University of Warsaw Faculty of Chemistry

Chemical Technology Division

Fundamentals of Chemical Technology and Chemicals Management Laboratory

Combustion and thermal degradation of polymers

Theoretical background for experiment 20

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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.
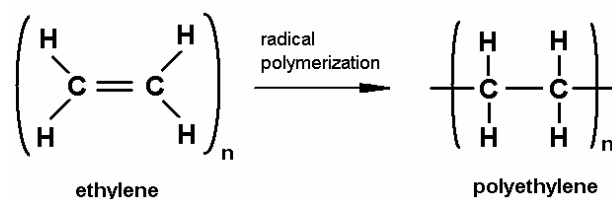

Figure 1. The polymerization of ethylene in to poly(ethylene).

Examples of repeating unit s of other polymer chains are shown in Figure 2. The list given below doesn't contain the full list of mers in whole existing polymers.

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

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

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

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

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

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

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

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

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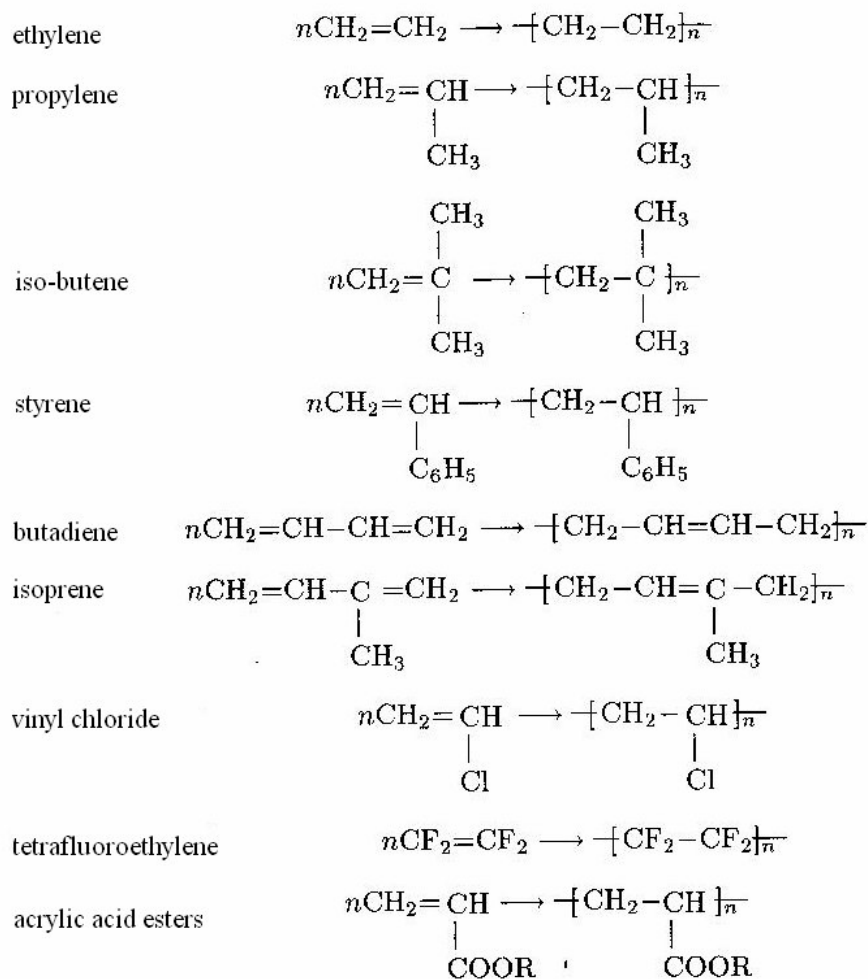$\quad\quad\quad\quad\quad\quad\quad\quad COOR \quad\quad\quad\quad COOR$

Figure 2. The repeating unit of some polymer chains.

There are in the literature different classification of synthetic polymers. The most common are presented in this material.

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 in 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 in Figure 4. Branched polymer chain is constituent with a main chain in which are present one or more substituent side chains or branches.
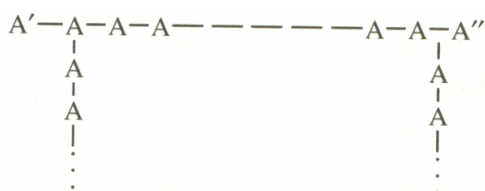
$$A'-A-A-A-\;-\;-\;-\;-A-A-A''$$

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 in Figure 5. Examples of this type polymers are star-shaped and comb-shaped polystyrene.
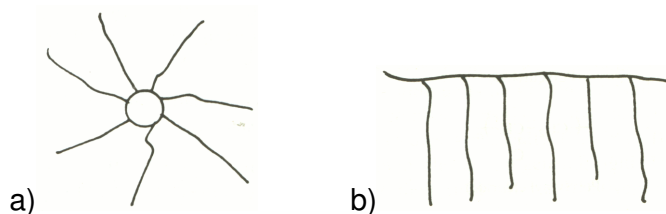

a)   b)

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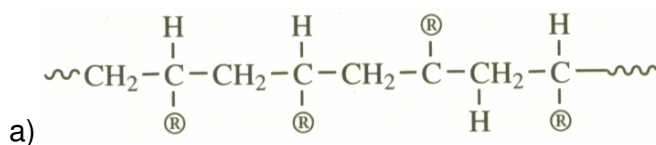
$$A-A-A\cdots A-B-B\cdots B$$

and the random or static copolymer:

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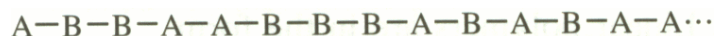
An example is the polystyrene-poly(methyl methacrylate) copolymer.

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.
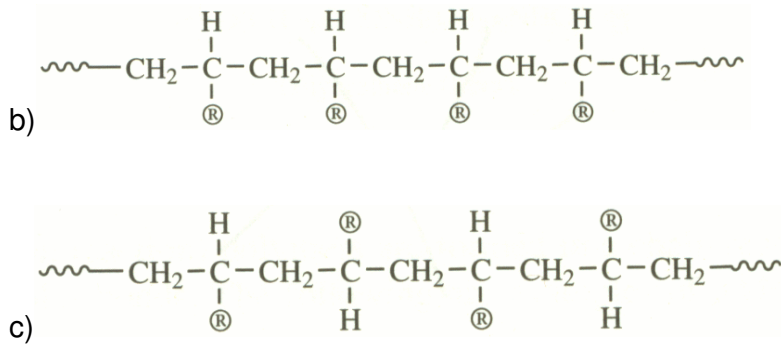

a)

b)

$$\text{\textasciitilde\textasciitilde} CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2 \text{\textasciitilde\textasciitilde}$$

c)

$$\text{\textasciitilde\textasciitilde} CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{\textcircled{R}}{|}}{C}}-CH_2-\underset{\underset{\textcircled{R}}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{\textcircled{R}}{|}}{C}}-CH_2 \text{\textasciitilde\textasciitilde}$$

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 the large industrial scale may be classified in three categories: plastics (including thermoplastics), synthetic fibers and synthetic rubbers.

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

As synthetic fibers, polymers which include cellulosics (such as rayon and acetate) and noncellulose (such as polyester and nylon).

To the last category, synthetic rubber belongs 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. The examples of addition polymers in Figure 7 are presented.

$$+CH_2-CH_2\overline{)}_n$$

Polyethylene

$$+CH_2-\underset{\underset{Cl}{|}}{CH}\overline{)}_n$$

Poly(vinyl chloride)

$$+CH_2-CH\overline{)}_n$$

Polystyrene

$$+CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}}\overline{})_n$$
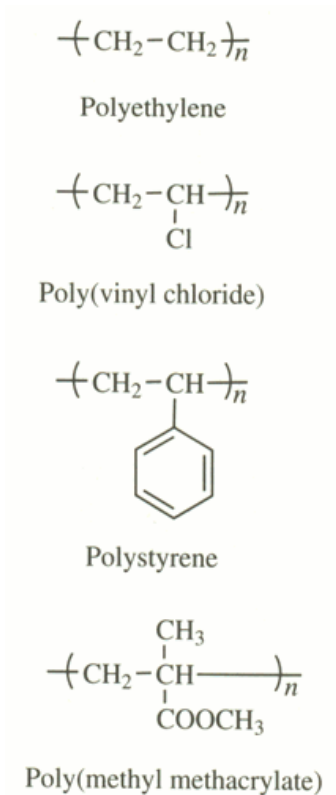
Poly(methyl methacrylate)

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.

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

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

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

Polyester (fiber)

$$+O(CH_2)_6OCONH(CH_2)_6NHCO\,]_x$$

Polyurethane (fiber)

$$+NH(CH_2)_6NHCONH(CH_2)_6NHCO\,]_x$$

Polyurea
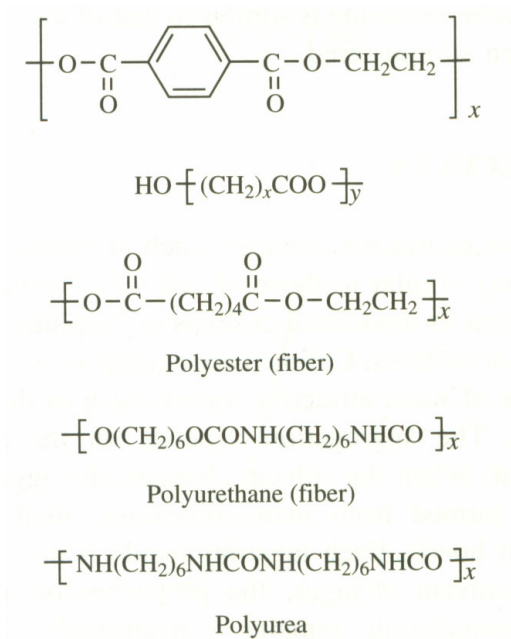
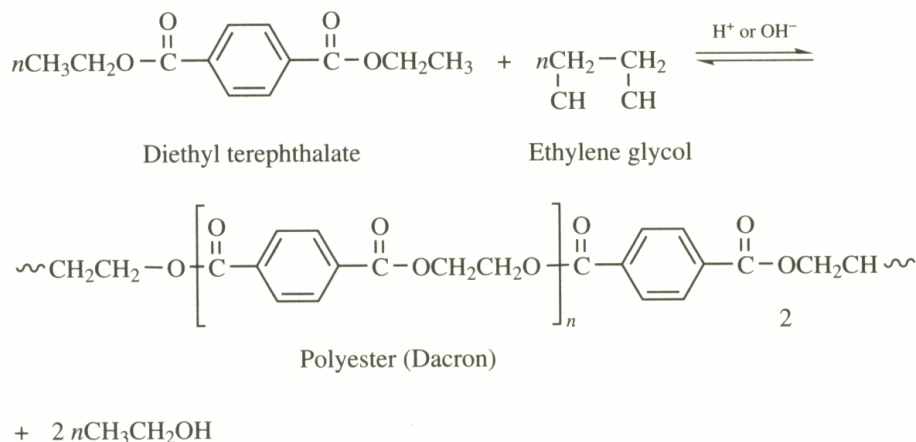Figure 8. Examples of condensation polymers.

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. As it was mentioned previously 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 three steps: initiation, chain propagation and termination. Contrary, in stepwise polymerization, there is no initiation, propagation or termination.
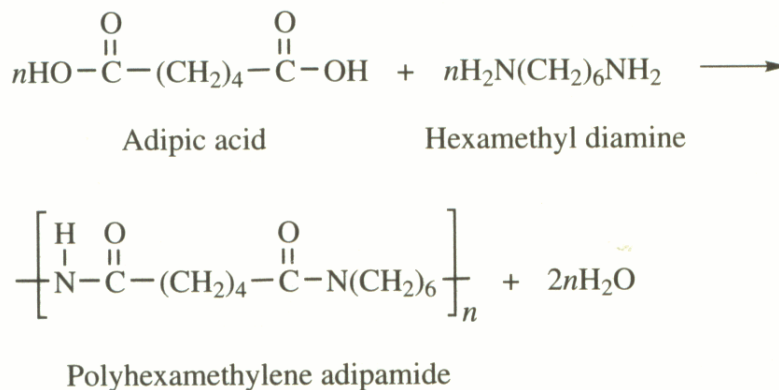
Stepwise polymerization

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:

$$n\text{CH}_3\text{CH}_2\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\underset{}{\bigcirc}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OCH}_2\text{CH}_3 \quad + \quad n\text{CH}_2-\text{CH}_2 \underset{\text{CH} \quad \text{CH}}{} \quad \overset{\text{H}^+ \text{ or OH}^-}{\rightleftharpoons}$$

Diethyl terephthalate   Ethylene glycol

$$\sim\sim\text{CH}_2\text{CH}_2-\text{O}\left[\overset{\overset{\text{O}}{\|}}{\text{C}}-\underset{}{\bigcirc}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OCH}_2\text{CH}_2\text{O}\right]_n\overset{\overset{\text{O}}{\|}}{\text{C}}-\underset{}{\bigcirc}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OCH}_2\text{CH}\sim\sim$$
                                                                                2

Polyester (Dacron)

+ $2\,n\text{CH}_3\text{CH}_2\text{OH}$

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

$$n\text{HO}-\overset{\overset{\text{O}}{\|}}{\text{C}}-(\text{CH}_2)_4-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OH} \quad + \quad n\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2 \quad \longrightarrow$$

Adipic acid   Hexamethyl diamine

$$\left[\overset{\overset{\text{H}}{|}}{\text{N}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-(\text{CH}_2)_4-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{N}(\text{CH}_2)_6\right]_n \quad + \quad 2n\text{H}_2\text{O}$$

Polyhexamethylene adipamide

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)

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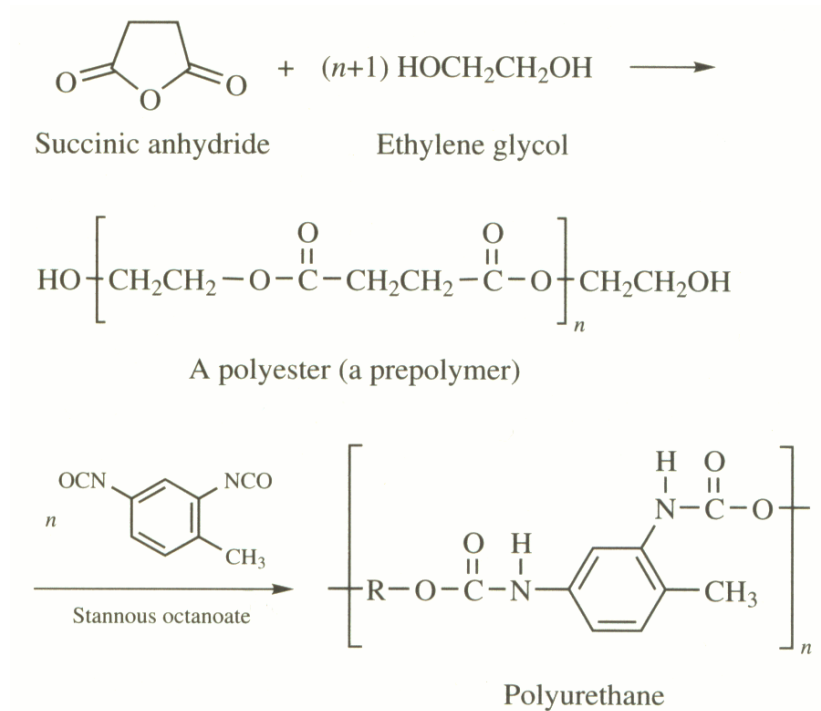
4. Polycarbonate synthesis – by the reaction of the simplest diacidchloride, phosgene, with bisphenol A in the presence of a base. An example of reaction is given below:
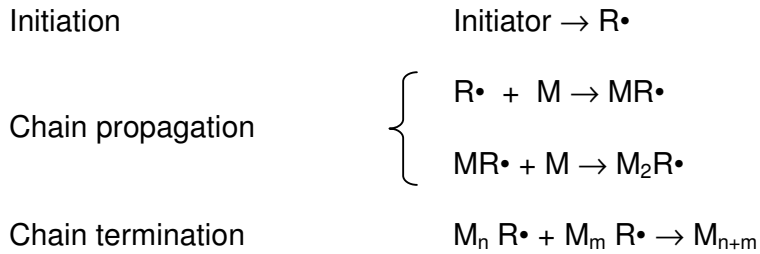

Bisphenol A   Phosgene

Pyridine

20–30 °C

+ $2\,n$HCl
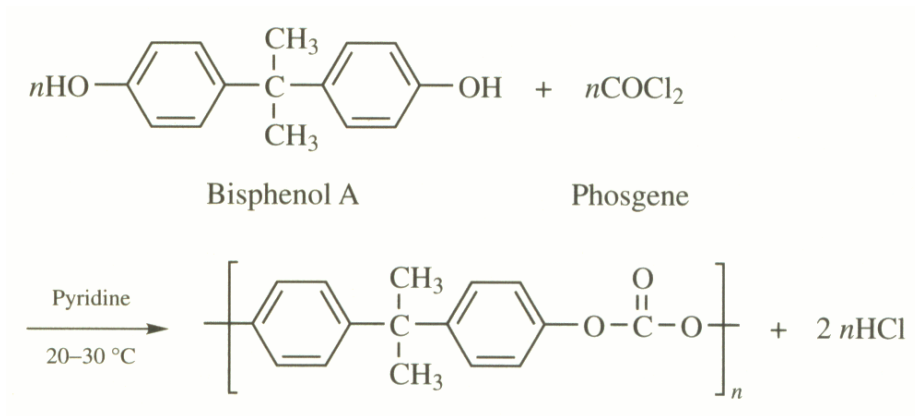
The chain polymerization depending on the mechanism of the reactions is classified as: radical polymerization and ionic polymerization.

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

Initiation   Initiator $\rightarrow$ R•

$$R• + M \rightarrow MR•$$
Chain propagation
$$MR• + M \rightarrow M_2R•$$

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

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. The reactions are presented below.

Initiation:
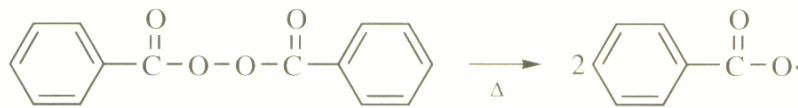
Benzoyl peroxide
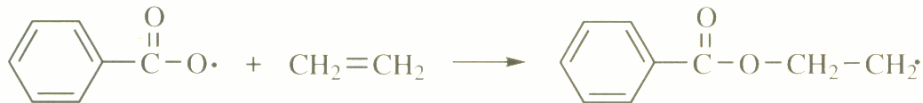
Ethylene (monomer)

Propagation:

Termination:

$$2R\text{\textasciitilde}CH_2-CH_2^{\cdot} \longrightarrow R\text{\textasciitilde}CH_2-CH_2-CH_2-CH_2\text{\textasciitilde}R-$$
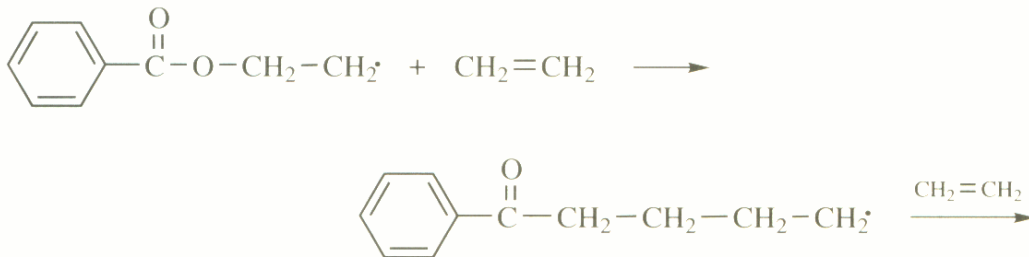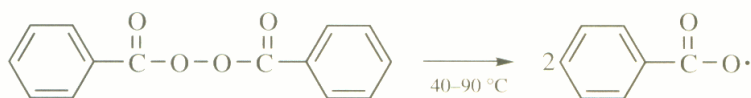
Most of the initiators used in the free-radical polymerization are aliphatic azo compounds and peroxides such as the following:

Azobisisobutyronitrile (AIBN)
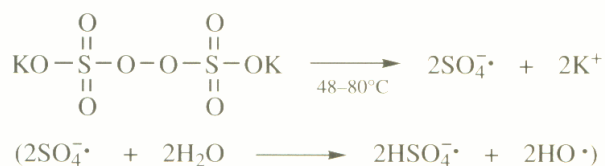
Potassium persulfate

Benzoyl peroxide (lucidol)

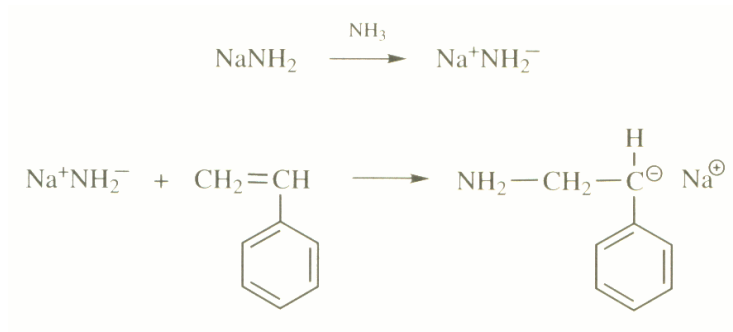Methods of free-radical polymerization are the following:
1. bulk polymerization – synthesis without solvent
2. solution polymerization – synthesis with (inert) solvent
3. precipitation polymerization – using solvent (such as methanol) to precipitate out the polymer
4. suspension polymerization – adding an initiator to the suspension in aqueous solution
5. emulsion polymerization – adding an initiator (such as potasium persulfate) to the emulsion of water insoluble monomers (such as styrene) in aquous soap solution.
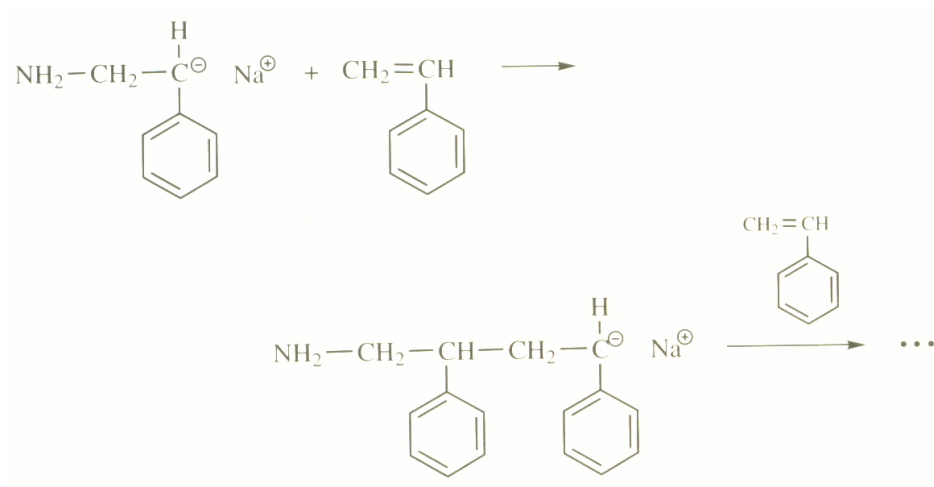
Ionic polymerization
There are two types of ionic polymerization: anionic and cationic. The formers involve carbanions C^- and the later involves carbonium C^+ ions. Catalysts and cocatalysts are needed in ionic polymerization.
In anionic polymerization as catalysts are used: alkali metals, alkali metal 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.
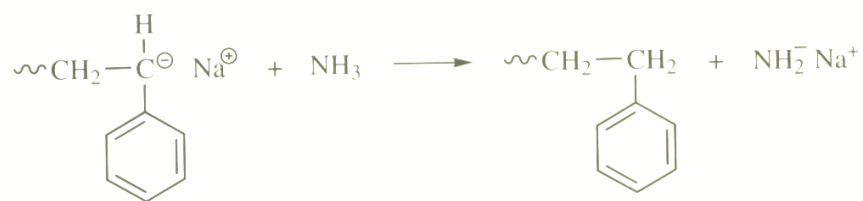
Initiation

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

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

Propagation

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

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

Termination

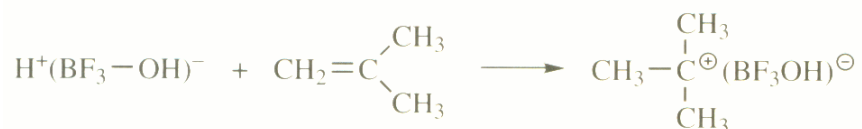$\sim CH_2{-}\overset{H}{\underset{(C_6H_5)}{C}}{}^{\ominus} Na^{\oplus} + NH_3 \longrightarrow \sim CH_2{-}CH_2(C_6H_5) + NH_2^- Na^+$
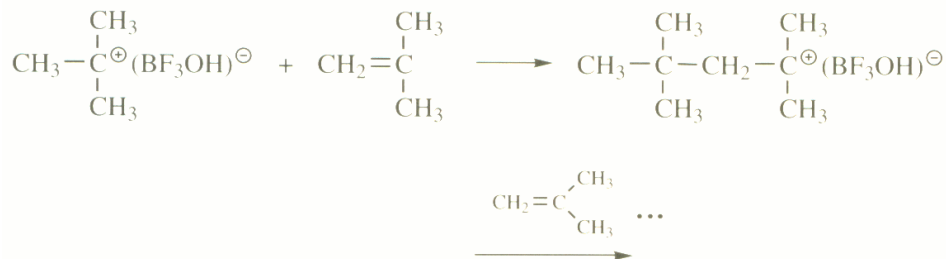
Depending on catalysts the chain growth in anionic polymerization can go through two, three four or more directions not only in one direction as shown in the above example.

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. Usaually there are: water and isobutene. Below the synthesis of polyisobutene as an example of cationic polymerization is given.
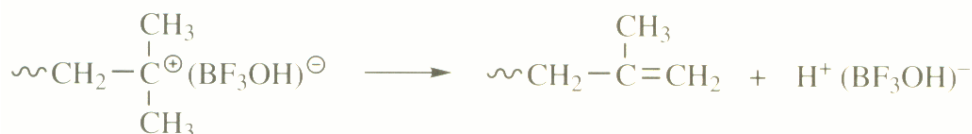
Initiation

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

$$H^+(BF_3-OH)^- \ + \ CH_2{=}C\binom{CH_3}{CH_3} \longrightarrow CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}{}^{\oplus}(BF_3OH)^{\ominus}$$

Propagation

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

$$CH_2{=}C\binom{CH_3}{CH_3} \ \cdots \longrightarrow$$

Termination

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

Modes of polymer degradation

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.

Thermal degradation refers to the case where the polymer, at elevated temperatures, starts to undergo chemical changes without the simultaneous involvement of another compound. Often it is rather difficult to distinguish between thermal and thermo-chemical degradation because polymeric materials are only rarely chemically "pure". Impurities or additives present in the material might react with the polymeric matrix, if the temperature is high enough.

Mechanically initiated degradation generally refers to macroscopic effects brought about under the influence of shear forces. Apart from the important role polymer fracture plays in determining the applications of plastics, it should also be pointed out, that stress-induced processes in polymeric materials are frequently accompanied by bond ruptures in the polymer main-chains. This fact can be utilized for example for the mechano-chemical initiation of polymerization reactions with the aim of synthesizing block- and graft-copolymers.

Photodegradation or light-induced polymer degradation, or, concerns the physical and chemical changes caused by irradiation of polymers with ultraviolet or visible light. In order to be effective, light must be absorbed by the substrate. Thus, the existence of chromophoric (light absorbing) groups in the macromolecules (or in the additives) is a prerequisite for the initiation of photochemical reactions. Generally, photochemically important chromophores absorb in the UV range (i.e. at wave lengths below 400nm). The importance of photodegradation of polymers derives, therefore, from the fact that the ultraviolet portion of the sunlight spectrum can be absorbed by various polymeric materials. The resulting chemical processes may lead to severe property deteriorations.

Degradation arising in high energy radiation such as electromagnetic radiation (X-rays, γ-rays) or particle radiation (α-rays, fast electrons, neutrons, nuclear fission products) is not specific with respect to absorption. The existence of chromophoric groups is no prerequisite as in the case of photodegradation since all parts of the molecule are capable of interacting with the radiation. The extent and character of chemical and physical changes depend on the chemical composition of the irradiated material and on the nature of the radiation. High energy radiation-induced alternations of polymeric materials are important for their utilization in fields of high radiation flux, e.g. in nuclear reactors. A great body of useful applications is based on the fact that the absorption of high energy radiation causes the generation of reactive intermediates (free radicals and ions) in the substrate. Thus high energy irradiation is a method quite generally applicable for the initiation of chemical reactions occurring via free radical or ionic mechanisms.

Biologically initiated degradation is strongly related to chemical degradation as far as microbial attack is concerned. Microorganisms produce a great variety of enzymes which are capable of reacting with natural and synthetic polymers. The enzymatic attack of the polymer is a chemical process which is induced by the microorganisms in order to obtain food (the polymer serves as a carbon source). The microbial attack of polymers occurs over a rather wide range of temperatures. Optimum proliferation temperatures as high as $60^{\circ}C$ or $70^{\circ}C$ are not uncommon.

Chemical degradation refers, in its strict sense, exclusively to processes which are induced under the influence of chemicals (e.g. acids,, bases, solvents, reactive gases etc.) brought into contact with polymers. In many such cases, a significant conversion is observed. Because the activation energy for these processes is high the chemical degradation occurs only at elevated temperatures.

It should be emphasized the strong inter-relationship between the various modes of polymer degradation. Frequently, circumstances prevail that permit the simultaneous occurrence of various modes of degradation. Typical examples are:
- environmental processes, which involve the simultaneous action of UV light, oxygen and harmful atmospheric emission;
- oxidative deterioration of thermoplastic polymers during processing, which is based on the simultaneous action of heat, mechanical forces and oxygen.

Detection of polymer degradation

Among the various methods for the detection of chemical changes in polymers those based on molecular size determinations play an eminent role, as far

as linear (non-crosslinked) polymers are concerned. Since synthetic polymers usually consist of a mixture of chemically identical macromolecules of different size, the molecular size- or molecular weight-distribution (MWD) are important properties which characterize a polymer. The MWD can be readily carried out with the aid of gel permeation chromatography (GPC).

Apart from MS- and MWD-determination, which are powerful in detecting degradation in linear soluble polymers, there is wealth of conventional analytical methods which are usually also applied in order to demonstrate chemical changes in polymers. When a gaseous low molecular weight products are formed in the degradation process they can be readily separate from the polymer specimen and easily analyzed qualitatively and quantitatively.

As far as chemical changes in bulk polymers are concerned, spectroscopic methods, such as infrared (IR) and ultraviolet (UV) absorption spectroscopy, are used to detect the formation or disappearance of chromophoric groups. Nuclear magnetic resonance (NMR) technique have proved helpful to analyze structural changes. The detection of reactive intermediates as free radicals can be monitored with electron spin resonance (ESR) spectroscopy.

There are various other analytical techniques, such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC) which are important in special fields of degradation. DTA and DSC are used in studies of thermal degradation.

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