

Chemistry of polymer

Polymeric material

Up to this point we have studied the properties of small molecules. However, life is fall with extremely large molecules. The basic molecules of life starch, cellulose, proteins and nucleic acids are formed of large number of repeated similar or unsimilar small molecules weight unites. Such molecules are called polymers a term introduced by Berzelius in 1830. We will now look at how such polymers can be making and examine some of their characteristics then will look into molecules of nature.

Monomers and polymers:

If we look at polymer poly lactic acid we can readily note that it is composed of units and

Should have resulted from consecutive esterification of carboxylic group of that acid with its hydroxyl group.

Poly Lactic acid

The process by with polylactic acid is formed from lactic acid is called polymerization. Lactic acid is thus a monomer and when self condensed it produces a dimmer and the letter when condensed with further one molecule it produces a trimmer.

The concept of polymerization can be illustrated graphically in general sense

By representing the "monomer" as astic and represent the functional group as ball (1) and (2)

In lactic acid 2 and 1 are different but this is not a condition: polyesters can be formed via condensation of a dicarboxylic acid and a diol.

Chemistry of polymer

It is easy to visualize the monomer units required to from a poly ester. The functional group in the polymer, an ester, is directed to functional groups from which it is made. However, as we will see, many polymers are formed by linking monomer units to getter by a carbon-carbon bond. It is all way difficult, if not impossible, to distinguish C-C bonds between monomer units from those in the monomer it self. For example ethylene undergoes polymerization to form long hydrocarbon chains in which C-C bonds are indistinguishable.

Linear and branched polymers:

In polyethylene and polylactic acid. Similar polymers monomer molecule are linked to each other linearly and such monomer are called "linear polymers" polymer molecules are attracted thus to each other only by vander wall's forces and by dipole interaction although these are very

Chemistry of polymer

weak the fact that they are repeated hundreds of times makes these enough to give such polymers rigidity and they are thus either solids or viscous liquids. The rigidity decreases by raising temperature as result of rupture of the attraction forces.

In contrast, other extremely large, multi dimensional molecules have distinctly different properties from those of linear polymers. These polymers are said to be branched or cross-linked. In such a polymer, chemical bonds interconnect chains, resulting in a complex network. One example is diamond, is which the smallest repeat unit is a single carbon that is connected to four other carbon bonds. In fact diamond is made under such extreme conditions of high temperature and pressure that scientists have been unable to define in detail how it is formed. Non etheles the bonding of each carbon to four partners in diamond lictice results in a material that is connected in three dimensions by very strong, carbon-carbon bonds. As a consequence, diamond does not melt or soften as it is heated and is totally insoluble in all known solvents.

The structure graphite is some what analogies, except that the carbon bonds are $SP²$ hyperdised and thus each carbon is linked to only three neighboring carbons. Because of the planner arrangement of bonding to such a carbon, graphite is composed of sheets resembling fused polyaromatic arrays.

5

Because each sheet is planner, these is a fairly strong attraction between the carbon nuclei of one sheet and the π electrons cloud of the adjust sheets, and graphite exhibit the same isolubility as dose diamond. Although these vander waals interaction are relatively strong, the attraction between the sheets changes very little as one sheet slides on the other. Thus sheets can be moved with virtually no resistance making graphite excellent lubercant. Diamond and graphite are examples of the three dimensional and two dimensional polymers respectively, in which the monomer units are identical.

Now we have looked at

1- **Linear polymers**: Derived from monomer that have only two possible attachment points.

2- **Branched polymers**: These are polymers that has three ar four attachment points

A three dimension network of chemical bonds in a polymer generally leads to a material that is less harder and less flexible than the corresponding linear polymer with similar functional groups. Polymers can also be made from mixtures of different monomer, which one unite having three bonds and other only two:

I & II represent alcohol which 1 & 2 &3 represent carboxylic acid derivatives.

Molecular Structure of Polymers

• **a- Linear**

– High Density Polyethylene (HDPE), PVC, Nylon, Cotton

• **b- Branched**

Polyethylene (LDPE)

- **c- Cross-linked**
	- Rubber
- **d- Network**
	- Kevlar, Epoxy

Types of polymerization:

The chemical transformations that result in polymers can be divided into two major classes:

(A)- Condensation polymerization: As an example OH fraction in hydroxy acid can condense with its carboxulic group producing polyester via elimination of water.

(B)- Addition polymerization: This results ferom addition of one molecule to another link can of polyethaylene.

Type of polymer according to their physical properties

• **thermoplastics**

It is a solid material at normal temperatures, but it softens with heat and turns into something like a paste, and if the heat is increased, it melts, and it is used in the manufacture of plastics and synthetic fibers, such as Polyethylene - polystyrene - polyvinyl chloride – polypropylene

thermosetting polymers

These polymers undergo chemical changes when heated, so the polymer chains become entangled in them, and after their thermal treatment, these polymers become insoluble,, poor conductivity of heat and electricity. These polymers are used as insulating materials in household electrical industries, such as phenolformaldehyde resins, urea-formaldehyde resins.

Addition polymerization

Radical polymerization: example (Polystyrene)

Polymers up to 1,400,4000 mw (50,000 unit) can be made link other linear polymers it is flexible and some are even stretshiabl and can these be shaped if heated. Materials this is called plastics from greek plastikos that mean.

Ionic polymerization:

i) Cationic polymerization:

The types of monomers necessary for cationic polymerization are limited to [olefins](https://en.wikipedia.org/wiki/Olefins) (alkene)with [electron-donating substituent's](https://en.wikipedia.org/wiki/Electron-donating_substituent) (oxygen and nitrogen-based functionalities)and heterocycles

• **Olefins**

Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electrondonating groups make the olefin nucleophilic enough to attack [electrophilic](https://en.wikipedia.org/wiki/Electrophile) initiators or growing polymer chains. Some reactive olefin monomers are shown below in order of decreasing reactivity, with [heteroatom](https://en.wikipedia.org/wiki/Heteroatom) groups being more reactive than alkyl or aryl groups.

Cationic polymerization link anionic polymerization have not to terminate and the length of polymer chain can be increased by addition more monomers. Such polymers are called living polymers. Cationic polymerization can be initiated by adding alkyl lithium to ethylene. All types of polymerization are exothermic with 20 kal / mol for each addition. Cationic and anionic polymers can have higher mol.wt rigid and insoluble

Poly ethylene:

Substituted ethylene are also polymerisable grieves new polymers with different properties.

Chemistry of polymer

Natural rubber :-

Rubber, also called India rubber, latex, Amazonian rubber, *caucho*, or *caoutchouc*, as initially produced, consists of [polymers](https://en.wikipedia.org/wiki/Polymer) of the organic compound [isoprene,](https://en.wikipedia.org/wiki/Isoprene) with minor impurities of other organic compounds. [Thailand](https://en.wikipedia.org/wiki/Thailand) and [Indonesia](https://en.wikipedia.org/wiki/Indonesia) are two of the leading rubber producers. Types of [polyisoprene](https://en.wikipedia.org/wiki/Polyisoprene) that are used as natural rubbers are classified as [elastomers.](https://en.wikipedia.org/wiki/Elastomer)

Butadiene polymerization:

(Rubber: Butadiene and other conjugated diene also form polymers. For example, the polymer derived from isoprene (2-methyl butadiene) is synthetic rubber. The rubber tree and several other plants produce a similar natural polymer known as latex rubber, which differ from synthetic rubber in that essentially all of its double bonds have a cis configuration. Chloroprene (2-chlorobutadiene) a monomer structurally similar to isoprene, lead to a synthetic rubber called neoprene.

n

isoprene

synthetic rubber.

Cl Cl Cl n

Chloroprene

Neoprene

Replacement of the methyl group of isoprene with a chlorine atom reduces the ability of neoprene is not resistant to gasoline and oils than synthetic rubber.

Although synthetic and naturally occurring rubbers are similar in many ways, some of their properties differ. The synthetic polymer consists of very diverse mixture of structures, whereas the structure of natural polymer is very constant. Radical polymerization begins by formation of bond between a radical initiator and one of the terminal atoms, resulting in a stabilized allyl radical.

Two sites in an allyl radical bear radical character. Therefore; addition of these type of species to another butadiene molecule occurs with two different region chemical outcomes; bond formation occurs either at C-2 or at C-3. Two dimmers are formed, one linear and one branched. As each additional butadiene molecule adds to a growing chain, there are two possible outcomes: Linear or branched addition. Furthermore, both cis and trans geometrical isomers will be formed, further expanding the number of different species formed. Thus, synthetic rubber is quite a complex mixture.

In contrast to synthetic rubber, latex rubber is produced in living plant through catalysis by enzymes. These natural catalysts produce a polymer in which essentially all double bonds have the cis geometry. For this reason, there is structure diversity a many the polymer molecules found in natural rubber.

Cross-Linking in polymers:

Most of the polymers described so far are derived from monomers with two bonding sites. As a result, the polymer chains are held together only by relatively weak vander wals attractive interactions. In contrast, glass is a rigid polymeric material in which tetravalent dimensional covalent net work

Chemistry of polymer

Cross-linking is a process in which a bifunctional molecule (such as a diene) participates in polymerization and is incorporated into two separate polymer chains.

Polymerisation of a mixture of simple alkene (such as styrene) with a diene (such as P-divinyl benzene) allows each of two alkene units of the diene to be incorporated into a separate chain, thus linking the chains together. A molecule such as divinyl benzene an believed a monomer capable of forming four bonds and these of establishing cross links between growing monomer chains.

The extent of cross-linking attained depends on the relative concentration of styrene and divinyl benzene. But, if divinyl benzene constitutes only very small % of the mixture, the resulting Plastic is much more rigid than polystyrene itself because of additional covalent bonds between the chains.

Diene polymers such as latex or neoprene rubber can also be made more rigid by cross-linking with nonconjugated dienes. One such linking agent is 5-vinylnor bornene, large quantities of with which is produced each year by the Diels –Alder reaction of butadiene with cyclopentadiene

The stretched double bond in 5-vinylnorbornen is more reactive them the monosubstituted alkene substituent and these the former is in corporated in individual chains while the majority of the latter remain unreacted. When polymerization has consumed most of the available alkene, the less reactive double bond participate in cross-linking of polymer chains. In this way cross-linking is delayed until late in polymerization, resulting in quite long chains. The incorporation of 5 vinylmorbornene in a monomer nature resulting a more rigid polymer by enhancing degree of cross linking between chains.

Attentively, polymer chains can be linked by sulfur bridges. Transformation of the rather of common and soft latex rubber into the much more rigid material used as example in automobile tires is a accomplished by heating with sulfarin a process known as **vulcanization**, which was discovered by accedant by chairles goody ear (the term vefes tovealcan, the roman god of fire, who was thought to be very strong). The reaction almost certainly invrus radicals, but the mechanism is not well understood. The bridges are depicted here as resulting from simple allylic substitution of sulpher for hydrogen

Chemistry of polymer

s heat () with the du y ad on i given a let $\frac{1}{18}$ by t c x i as is a let $\frac{1}{18}$ by t c x i as is a let $\frac{1}{18}$ by t c x i as is a let $\frac{1}{18}$ by t c x i as is a let $\frac{1}{18}$ by t c x i as is a let $\frac{1}{1$ Neither the original polymer nor the cross linked rubber derived from isoprene only functionality that produces color. **The characteristic black color of the rubber is caused by the presence of carbon black**, a material similar to graphite, which ads as lubricant and impedes a greater life time to the rubber under conditions of repeats flexing. Large quantities carbon black is produced in easter Europe. Unfortunately, the outdated technologies in this region have resulted in emission of substantial amounts of carbon black into the atmosphere causing,

significant industrial pollution.

Heteroatom containing additional polymers:

Substituted vinyl polymers have very low solubility in water because they lack any functional group that can form hydrogen bonds. Now we then to polymers that incorporates oxygen in the form of alcohol or ether functional groups. The attachment of heteroatom to a carbon framework increases solvent-solute interactions, enhancing solubility of heteroatomcontaining carbons.

Carbon-linked monomer units: polyols:

The polyol known **as poly (vinyl alcohol)**, or **PVA** is highly watersoluble. Its name might seem to imply that, this polymer is made from vinyl alcohol, but this enol is not present in significant amounts in equilibrium with keto form, acetaldehyde.

Radical polymerization of vinyl acetate is used to form poly (vinyl acetate), a polymer with a hydrocarbon chain substituted with acetate ester. The ester are cleaved by awd or base–catalyzed reaction with methanol, forming methyl acetate and PVA. The resulting polymer is mach more soluble in water than are hydrocarbon polymers such as polyethylene and polystyrene but a lower surface tension than pare water. (Viscosity is increased because the long polymer molecules are quite viscous, and the surface tension is partially disrupted by the polymer).

Poly (vinyl alcohol) is therefore included in products ranging from hair spray and styling gels to lubricants for molding rubber.

Heteroatom-linked monomer units:

The addition polymers discussed so far have carbon-carbon bonds linking the polymer units. However, there are also important classes of addition polymers in which the monomer units linked by heteroatoms.

Polyethenes.

A very important class of addition polymers is formed by addition polymerization of simple epoxides. The addition of nucleophile such as OH to ethylene oxide results in ring opining and yields the monoanion of ethylene glycol. This ion can also serve as a nucleophile, reacting with another molecule of ethylene oxide.

Polyethaylene glycol

This polymerization is quit similar to anionic polymerization of ethylene. Each step in these ring opening polarization releases ring strain of a three membered epoxide ring and is thus exothermic by approximately 15 k cal/mol.

The resulting polymer is called poly (ethylene glycol), or PEG, synthetic PEGS are used in cosmetic creams, lotions, and deodorants and in antistatic agents. These plastics are marketed commercially as carbon waxes and under other trade names. They have high water solubility because of hydrogen bonding to ether oxygen atoms and have many of

the same applications as poly (vinyl alcohol). Naturally occurring cyclic polyethenes were important in the biological transport of cations across membranes.

Polyacetals:

Another oxygen-containing polymer is paraformaldehyde, poly acetate formed by addition polymerization of formaldehyde, a reaction that takes place as an agues solution of formaldehyde.

Note that the backbone of the polymer is formed of acetal linkages and that both ends are hemiacetals, which are active sites for further chain growth. Note, also, that all atoms of the monomer are retained within the polyacetal, making it an addition polymer. This addition polymerization is only slightly exothermic. As a result paraformaldehyde undergoes depolymerization in water, reforming formaldehyde. Because formaldehyde is strong antibacterial agent, aqueous solutions of paraformaldehyde are used as disinfectants, and the polymer is the active ingredient in same contraceptive creams.

Polyacetals made from formaldehyde, as well as polyacetal and polyketals made from aldehydes and ketanes are strong plastics that are resistant to fatigue (breaking after repeated flexing) and have high electrical resistance, making them quite useful as components for computer hard were and automobile parts. To stabilize these materials toward hydrolysis, the hemiacetals (or hemiketals) at the ends or "capped" by reaction ether with acetic anhydride (to form esters) or ethylene oxide. Polyacetals or (polyketals) require more strongly acidic or basic condition for their hydrolysis than does paraformaldehyde.

Condensation polymers

Unlike an addition reaction in all atoms of the reactants are incorporated with in the product, a condensation reaction forms a more complex organic molecule from two or less complex one, with the expulsion of a small molecule. Some examples of condensation reactions include esterification, aldol, and claisan condensation. In all these water is formed as a byproduct. When such a reaction is repeated many times with an appropriately functionalized monomer, a condensation polymer is produced.

Polyesters:

Because interaction of dicarboxylic acids with diols to form polyesters produces one equivalent of water for each link formed in polymer chain, poly ester formation is a condensation polymerization. If esters are used in place of the carboxylic acids, the reaction is a trans esterification. Dacron is communally important condensation polymer used as a fiber and also as a film called Mylar. It is formed by reaction of dimethyl terphthalate with ethylene glycol, a trans esterification in which methane is produced as a by-product:

Polycarbonates:

Are condensation polymers that result from trans esterification. A diol often employed reaction is bisphenol **A** (the **A** comes from acetone), produced by reaction of phenol and acetone in presence of lewis acid.

Bisphenol **A**

 Because phenols are better leaving groups these are aliphatic alcohols, diphenyl carbonate is more reactive in transformation than is, for example dimethyl carbonate. The polycarbonate formed from bisphenol of has many of the same propriates as Plexiglas or polystyrene. All these materials have high optical clarity, but the polycarbonate is more stronger and more rigid, with great impact resistance.

Polysaccharides:

Polysaccharides are naturally occurring condensation polymers. In starsh (known as amylose) the acetal function in one molecule condenses with OH group at C-4 of other function though α -linkage. Amylose is water insoluble despite the fact that at is formed from as many as 4000 glucose units. On the other hand amylopectine is also poly glucose but water soluble as a result of the fact that it is braced at C-6 and is of more than million glucose unites.

Cellulose

Cellulose is a biological polymer formed via condensation of several anits of β-glucose at C-1 and C-4.

Cellulose is typically formed from 3000 to 3500 glucose units however it is water insoluble as a result of stereochemistry that permit adherence of chins by vander wal forces.

Acylation by acetic anhydride produces acetyl cellulose which is transparent and is used in photographic films.

Polyamides;

A polymeric condensation product formed from a diacid and a diamine is called polyamide. In a route similar to that for polyester formation adepic acid and 1,6-diaminohexane react at high temperature to form a polyamide known as **nylon 66**. (the numbers refer to the number of carbon atoms of acid and amine).

Nylon 66

There is also **nylon 6** produced by the polymeric ring opening induced by the catalytic interaction of Nucleophilic with carpolactan.

Beckmann rearrangement of cyclohexanone oxime

The seven member cyclic amide is produced industrially through Beckmann rearrangement of cyclohexanone oxime. By salphonic acid with is neutralized by ammonia producing ammonia sulphate which solid as fertilizer.

The term condensation and addition refer to the method by which polymers are produced and therefore are not necessarily provide clues to characters of a polymer.

Nylon 66 is produced by the condensation polymerization (with loss of water) of two diffract six-carbon monomers, one of a diacid and other of a diamin. Nylon 6 on the other hand results of addition polymerization of a single six-carbon monomer (the cyclic amide). Both nylon 66 and nylon 6 are useful plastics that form very long lasting, and flexible fibers; the flexibility is due, in part, to conformation at freedom of the chains.

PPTA polymer

Condensation polymerization of terphthalic acid with p-phenylene diamine results in a polymer known as PPTA (p-phenylenterephdiamine) which have very unusual properties.

In contrast with nylon 6 and 66, which have considerable conformation freedom, PPTA is quite rigid. As a result tris polymer can be formed into fibers that have great tensile strength and resists both compression and elongation. PPTA is five times stronger than steel on a per-weight basis. Fibers spun from this polymer are marketed as Kevlar and are used in applications such as bulletproof vests that require high strength and low weight.

Polypeptides:

The amide linkage in a polyamide resembles those found in polypeptides and proteins, which are natural polymeric materials derived from a aminoacids. This linkage is referred to us a peptide bond, and thus the term polypeptides explicitly refer to the repeating amide linkage. In polypeptides (and proteins), the monomer units are linked by amide groups formed by a condensation reaction between amino groups of one, α -amino acids and the carboxylic group of another.

Polypeptides and proteins are naturally occurring polymers that have many different forms and a variety of functions. The difference between the term polypeptide and protein refers to molecular size. Polypeptides are a polymer containing more than 100 amino acids and proteins are larger molecules.

The synthetic (manufacture) polyamides are clavelayzed to minic the properties fond in silic and natural animal hairs such as wool, both composed mainly of polypeptides silk is polymer with amino acid glycine and alanine. **Wool** is structurally more complex, having sulfur sulfur bonds that link individual chains to the another and forms matrix some what like that of vulcanized rubber. These bonds in wool are the result of significant amounts of the sulfur containing amino acid system.

Although a bond between two sulfurs may usual it is non ethelens very easily upon exposed of thiol functional groups to oxidants, and even molecular oxygen will effect this transformation. S-S bonds play a crucial role in many biological processes.

Silk

Poly urethane:

O O N H

A urithane

Similar in structure to polyamids are poly urethanes, which have one of components of chain a urethane (or carbonate) group. Urethanes are formed by reaction of isocyanets with alcohols.

Typically reacting a low molecular weight polyester with terminal hydroxyl group with pis isocyante.

When a compound with a low boiling point (for example $CO₂$ or volatile hydrogen such as methane or ethane) is dissolved under pressure in one of starting materials and then allowed to expand and vaporize while polymerization proceeding, the polyurethane obtained has tiny "void" spaces sealed of by surrounding polymer. The resulting poly urethane form is a valuable lightweight material for building insulations and padding.

Extensively Croos-Linked Polymers

Even in vulcanized rubber, the number of cross-linking bonds is usually small in comparison with polymer units. On the other hand, monomers with three or more points of comedian produces polymers that extend in two and three dimensions rather than having a linear arrangements as in simple polymers such as polyethylene. These extensively cross-linked polymers are often very hard. **Bakelite** is one

example: it is a resin (a highly viscose polymer glass) derived from reaction of phenol and formaldehyde.

Epoxy resins

Epoxy resins constitute another important class of cross-linked polymers that have many applications as structural materials. Includes in this class are the commonly used epoxy glues, many laboratory bench tops are made of epoxy resin and microelectronic chips are encapsulated in this material. Because such resins are expensive, a filter is added in the same way that sand and small stones are added to cement to make convert. (for microchips the filter is silicon dust). The chemistry of epoxy resins is straight formed but the structures are complex; for their reason, block diagrams are often used to represent structures such as bisphenol as.

Bisphenol - A

Reaction of bisphenol **A** with epichlorohydrine results in formation of a bis-epoxide: this in when reaction with additional bisphenol **A** in one to one ration, forming first a simple 1:2 adduct. This epoxy alcohol then reacts either with more PPA to form a diol or with more bis-epoxide to form larger bisepoxide. These reactions non tinue, ultimately forming a mixture of short polymers composed of diols, epoxy alcohols, and bisepoxides. This mixtures is still fluid and is clear, nearly odorless component of two part epoxy glues. This reaction of this complex mixture of linear polymer with a triamin, the fishy smelling component, leads to the opening of terminal epoxides and the formation of three dimentionaly linked not work that is much more rigid than the original resin.

Example of gallery with epoxy resin

Chemistry of polymer

The Nylon Story

- **1- In 1928 DuPont asked prof. Carothers to do also basic research on petrochemicals in direction of polymers.**
- **2- He selected condensation polymerization as a direction for his work**
- **3- Initially he investigated condensing diesters with diols but removal of water from reaction proved a tidous process in industry and his discoveries in this area could not be scaled up.**
- **4- He shifted to condensation of diamines with diacids.**
- **5- Several types of polyamides were obtained.**

Chemistry of polymer

6- Synthesis of Adepic acid and hexamethylenediamine Three steps from benzene to adipic acid

This is expensive and multistageouses

7- Other routes to hexamethylenediamine were thus investigated.

How

hexamethylene diamine

8- Other source to diamines were considered. Successful synthesis of tetramethylenediamine afforded nylon 4, 6.

diamine

reacts with adipic acid to produce nylon 4,6

9- Monsanto process (Dr. Emanuel Baizer).

10- Purity of both monomers is essential to get long chains as impurity can stop chain growth. This is achieved by crystallization and in this way both nylons 6,6 and could be produced Nylon made from single monomer.

Nylon 6

Reference :-

1- An Introduction to Polymer Chemistry (book) 2-some publication of prof.M.H.Elnagdi 3-polymer chemistry (springerlink)