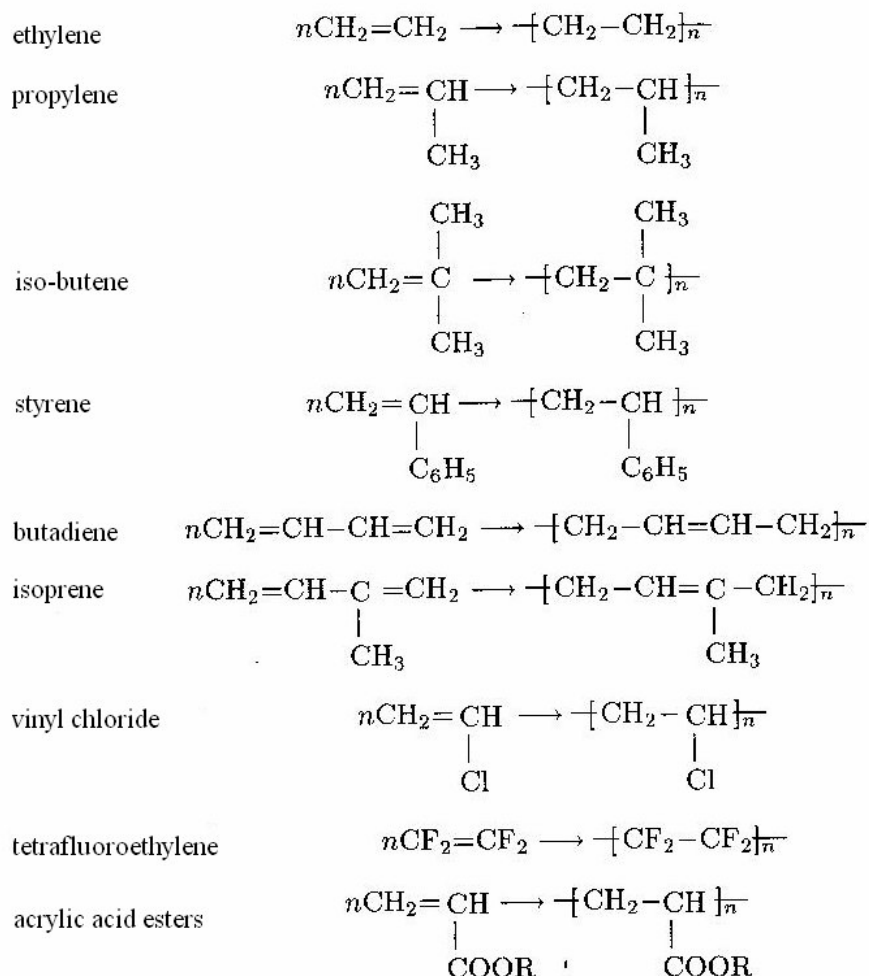$\qquad\qquad\qquad\quad COOR \qquad\quad COOR$

Figure 2. The repeating unit of some polymer chains.

Taking into account the polymer chain structure polymers are classified into two structural categories: linear polymers (a single backbone without branches) and branched polymers. Linear polymer chain is in the form showing on Figure 3 where A is the basic structural unit, x is the degree of polymerization and A' and A" are called the end groups.

$$A'-A-A\cdots A''$$

Figure 3. Linear polymers form

Branched polymer chain is in the form presented on Figure 4. Branched polymer chain is constituent with a main chain in which are present one or more substituent side chains or branches.

3

$$A'-A-A-A-------A-A-A''$$
$$\qquad\ |\qquad\qquad\qquad\qquad |$$
$$\qquad\ A\qquad\qquad\qquad\qquad A$$
$$\qquad\ |\qquad\qquad\qquad\qquad |$$
$$\qquad\ A\qquad\qquad\qquad\qquad A$$
$$\qquad\ |\qquad\qquad\qquad\qquad |$$
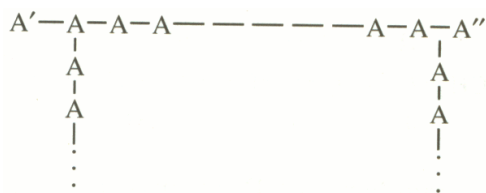$$\qquad\ \vdots\qquad\qquad\qquad\qquad \vdots$$

Figure 4. Branched polymers form

To branched type of polymers belong star, comb, brush and dendronized polymers as well dendrimers. The most well-known branched polymers are shown on Figure 5. Examples are star-shaped and comb-shaped polystyrene.
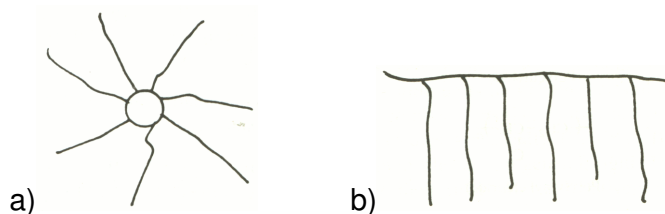
a)   b)

Figure 5. a) the star-shaped polymer, b) the comb-shaped polymer.

In terms of repeating units (mers) polymers are classified into two types: homopolymers and copolymers. A homopolymer is one in which only one monomer constitutes the repeating units. The examples of homopolymer are: polystyrene, polyethylene, polyvinyl chloride.
A copolymer consists of two or more different monomers as repeating units, such as the diblock copolymer:

$$A-A-A\cdots A-B-B\cdots B$$

and the random or static copolymer:

$$A-B-B-A-A-B-B-B-A-B-A-B-A-A\cdots$$
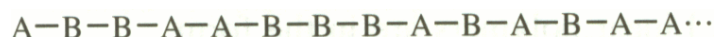
An example is the polystyrene-poly(methyl methacrylate) copolymer.

In terms of stereoregularity synthetic polymers may have trans and gauche forms, similar to some small molecules (e.g., ethane). Because of the steric position of substituents along the chain, the heterogeneity of the chain structure may be classified into atactic, isotactic and syndiotactic forms. Examples of these forms are presented in Figure 6.

$$\sim CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \circledR}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \circledR}{|}}{C}}-CH_2-\overset{\overset{\displaystyle \circledR}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \circledR}{|}}{C}}\sim$$
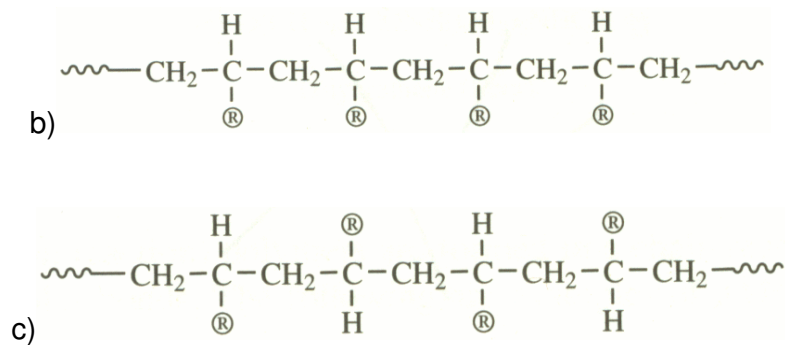
a)

b)

c)
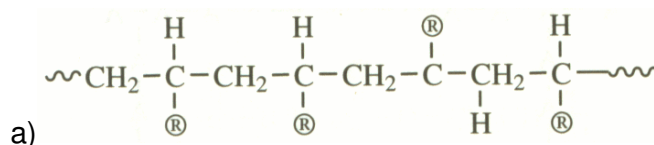
Figure 6. The heterogeneity of the chain structure: a) atactic polymer - no regularity of R groups; b) isotactic polymer – regularity of R groups; c) syndiotactic polymer – regularity involves trans and gauche forms in a uniform manner.
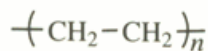
Synthetic polymers that are commercially manufactured in the quantity of billions of kilos may be classified in three categories plastics (including thermoplastics), synthetic fibers and synthetic rubber.

To plastics are classified polymers which include thermosetting resins (e.g., urea resins, polyeters, epoxides as well as thermoplastic resins (e.g., low-density as well as high-density polyethylene, polystyrene, and polypropylene.

As synthetic fibers, polymers which include cellulosic (such as rayonand acetate) and nonlellulose (such as polyester and nylon;

To the last category, synthetic rubber belong the following examples of polymer: styrene-butadiene copolymer, polybutadiene, ethylene-propylene copolymer).
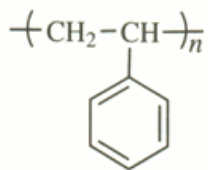
In 1929 Carothers classified synthetic polymers into two basic classes according to the method of preparation: addition polymers and condensation polymers. Addition polymers (also called chain reaction polymers) are formed in a chain reaction of monomers which have double bonds. On Figure 7 examples of addition polymers are presented
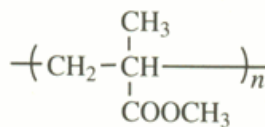
$$+CH_2-CH_2\frac{}{n}$$

Polyethylene

$$+CH_2-CH\frac{}{n}$$
$$\quad\quad\quad |$$
$$\quad\quad\quad Cl$$

Poly(vinyl chloride)

$$+CH_2-CH\frac{}{n}$$

Polystyrene

$$\quad\quad\quad CH_3$$
$$\quad\quad\quad |$$
$$+CH_2-CH\longrightarrow\frac{}{n}$$
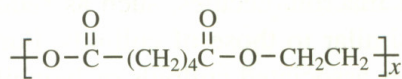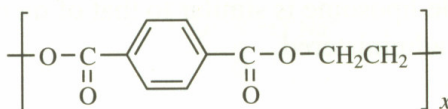$$\quad\quad\quad |$$
$$\quad\quad\quad COOCH_3$$
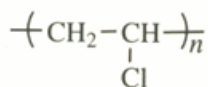
Poly(methyl methacrylate)

Figure 7. Examples of addition polymers.

Condensation polymers (called stepwise reaction polymers) are the products of the reaction occurring between two polyfunctional molecules by eliminating a small molecule, for example, water. Examples of condensation polymers are given in Figure 8.

$$\left[O-\underset{O}{\underset{\|}{C}}-\underset{}{\bigcirc}-\underset{O}{\underset{\|}{C}}-O-CH_2CH_2\right]_x$$

$$HO\left[(CH_2)_xCOO\right]_y$$

$$\left[O-\underset{O}{\underset{\|}{C}}-(CH_2)_4\underset{O}{\underset{\|}{C}}-O-CH_2CH_2\right]_x$$

Polyester (fiber)

$$\left[O(CH_2)_6OCONH(CH_2)_6NHCO\right]_x$$

Polyurethane (fiber)

$$\left[NH(CH_2)_6NHCONH(CH_2)_6NHCO\right]_x$$
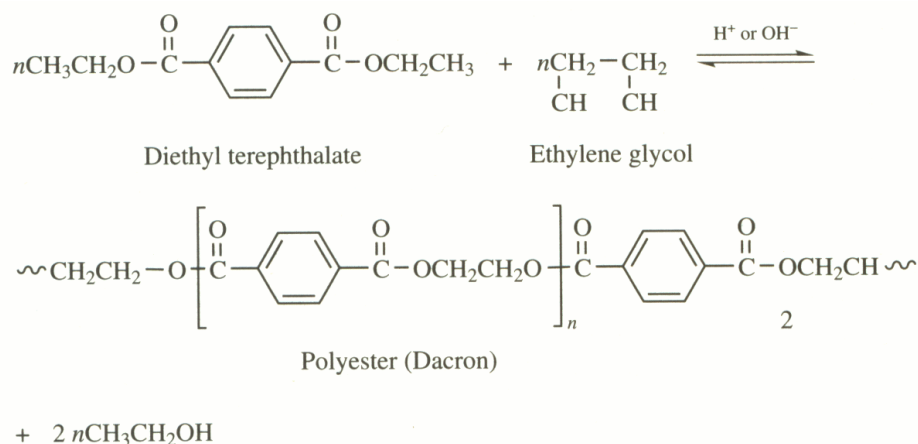
Polyurea

Figure 8. Examples of condensation polymers.

Polymerization is the name of reaction of combining a many monomer molecules into a covalently bonded chain without presence low molecular weight products like water. Such a continuously linked polymer chain consists mainly of carbon atoms. The simplest example of synthetic polymers is polyethylene. The repeating unit in this polymer is based on ethylene monomer. In polymer backbones except carbon atoms also oxygen ones are present, for example in polyethylene glycol.

Commonly polymerization reactions are divided on chain polymerization and stepwise polymerization. In a chain polymerization are present the steps: initiation, chain propagation and termination. Contrary, in stepwise polymerization, there is no initiation, propagation or termination.

Stepwise polymerization
The polymerization depends entirely on the individual reactions of the functional groups of monomers. The four types of stepwise polymerization are the synthesis of polyester, polyamide, polyurethane and polycarbonate. The examples of stepwise polymerization are given below:

1. Polyester synthesis– by the direct reaction of a diacid and a diol at high temperatures. The example given below is the synthesis of Dacron:


Diethyl terephthalate   Ethylene glycol

Polyester (Dacron)

$+ \quad 2\,nCH_3CH_2OH$

2. Polyamide synthesis – using two difunctional monomers. As example is the synthesis of 66 nylon:

Adipic acid   Hexamethyl diamine

Polyhexamethylene adipamide

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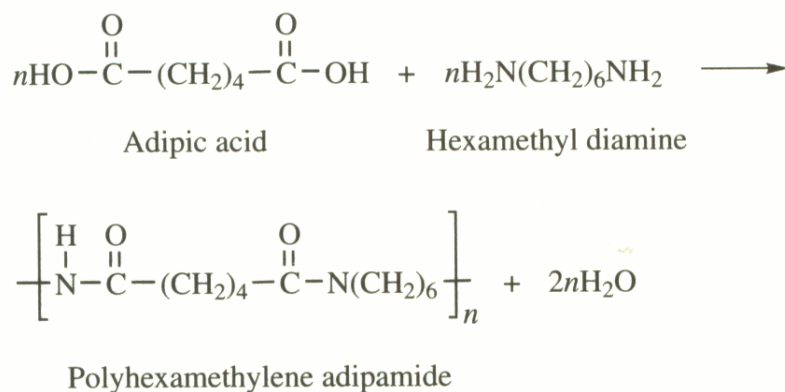
3. Polyurethanes (polycarbamates) synthesis – by the reaction of a diisocyanate with a diol. Reactions are usually carried out in solutions. The example of polyurethane synthesis is the following:

Succinic anhydride   Ethylene glycol

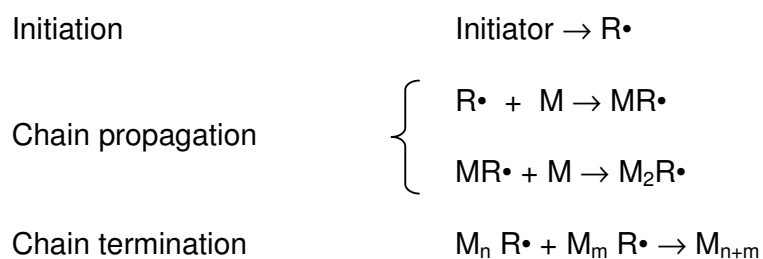A polyester (a prepolymer)

Stannous octanoate

Polyurethane
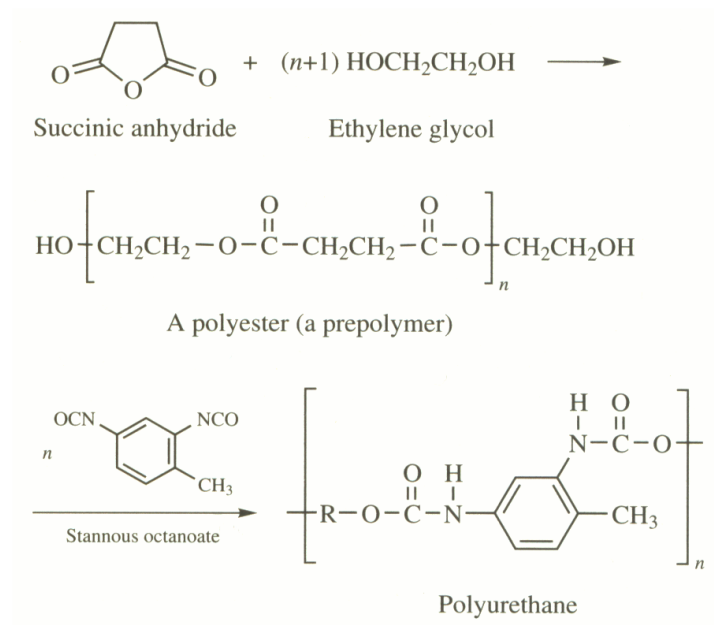
4. Polycarbonate synthesis – by the reaction of the simplest diacidchloride, phosgene, with bisphenol A in the presence of a base. An example of reaction is given below:

Bisphenol A   Phosgene

Pyridine
20–30 °C
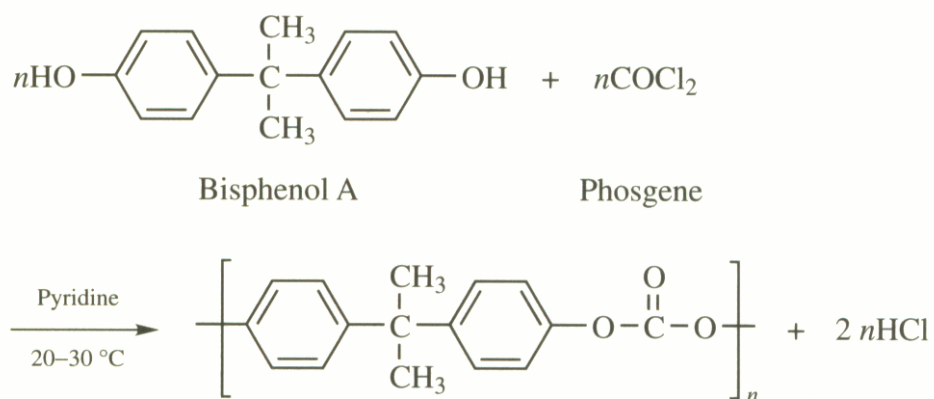
The chain polymerization depending on the mechanism of the reactions is classified as: radical polymerization and ionic polymerization.
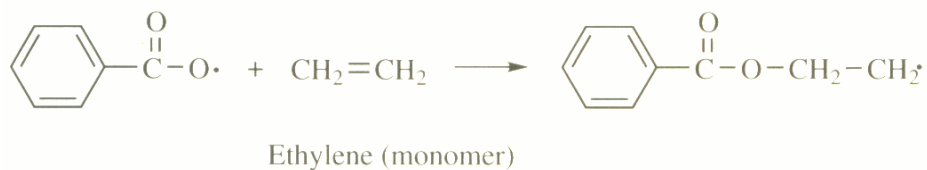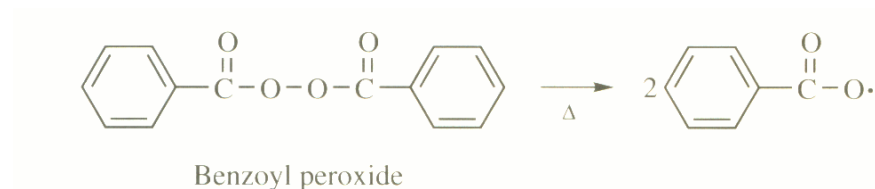
Radical polymerization

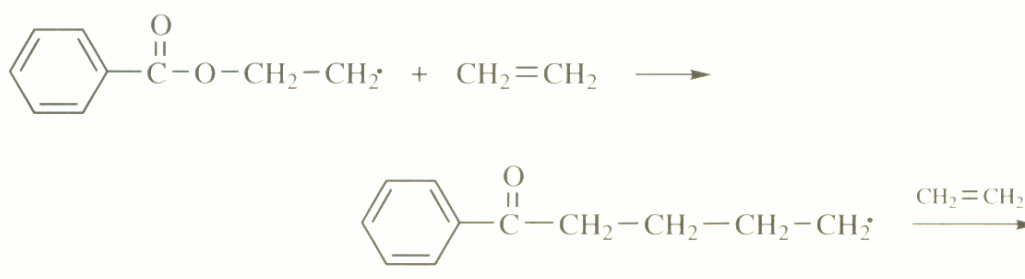The reaction scheme for free-radical polymerization can be expressed as follows:

Initiation   Initiator → R•

Chain propagation
$$\begin{cases} R\bullet + M \rightarrow MR\bullet \\ MR\bullet + M \rightarrow M_2R\bullet \end{cases}$$

Chain termination $M_n R\bullet + M_m R\bullet \rightarrow M_{n+m}$

where M represents a monomer molecule and R• a free radical produced in the initial step.
An example of free-radical polymerization is the synthesis of polyethylene.

Initiation:

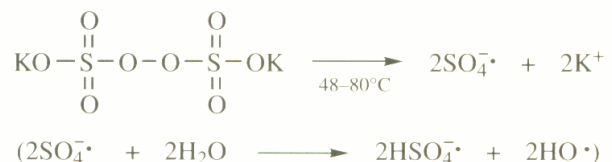Benzoyl peroxide

Ethylene (monomer)
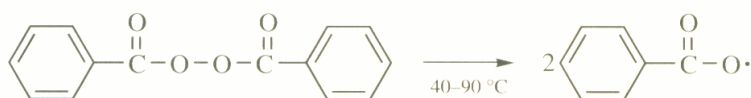
Propagation:

Termination:

Most of the initiators used in the free-radical polymerization are aliphatic azo compounds and peroxides such as the following:

Azobisisobutyronitrile (AIBN)

Potassium persulfate

Benzoyl peroxide (lucidol)

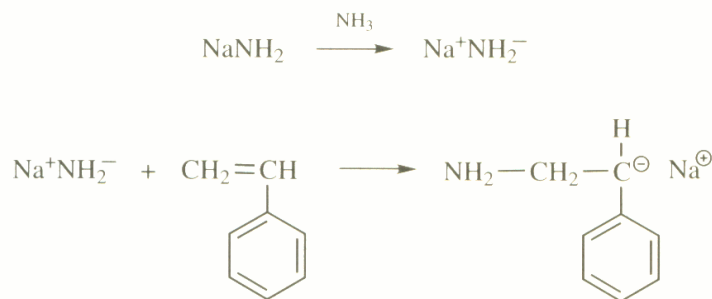Methods of free-radical polymerization are the following:
1. bulk polymerization – synthesis without solvent
2. solution polymerization – synthesis with (inert) solvent
3. precipitation polymerization – using solvent (such as methanol) to precipitate out the polymer
4. suspension polymerization – adding an initiator to the suspension in aqueous solution
5. emulsion polymerization – adding an initiator (such as potassium persulfate) to the emulsion of water insoluble monomers (such as styrene) in aqueous soap solution.
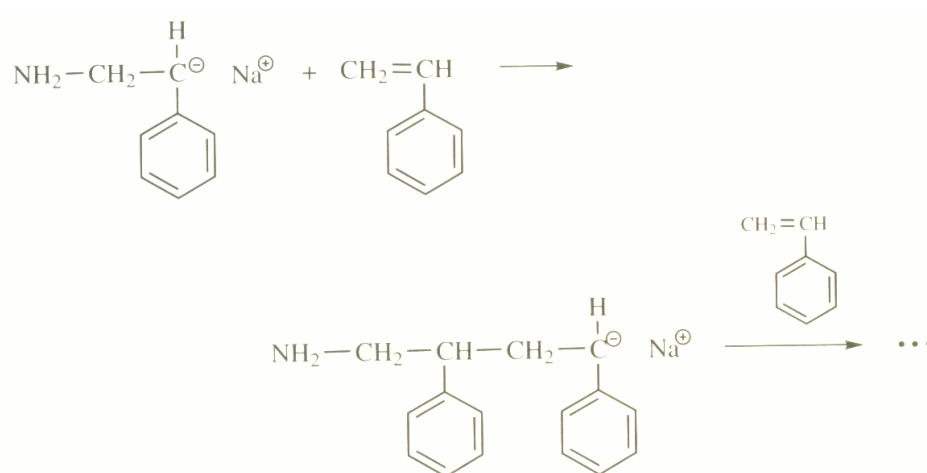
Ionic polymerization

There are two types of ionic polymerization: anionic and cationic. The formers involve carbanons C^- and the later involves cabonium C^+ ions. Catalysts and cocatalysts are needed in ionic polymerization.

In anionic polymerization as catalysts are used: alkali metals, alkali metal amides, alkoxides, and cyanides. The cocatalysts usually are: organic solvents, such as heptane. Below the synthesis of polystyrene as an example of anionic polymerization is given.
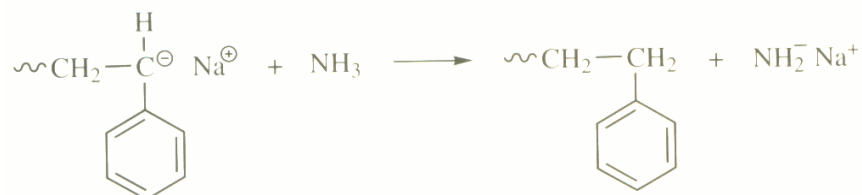
Initiation:

$$NaNH_2 \xrightarrow{NH_3} Na^+NH_2^-$$

$$Na^+NH_2^- + CH_2{=}CH\text{-}(C_6H_5) \longrightarrow NH_2\text{-}CH_2\text{-}\overset{H}{\underset{(C_6H_5)}{C}}{}^{\ominus}\ Na^{\oplus}$$

Propagation:

$$NH_2\text{-}CH_2\text{-}\overset{H}{\underset{(C_6H_5)}{C}}{}^{\ominus}\ Na^{\oplus} + CH_2{=}CH\text{-}(C_6H_5) \longrightarrow$$

$$NH_2\text{-}CH_2\text{-}\underset{(C_6H_5)}{CH}\text{-}CH_2\text{-}\overset{H}{\underset{(C_6H_5)}{C}}{}^{\ominus}\ Na^{\oplus} \xrightarrow{CH_2{=}CH\text{-}(C_6H_5)} \cdots$$

Termination:

$$\sim CH_2\text{-}\overset{H}{\underset{(C_6H_5)}{C}}{}^{\ominus}\ Na^{\oplus} + NH_3 \longrightarrow \sim CH_2\text{-}CH_2\text{-}(C_6H_5) + NH_2^-\ Na^+$$
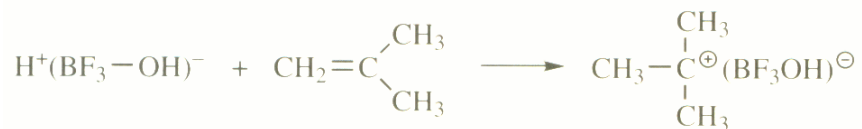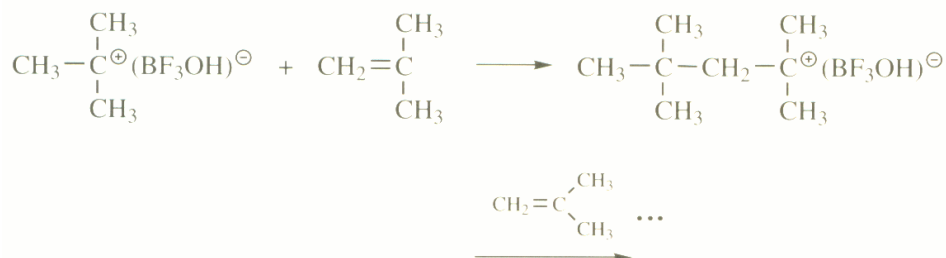
Depending on catalysts the chain growth in anionic polymerization can go through two, three four or more directions not only in one direction as shown in the above example.

In cationic polymerization as catalysts are used Lewis acids and Friedel-Crafts catalysts such as BF_3, $AlCl_3$, and $SnCl_4$ and strong acids such as H_2SO_4. The cocatalysts are needed also. Usually there are: water and isobutene. Below the synthesis of polyisobutene as an example of cationic polymerization is given.

Initiation:

$$H_2O + BF_3 \longrightarrow H^+(BF_3OH)^-$$

$$H^+(BF_3-OH)^- + CH_2=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^\oplus}}(BF_3OH)^\ominus$$

Propagation:

$$CH_3-\overset{CH_3}{\underset{CH_3}{C^\oplus}}(BF_3OH)^\ominus + CH_2=\overset{CH_3}{\underset{CH_3}{C}} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C^\oplus}}(BF_3OH)^\ominus$$

$$CH_2=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} \quad \dots$$

$$\longrightarrow$$

Termination:

$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^\oplus}}(BF_3OH)^\ominus \longrightarrow \sim CH_2-\overset{CH_3}{C}=CH_2 + H^+(BF_3OH)^-$$

Polymer degradation and depolymerization

Polymer degradation is mainly caused by chemical bond scission reactions in macromolecules. It does not appear meaningful therefore, to distinguish between different modes of polymer degradation. For practical reason, however, it is useful to subdivide the polymer degradation according to its various modes of initiation. There are: thermal, mechanical, photochemical, radiation chemical, biological and chemical degradation of polymeric materials. Modes of polymer degradation in details are described in theoretical background for experiment 20 (www.   ).

The peculiar process category causing changes in macromolecules and plastics is depolimerization (is the process converting polymer into a monomer, mixture of monomers or oligomer). According to definition, depolimeryzation it is a process of polymer chain decomposition till monomers or oligomers which undergo at high temperature or hydrolytic agents. So, there are distinguishing thermal and chemical depolymerization suitable.

Commonly, as thermal depolymerization is classified chemical reaction in which polymer chain converses to monomer at high temperature. The monomer yield in this reaction is satisfied for a few polymers only. As an example can be given produced in commercial scale methyl polymethacrylate (PMMA), polystyrene (PS) as well as methacrylate resins (ethyl- and buthyl polymethacrylate) produced in smaller scale. Depolymerization occurs during thermal decomposition of poly (dimethylsiloxanes) too. There are formed cyclic oligomers, mainly hexamethyltrisiloxane. Such oligomers are used as monomers in polysiloxanes synthesis. It is necessary to underline that during heating bulk of polymers degradates instead depolymerization.

Common regularity is that thermal depolymerization undergoes additive polymers (yields in addition polymerization). Contrary, polycondensation polymers don't depolymerize thermally.

Below are given example of thermal depolymerization of some polymers:

- thermal depolymerization of polystyrene (yield ~70%) undergoes according to relation:
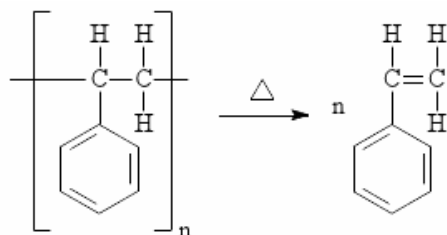
- thermal deplymerization of methyl polymethacrylate (yield 90%) undergoes according to relation:
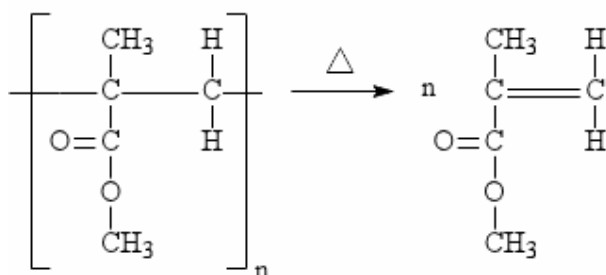
Chemical depolymerization point is that chemical compounds containing active hydrogen atoms react with polar groups in the main chains of polycondensate (condensation polymer). Usually, this reaction goes as acid or basic hydrolysis of amide, ester or urethane bonds.

Poly(ethylene terephthalate) PETP is the polymer mainly treated with the chemical depolymerization. Except it, depolymerization is possible for polycarbonates and polyurethanes (mostly polyurethane foams).

PETP chemical depolymerization goes as a hydrolysis at acidic medium according to relation:
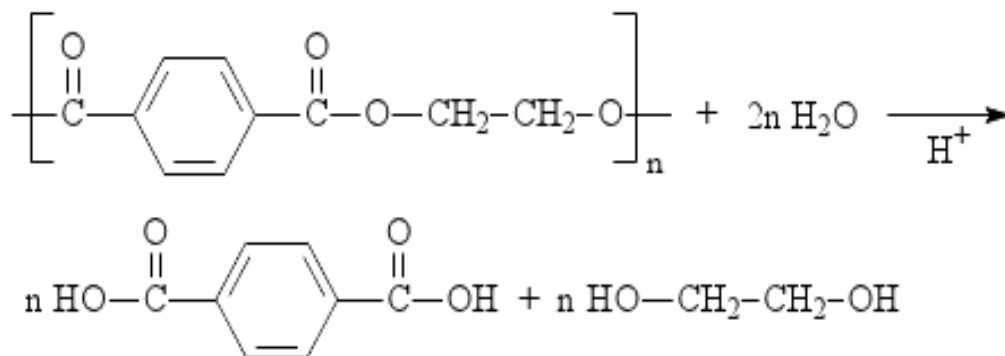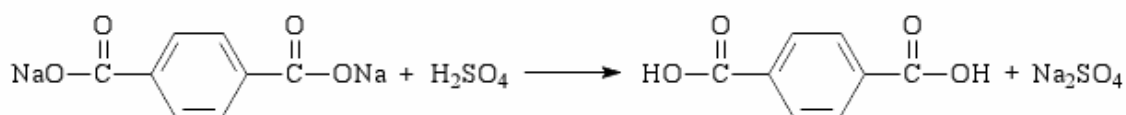
The main reaction products are monomers: terephtalic acid and ethylene glycol.

In case of PETP hydrolysis in basic medium the reaction products are: ethylene glycol and sodium terephthalate according to relation:
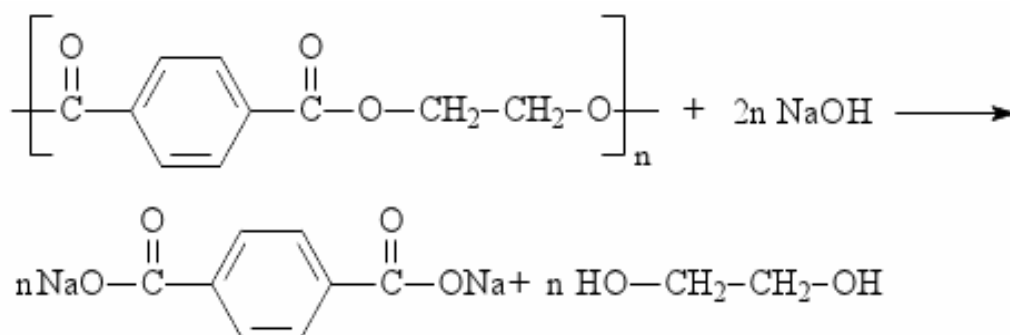

and next treating sodium terephthalate with sulphyric acid VI as a product a therephthalate acid is obtaining:

:

Another option of PETP depolymerization is alcoholysis (for example methanolysis – methyl alcohol action). Dimethyl terephthalate (DMT) is getting as the product. DMT is used as a monomer in PETP synthesis. The PETP methanolysis is going according to relation:
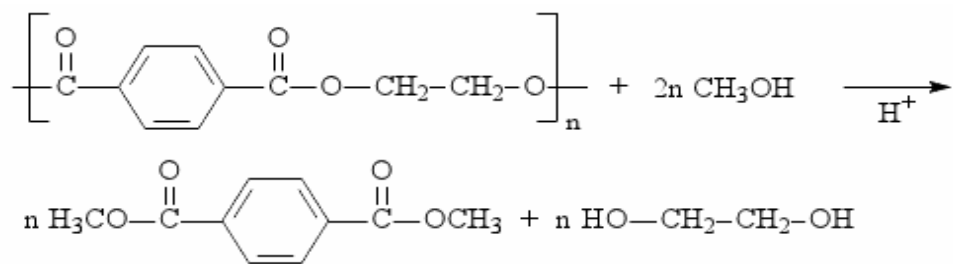
Except given above there are possible depolymerizations under different chemical reagents as for example autooxidants such as L-ascorbic acid, iron (II) sulfate, enzymes (for example cysteine).

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