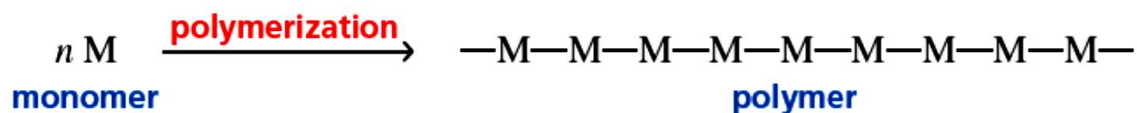


Polymer Chemistry

A polymer is a large molecule made by linking together repeating units of small molecules called monomers. The process of linking them together is called polymerization.



Classification of Polymers

Polymers cannot be classified under one category because of their complex structures, different behaviours and vast applications. We can, therefore, classify polymers based on the following considerations.

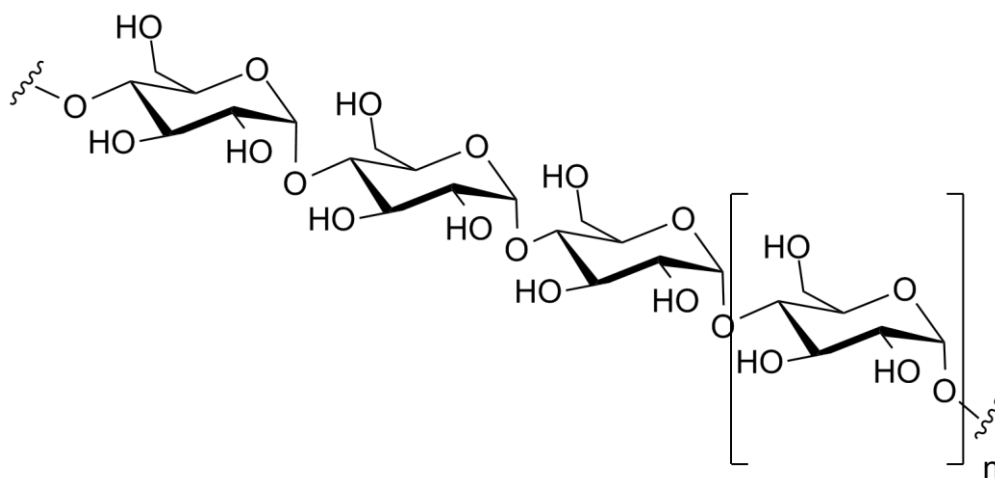
Classification of Polymers based on the Source of Availability

There are three types of classification under this category, namely, Natural, Synthetic, and Semi-synthetic Polymers.

Natural Polymers: They occur naturally and are found in plants and animals.

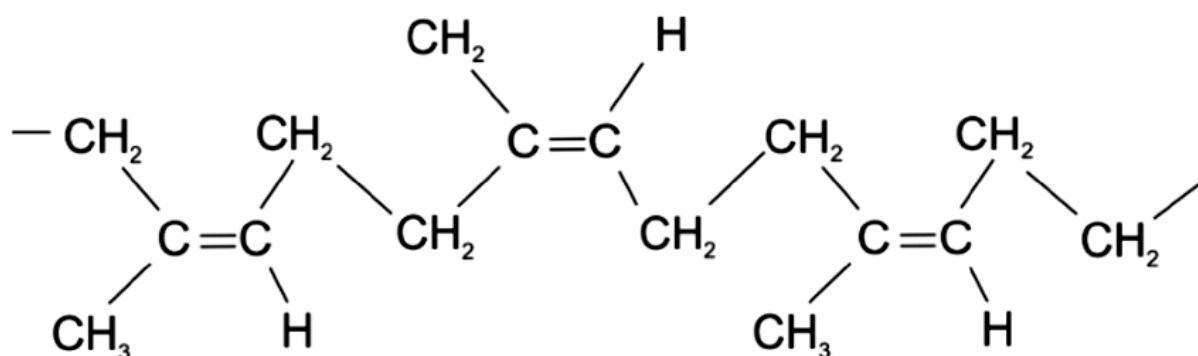
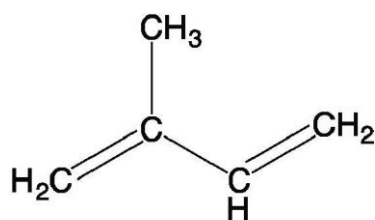
Polymer from plants

The polymer which are obtained from plant sources are called plant polymers. For example carbohydrate, cellulose and rubber. They are biodegradable polymers which are also called biopolymers.

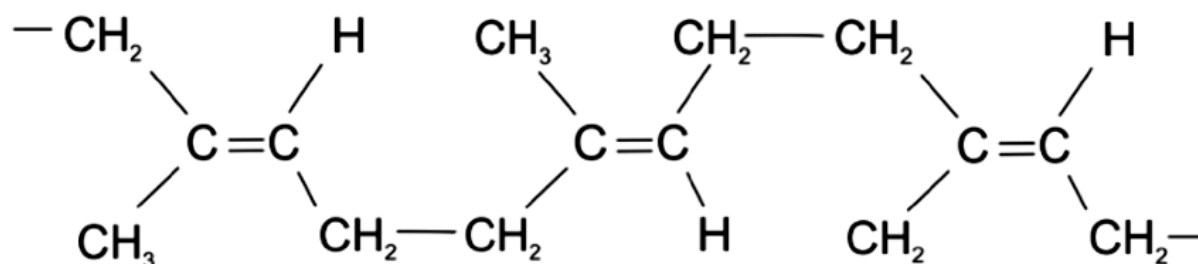


Linear Polymer of α glucose is amylose.

Linear polymer of isoprene is called natural rubber.



Natural rubber



Gutta-percha

Polymer from animals

Polymers which are obtained from animal sources are called polymers obtained from animals. For examples proteins, DNA etc obtained from animals. Proteins are polymers of amino acids.

Semi-synthetic Polymers: They are derived from naturally occurring polymers and undergo further chemical modification. For example, cellulose nitrate, cellulose acetate.

Nitrocellulose (also known as cellulose nitrate, flash paper, flash cotton, guncotton, pyroxylin and flash string, depending on form) is a highly flammable compound formed by nitrating cellulose through exposure to a mixture of nitric acid and sulfuric acid. One of its first major uses was as guncotton, a replacement for gunpowder as propellant in firearms. It was also used to replace gunpowder as a low-order explosive in mining and other applications. Cellulose treated with sulfuric acid and potassium nitrate produces cellulose mononitrate. In 1855, the first man-made plastic, nitrocellulose (branded Parkesine, patented in 1862), was created by Alexander Parkes from cellulose treated with nitric acid and a solvent. In 1868, American inventor John Wesley Hyatt developed a plastic material he named Celluloid, improving on Parkes' invention by plasticizing the nitrocellulose with camphor so it could be processed into finished form and used as a photographic film. This was used commercially as "**celluloid**", a highly flammable plastic that until the mid-20th century formed the basis for lacquers and photographic film

Synthetic Polymers:

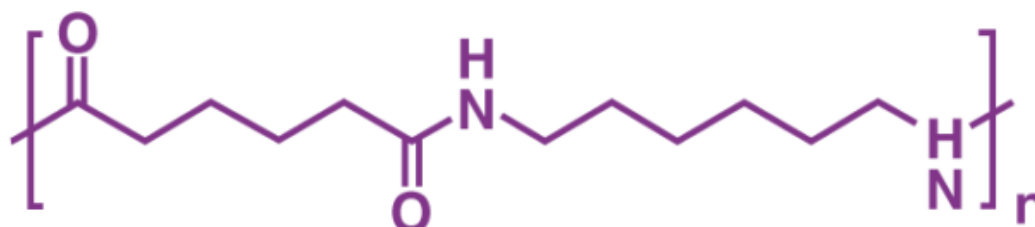
Synthetic polymers are those which are human-made polymers. Polymers are those which consists of repeated structural units known as monomers. Polyethylene is considered to be as one of the simplest polymer, it has ethylene as the monomer unit whereas the linear polymer is known as the high density polyethylene-HDPE. Many of the polymeric materials have chain-like structures which resemble polyethylene.

Synthetic polymers are sometimes referred as “plastics”, of which the well-known ones are nylon and polyethylene. The polymers which are formed by linking monomer units, without the any change of material, are known to as addition polymers or also called as chain-growth polymers. All these are said to be synthetic polymers.

Some synthetic polymers which we use in our everyday life include nylons used in fabrics and textiles, Teflon used in non-stick pans, polyvinyl chloride used in pipes. The PET bottles we use are commonly made up of synthetic polymer called as polyethylene terephthalate. The covers and plastic kits comprises synthetic polymers such as polythene, and the tyres of vehicles are manufactured from the Buna rubbers. But on the other side, there also arises environmental issues by the use of these synthetic polymers such as the bio plastics and those made from petroleum as they are said to be non-biodegradable.

Nylone

Nylon belongs to the synthetic polymers family and is also known as polyamides. It was produced on February 28 in the year 1935 by person naming Wallace Carothers at the DuPont's research facility. Nylon is widely used polymers. The backbone of it called as amide causes it to become hydrophilic than other polymers. Nylon gets engaged in hydrogen bonding with water, not like the pure hydrocarbon polymers which make most of the plastics.



Structure of Nylon – 6,6

Properties of Nylon

Nylon is Lustrous, Elastic, Very strong, Damage resistant to oil and many chemicals, Does not absorb water and Dries quickly

Types of Nylon

Nylon 6 – It was developed by Paul Schlack. It is formed by ring-opening polymerization of caprolactum. **Nylon 510** – It is obtained from sebacic acid and pentamethylene diamine.

Nylon 1,6 – Nylons can also be synthesized from dinitriles using acid catalysis. For example, this method is applicable for preparation of nylon 1,6 from adiponitrile $(\text{CH}_2)_4(\text{CN})_2$, formaldehyde and water. **Nylon 66** – Wallace Carothers patented nylon 66 with the use of amide.

Uses of Nylon Clothing – Shirts, Foundation garments, lingerie, raincoats, swimwear and cycle wear.

Industrial uses – Conveyer and seat belts, parachutes, airbags, nets and ropes, tarpaulins, thread, and tents. It is used to make a fishnet. It is used as plastic in manufacturing machine parts

Classification of Polymers based on the Structure of the Monomer Chain

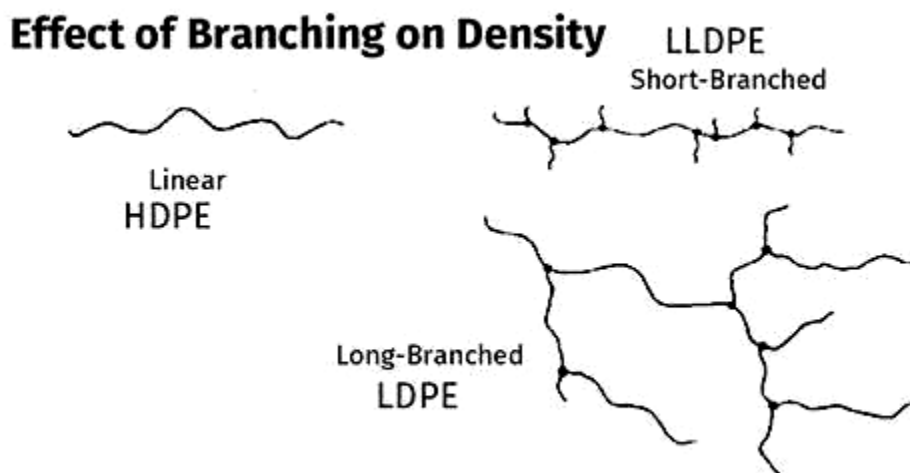
This category has the following classifications:

Linear polymers

The structure of polymers containing long and straight chains fall into this category. PVC, i.e. poly-vinyl chloride is largely used for making pipes and electric cables is an example of a linear polymer. The long chains are typically held together by the weaker van der Waals or hydrogen bonding. Since these bonding types are relatively easy to break with heat, linear polymers are typically thermoplastic. Heat breaks the bonds between the long chains allowing the chains to flow past each other, allowing the material to be remolded. Upon cooling the bonds between the long chains reform, i.e., the polymer hardens.

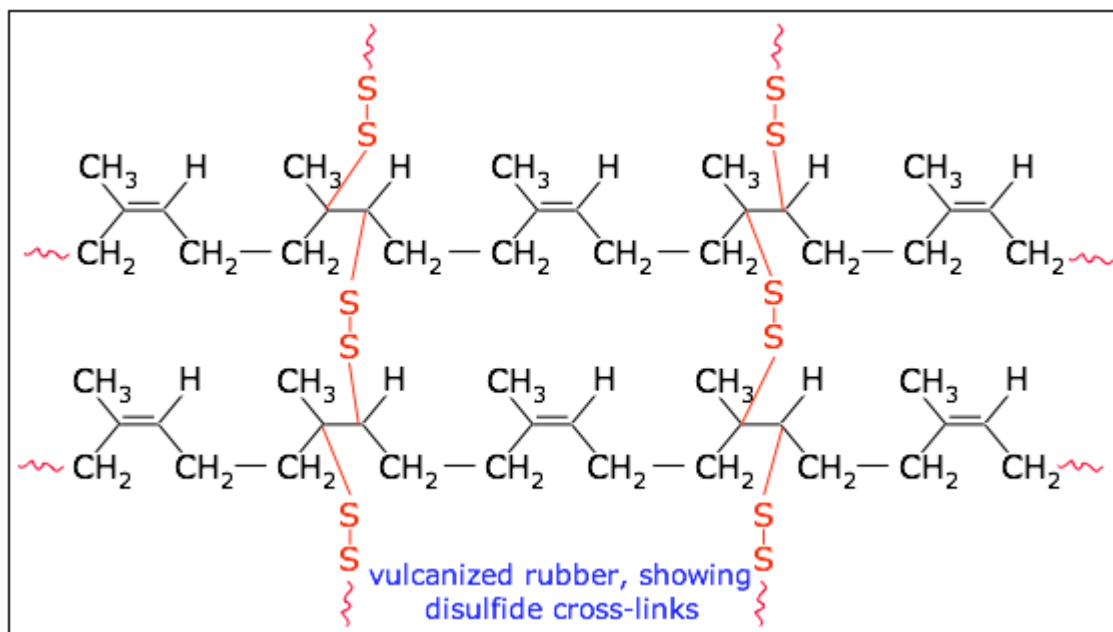
Branched polymers

When linear chains of a polymer form branches, then, such polymers are categorized as branched chain polymers. For example, Low-density polythene. It resembles linear polymers with the addition of shorter chains hanging from the spaghetti backbone. Since these shorter chains can interfere with efficient packing of the polymers, branched polymers tend to be less dense than similar linear polymers. Since the short chains do not bridge from one longer backbone to another, heat will typically break the bonds between the branched polymer chains and allow the polymer to be a thermoplastic, although there are some very complex branched polymers that resist this 'melting' and thus break up (becoming hard in the process) before softening, i.e., they are thermosetting.

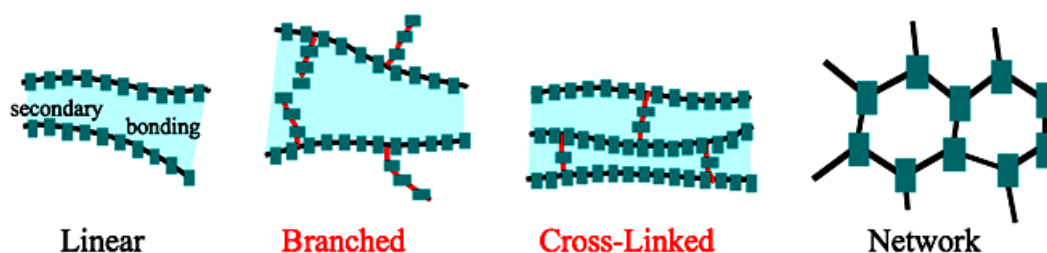
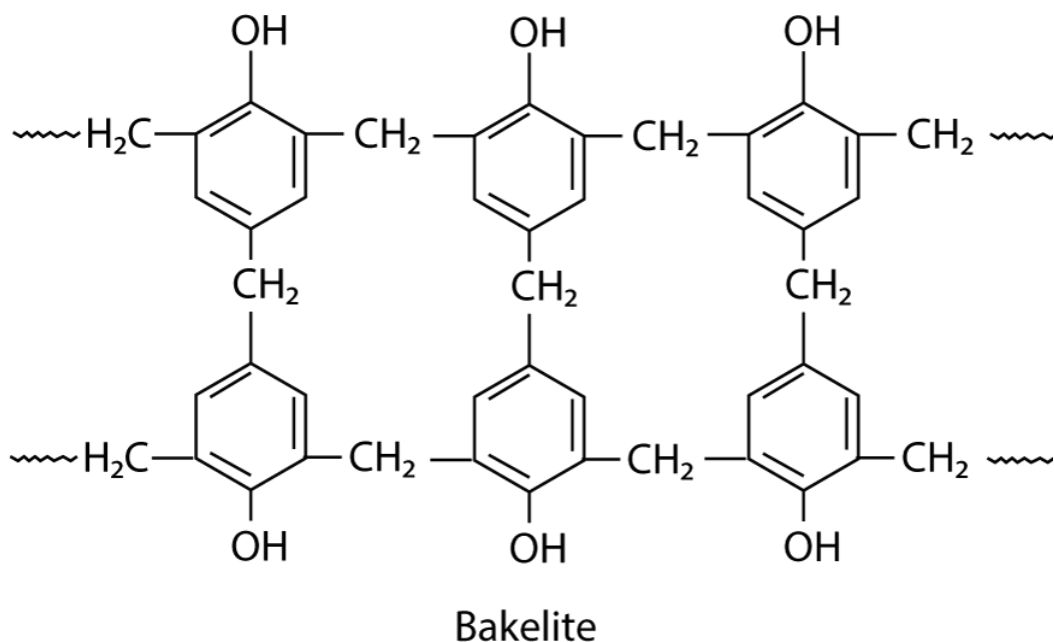


Crosslinked polymers

They are composed of bifunctional and trifunctional monomers. They have a stronger covalent bond in comparison to other linear polymers. Vulcanized rubber is in this category. It resembles ladders. The chains link from one backbone to another. So, unlike linear polymers which are held together by weaker van der Waals forces, crosslinked polymers are tied together via covalent bonding. This much stronger bond makes most crosslinked polymers thermosetting, with only a few exceptions to the rule: crosslinked polymers that happen to break their crosslinks at relatively low temperatures.



Networked polymers are complex polymers that are heavily linked to form a complex network of three-dimensional linkages. These polymers are nearly impossible to soften when heating without degrading the underlying polymer structure and are thus thermosetting polymers. Monomers do not have to be of a single atom type, but when referring to a specific monomer it is understood to be of the same composition structure. Bakelite is an example for network polymer.



Other Ways to Classify Polymers Classification

Based on Polymerization

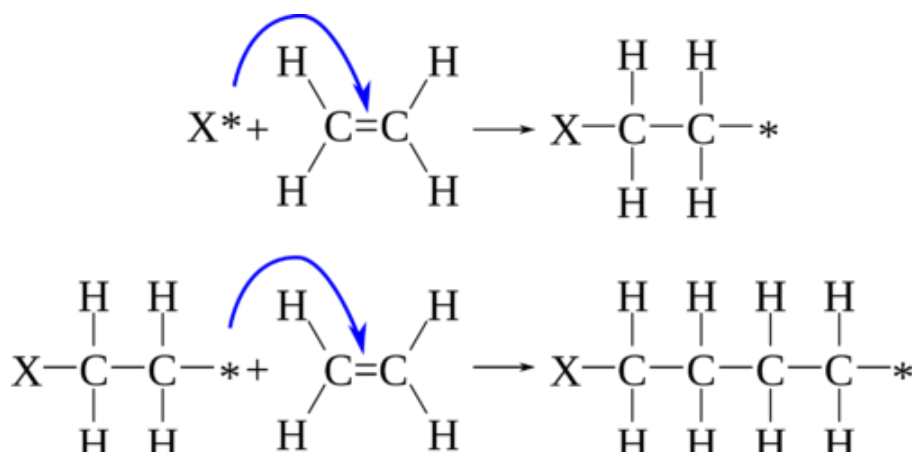
Addition Polymerization:

In polymer chemistry, an addition polymer is a polymer that forms by simple linking of monomers without the co-generation of other products. Addition polymerization differs from condensation polymerization, which does co-generate a product, usually water. Addition polymers can be formed by chain polymerization, when the polymer is formed by the sequential addition of monomer units to an active site in a chain reaction, or by polyaddition, when the polymer is formed by addition reactions between species of all degrees of polymerization. Addition polymers are formed by the addition of some simple monomer units

repeatedly. Generally polymers are unsaturated compounds like alkenes, alkalines etc. The addition polymerization mainly takes place in free radical mechanism.

Example, poly ethane, Teflon, Polyvinyl chloride (PVC)

Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.



The reactions above show the basic steps to form an addition polymer:

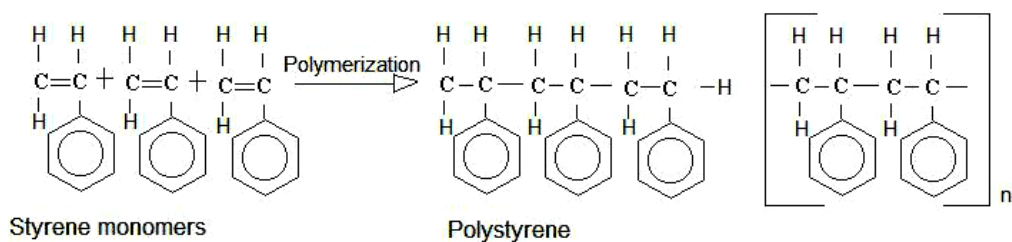
Initiation - a free radical initiator (X^*) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: $\text{H}-\text{O}-\text{O}-\text{H} \rightarrow 2\text{H}-\text{O}\cdot$. This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.

Propagation - the new free radical compound interacts with another alkane, continuing the process of chain growth (second step above).

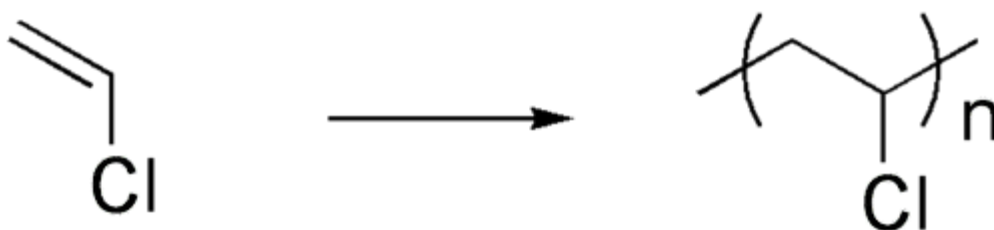
Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

Polyethylene can have different properties depending on the length of the polymer chains, and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates. Several other kinds of unsaturated monomers can be polymerized, and are

components in common household products. Polypropylene is stiffer than polyethylene, and is in plastic utensils and some other types of containers.



Polystyrene is used in insulation and in molded items such as coffee cups.

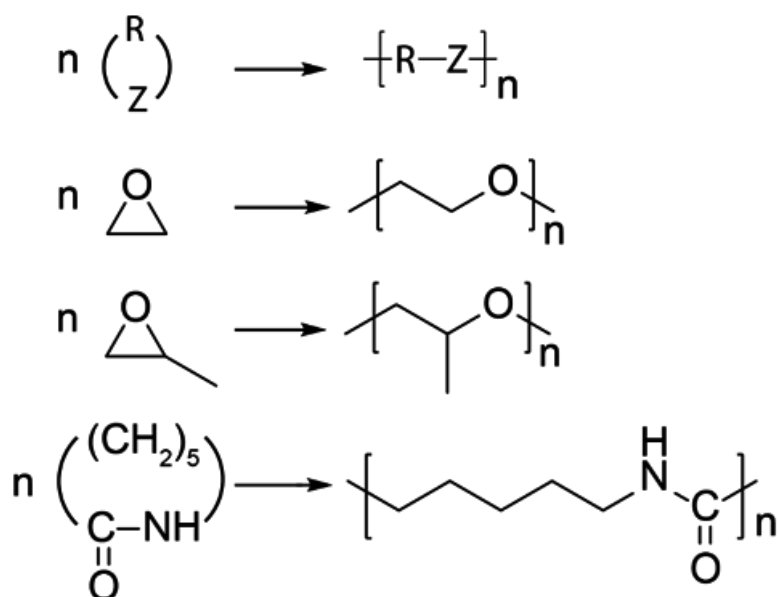


Copolymers

When two or more types of monomers undergo addition polymerization, the resulting polymer is an addition copolymer. Saran wrap, formed from polymerization of vinyl chloride and vinylidene chloride, is an addition copolymer.

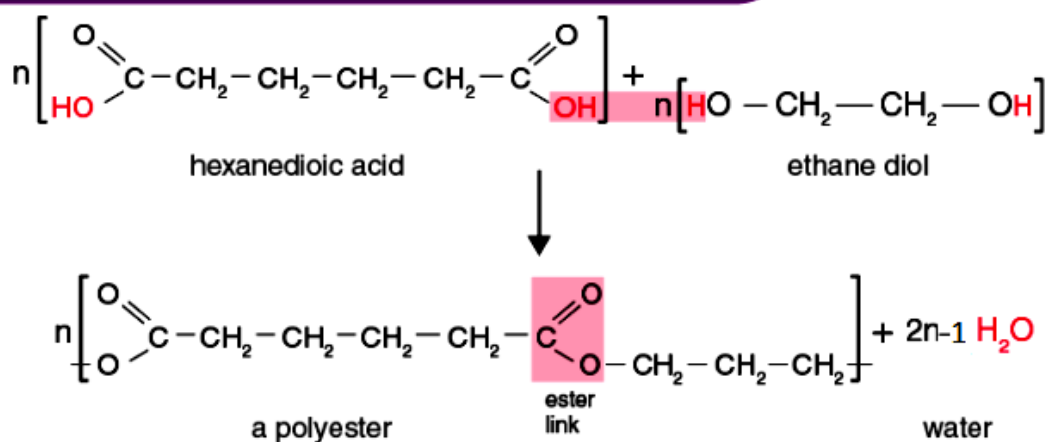
Ring-opening polymerization (ROP)

Ring-opening polymerization is an additive process but tends to give condensation-like polymers but follows the stoichiometry of addition polymerization. For example, polyethylene glycol is formed by opening ethylene oxide rings:



Condensation Polymerization: it is a form of a step-growth polymerization where smaller molecules or monomers react with each other to form larger structural units (usually polymers) while releasing by products such as water or methanol molecule.

CONDENSATION POLYMERISATION



Example, Nylon -6, 6, perylene, polyesters.

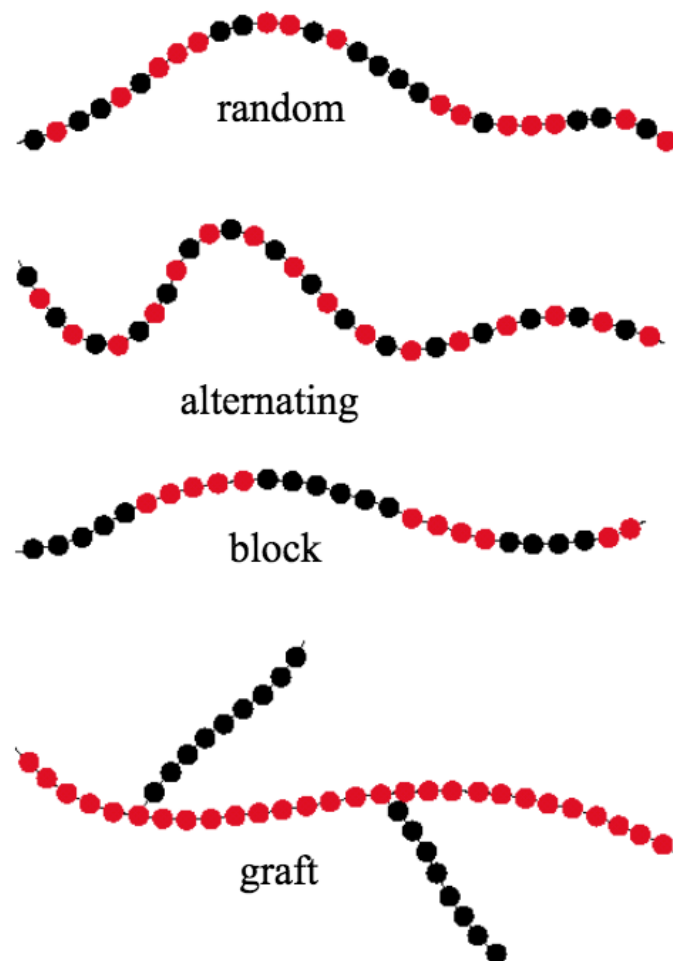
Classification Based on Monomers

Homomer: A homopolymer is a chain of chemically linked one type of small molecules (or monomers), whereas a copolymer (also called heteropolymer) can be chemically built of two or more types of monomers forming the same polymer chain.

When building a polymer from two distinct monomers, those polymers are referred to as copolymers. Next, we will look at how copolymers are classified. If a chemist is synthesizing a polymer utilizing two distinct starting monomers there are several possible structures, as shown in the figure below. The four basic structures are random, alternating, block, and graft. If the two monomers are randomly ordered then the copolymer is, not surprisingly, referred to as a random copolymer. In an **alternating copolymer**, each monomer is alternated with the other to form an ABABABA... pattern. Examples are styrene butadiene rubber

In **block copolymers**, more complex repeating structures are possible, for example AAABBBAAABBBAAA... Example is polystyrene-b-poly(methyl methacrylate) (where b = block)

Graft copolymers are created by attaching chains of a second type of monomer on the backbone chain of a first monomer type. One of the better-known examples of a graft polymer is high impact polystyrene, which consists of a polystyrene backbone with polybutadiene grafted chains.



Classification Based on Molecular Forces

Elastomers: These are rubber-like solids weak interaction forces are present. For example, Rubber.

Elastomers (rubbers) are special polymers that are very elastic. They are lightly cross-linked and amorphous with a glass transition temperature well below room temperature. The intermolecular forces between the polymer chains are rather weak. The crosslinks completely suppress irreversible flow but the chains are very flexible at temperatures above the glass transition, and a small force leads to a large deformation. Thus, elastomers have a low Young's modulus and very high elongation at break when compared with other polymers. The term elastomer is often used interchangeably with the term rubber, although the latter is preferred when referring to vulcanized rubbers.

Elastomers can be classified into three broad groups: diene, non-diene, and thermoplastic elastomers.

Diene elastomers are polymerized from monomers containing two sequential double bonds. Typical examples are polyisoprene, polybutadiene, and polychloroprene.

Nondiene elastomers include, butyl rubber (polyisobutylene), polysiloxanes (silicone rubber), polyurethane (spandex), and fluoro-elastomers. Non-diene elastomers have no double bonds in the structure, and thus, crosslinking requires other methods than vulcanization such as addition of trifunctional monomers (condensation polymers), or addition of divinyl monomers (free radical polymerization), or copolymerization with small amounts of diene monomers like butadiene. **Thermoplastic elastomers** such as SIS (Styrene isoprene) and SBS (Styrene butadiene styrene) block copolymers and certain urethanes are thermoplastic and contain rigid (hard) and soft (rubbery) repeat units. When cooled from the melt state to a temperature below the glass transition temperature, the hard blocks phase separate to form rigid domains that act as physical crosslinks for the elastomeric blocks.

Manufacturing elastomeric parts is achieved in one of three ways: injection molding, transfer molding, or compression molding. The choice of the molding process depends on various factors, including the shape and size of the parts, the required tolerance, as well as the quantity, type of elastomer, and raw material cost. As with almost any material, selecting the right elastomeric product for the application requires consideration of many factors, including mechanical and physical service requirements, exposure to chemicals, operating temperature,

service life, manufacturability of the parts, and raw material and manufacturing cost.

Fibers:

Strong, tough, high tensile strength and strong forces of interaction are present. For example, nylon -6, 6. Synthetic fibers are manmade fibers produced from petroleum- or coal-derived polymers or from natural occurring materials by chemical modification. They are generally semicrystalline polymers that are extruded and drawn in a variety of cross-sectional shapes. The fibers are uniaxially oriented during the melt, dry, or wet spinning process, which give the fibers high tenacity and strength.

Commercially produced fibers can be classified as cellulosic and noncellulosic fibers. Cellulosics are derived from naturally occurring cellulose through chemical reactions and processing. The most important types of cellulose based synthetic fibers are cellulose acetate (Acetate), regenerated cellulose (Viscose Rayon), Cuprammonium Rayon (Bemberg), and saponified acetate (Rayon).

Common non-cellulosic fibers include Nylon (1931), Olefin (1949), Acrylic (1950), Polyester (1953) and Spandex (1959). Of these, Polyester, Nylon and Acrylic are the most important fibers accounting for more than 80% of the world fiber market.

Thermoplastics: These have intermediate forces of attraction. For example, polyvinyl chloride.

All the plastic materials which can be softened and melted by heating, but they set again when cool are called thermoplastics. Thermoplastic polymers can be very broadly classified as amorphous or crystalline. Most thermoplastics suitable for use as matrices for high performance composite exhibit some degree of crystallinity because this type of structure has better resistance to chemical attack by field, hydraulic oil and paint stripper. With regard to behaviour at elevated temperatures, polymers are classified as either thermoplastics or thermosetting. Thermoplastic polymers have linear and branched structures they soften when heated and harden when cooled. In contrast, thermosetting polymers once they have hardened, will not soften upon heating; their structures are cross-linked and network.

Many thermoplastic polymers are reinforced with fibers. Reinforcement is used to improve physical properties – specifically heat deflection temperature. Glass fibers are the most

commonly used reinforcing material. The wear resistance and abrasion resistance of thermoplastic polymers are improved by the use of aramid reinforcing. Although fibers can be used with any thermoplastic polymer, the following are the most important.

Polycarbonate compounds using 10, 20, 30 and 40% glass fiber loading have their physical properties greatly improved.

Other polymers benefiting from the addition of glass fibers include polyphenylene sulfide, polypropylene and polyethersulfone.

Thermosetting polymers: These polymers greatly improve the material's mechanical properties. It provides enhanced chemical and heat resistance. For example, phenolics, epoxies, and silicones. Thermosetting Polymers are the type of polymers where the macromolecular chains tend to bond with one another forming the cross-linked 3D network. These polymers are also known as Thermosetting plastics or Thermosets. The definition of the word Thermosetting translates to a term which means setting permanently upon heating. Thus the Thermosetting Polymers get the hard texture after they are exposed to heating to their pre-Thermoset form.

The Thermosetting Polymers tend to have a cross-linked 3D structure. The chemical and physical properties of polymers are dependent on components behind the creation of polymers. Some of the fundamental properties of the Thermosetting Polymers are as follows. Thermosetting plastics tend to be heat resistant. However, when high intensity of heat is applied, they tend to decompose before they reach the melting point. The Thermosetting Polymers are brittle in nature owing to loss of elasticity when they are heated. Once cured or moulded, these polymers cannot be re-shaped through application of heat.

Due to thermosets having unique properties, they are highly useful for some of the daily requirements. The uses of the Thermosetting Polymers are as follows.

They are used for manufacturing permanent parts in a wide array of industries. Thermosets are used for producing electrical goods as well as components such as panels and insulators.

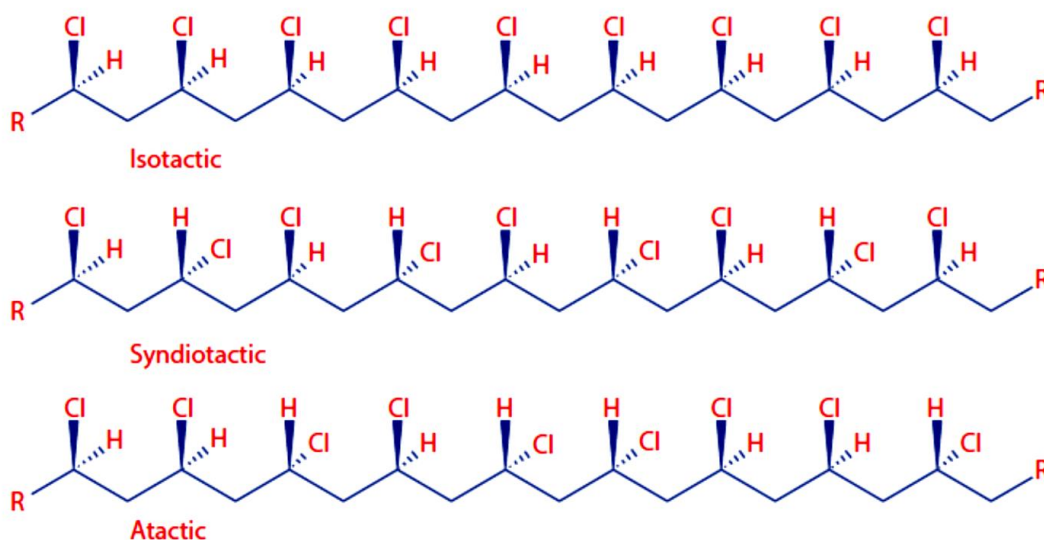
Thermosets are used for manufacturing construction equipment panels. Since they tend to be heat resistant, thermosets are used for manufacturing heat shields. In automobiles, thermosets are utilised for producing brake pistons. Thermosets are also used for various agricultural equipments that includes motors and feeding troughs.

The Examples of Thermosetting Polymers: The various examples of Thermosetting Polymers

include Bakelite, Epoxy Resin, Melamine Resin, Duroplast, and Urea-Formaldehyde. These different Thermosetting Polymers are used in a variety of applications across a wide range of industries.

Tacticity of polymers

In the early 1950s, Nobel laureate Giulio Natta used stereospecific coordination catalysts to produce stereospecific isomers of PP. Natta used the term tacticity to describe the different possible structures. As shown in Figure below the isomer corresponding to the arrangement DDDDDD or LLLLLL is called isotactic (same). The isomer corresponding to the DLDLDL alternating structural arrangement about carbon is called syndiotactic (alternating). The isomer arrangement that corresponds to some mix of stereo arrangements about the chiral carbons is called atactic (having nothing to do with). As noted above, the differences in stereoregularity around the chiral carbon influence the physical properties of the polymers. Thus, those with isotactic or syndiotactic arrangements are more apt to form compact crystalline arrangements, and those with atactic stereoregularity are more apt to form amorphous arrangements. Isotactic PP (i-PP) has an MP of about 160°C and it is highly crystalline whereas atactic PP (a-PP) melts at about 75°C and is amorphous. The term eutactic is used to describe either an isotactic or syndiotactic polymer or a mixture of both.



Composites

A composite is a material which is made up of two or more distinct (i.e. macroscopic, not microscopic) materials. A familiar composite is concrete, which is basically made up of sand and cement. Polymer composites are plastics within which fibers or particles are embedded. The plastic is known as the matrix, and the fibers or particles, dispersed within it, are known as the reinforcement. The reinforcement is usually stiffer than the matrix, thus stiffening the composite material. This stiffer reinforcement will usually be laid in a particular direction, within the matrix, so that the resulting material will have different properties in different directions.

MATRIX: There are a large number of classes of polymer that can be utilized in fabricating a composite material. The selection of a polymer type is a function of many items including application, cost, fiber type, manufacturing method, supply etc.

Polymer matrix composites (PMCs) are materials that use a polymer based resin as a matrix material with some form of fibers embedded in the matrix, as reinforcement. Both thermosetting and thermoplastic polymers can be used for the matrix material. PMCs are designed to transfer loads between fibers of a matrix. Some of the advantages with PMCs include their lightweight, high stiffness and their high strength along the direction of their reinforcements. Other advantages are good abrasion resistance and good corrosion resistance.

The function of the matrix in PMCs is to bond the fibers together and transfer loads between them. PMCs matrices are typically either thermosets or thermoplastics. Thermosets are by far the predominant type in use today. Thermosets are subdivided into several resin systems including epoxies, phenolics, polyurethanes, and polyimides. Of these, epoxy systems currently dominate the advanced composite industry.

Thermoset resins require addition of a curing agent or hardener and impregnation onto a reinforcing material, followed by a curing step to produce a cured or finished part. Once cured, the part cannot be changed or reformed, except for finishing. Some of the more common thermosets include epoxy, polyurethanes, phenolic and amino resins, bismaleimides (BMI, polyimides), polyamides.

Thermoplastics currently represent a relatively small part of the PMC industry. They are typically supplied as nonreactive solids (no chemical reaction occurs during processing) and

require only heat and pressure to form the finished part. Unlike the thermosets, the thermoplastics can usually be reheated and reformed into another shape, if desired.

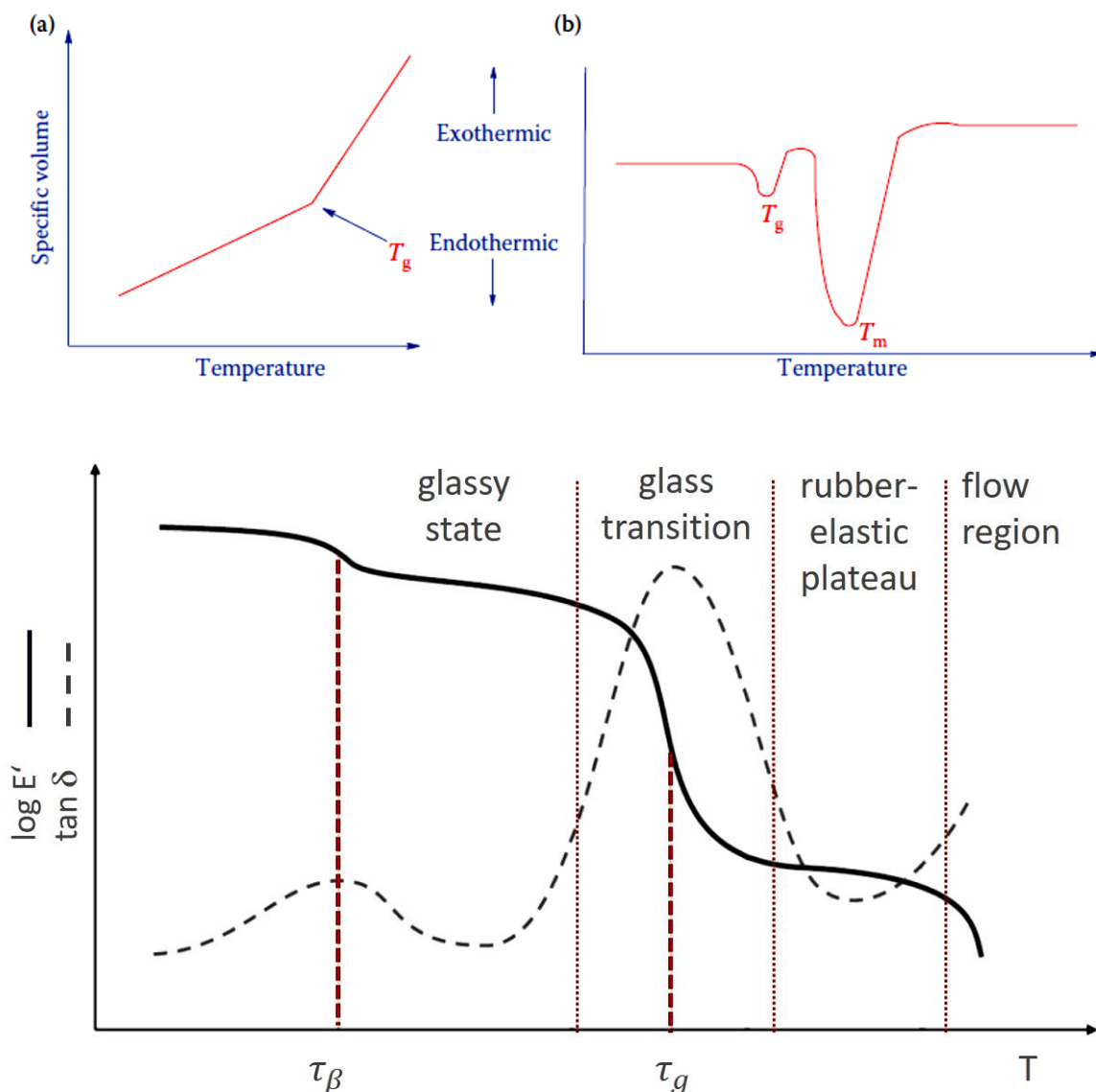
Dispersed Materials

Fiber-reinforced PMCs contain about 60 percent reinforcing fiber by volume. The fibers that are commonly found and used within PMCs include fiberglass, graphite and aramid. Fiberglass has a relatively low stiffness at the same time exhibits a competitive tensile strength compared to other fibers. The cost of fiberglass is also dramatically lower than the other fibers which are why fiberglass is one of the most widely used fiber. The reinforcing fibers have their highest mechanical properties along their lengths rather than their widths. Thus, the reinforcing fibers may be arranged and oriented in different forms and directions to provide different physical properties and advantages based on the application.

Carbon Nanotubes: Unlike fiber-reinforced PMCs, nonmaterial's reinforced PMCs are able to achieve significant improvements in mechanical properties at much lower (less than 2% by volume) loadings. Carbon nanotubes in particular have been intensely studied due to their exceptional intrinsic mechanical properties and low densities. In particular carbon nanotubes have some of the highest measured tensile stiffness and strengths of any material due to the strong covalent sp^2 bonds between carbon atoms. However, in order to take advantage of the exceptional mechanical properties of the nanotubes, the load transfer between the nanotubes and matrix must be very large. Like in fiber-reinforced composites, the size dispersion of the carbon nanotubes significantly affects the final properties of the composite.

Glass transition temperature

Polymers have a temperature boundary above which it is soft flexible and rubbery and below which it becomes hard, brittle and glass. This temperature below which a polymer is hard and above which it is soft, is called the glass transition temperature (T_g). The hard, brittle state is known as the glass state and the soft flexible state, as the rubbery state. On further heating the polymer becomes a highly viscous liquid and starts flowing. This state is known as viscous fluid state. The temperature at which this transition takes place is known as its flow temperature (T_f).



Factors influencing the glass temperature

The presence or absence of segmental and molecular motions decides whether a polymer is in a solid, rubbery or molten state. The nature and the magnitude of these motions depend on the size and geometry of the polymeric chain, flexibility of the chain segments etc.

The polymer has a greater crystallizability, if molecular geometry permits formation of a definite molecular orientation leading to a three-dimensional order. That is why polymers with a symmetrical structure are crystalline. Polymers with irregular chain backbone or randomly placed side groups are non-crystalline or amorphous. Chain mobilities are easier in amorphous polymers than in crystalline polymers.

The linear polymer chains made of C—C, C—O or C—N single bonds have a high degree of freedom of rotation. The presence of aromatic ring or cyclic structure in the chain backbone hinders the rotation. The presence of bulky side groups on the backbone carbon atoms also hinders the freedom for rotation. The higher the freedom to rotate higher is the chain mobility.

The intermolecular forces determine the magnitude of the molecular aggregates. In the case of hydrocarbon polymers, only Van der Waals forces act on the neighboring polymer chain and hence molecular aggregates are not that strong. Polymer chains can slip past easily. Polymer chain containing polar groups like $>C=O$, $>N-H$ etc are held together by dipolar attraction and intermolecular hydrogen bonding and so are unable to move that easily.

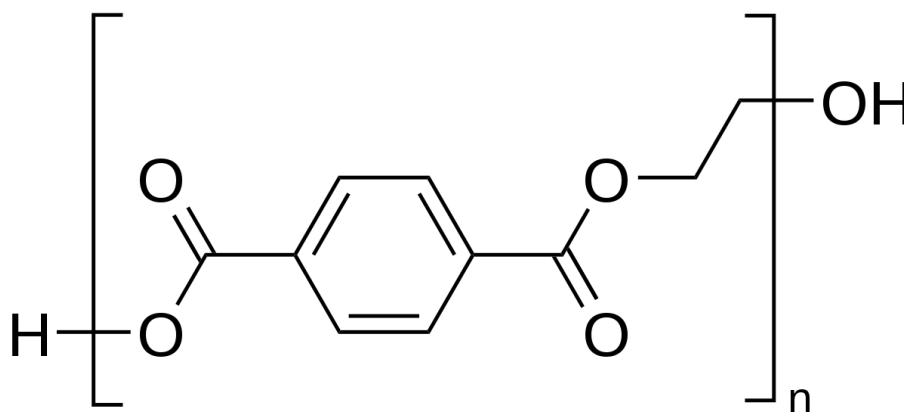
Hindrance to segmental rotation and intermolecular cohesive forces restricts the chain mobility and they are held down to positions of minimum potential energy. The thermal energy of the polymer (which naturally increases with temperature) however activates thermal vibrations of the chain elements. As the temperature is increased, these vibrations are able to get over the hindrance to segmental rotation and the intermolecular cohesion. When the restrictions are overcome at appropriate temperatures, segmental and molecular motion set in. The onset of these motions determines the T_g as well as the T_m of the polymer. Hence we see that the glass transition temperature and the melting temperature of a polymer depend on chain geometry, chain flexibility and molecular aggregates.

Examples

1. Polyethylene is made up of the repeating unit has a T_g value of -125°C . In this case T_g is quite low because (i) strong cohesive forces are absent (ii) the substituent group on carbon atoms is only hydrogen which is not bulky at all.
2. Nylon 6, a polyamide has a high T_g (50°C). It is due to the presence of a large number of polar groups in the molecules, leading to strong intermolecular hydrogen bonding between $>C=O$ and $>N-H$ groups.
3. The effect of the side group on chain mobility and hence on glass transition temperature can be studied by taking the examples of polystyrene and polymethyl styrene and also of poly methylmethacrylate.

The presence of $-\text{CH}_3$ group in polymethyl styrene and poly methylmethacrylate comes in a way of free rotation around $\text{C}-\text{C}$ bond of the chain backbone and hence hinders the chain mobility, resulting in an increase of around 70°C and 100°C in their T_g values over polystyrene and polymethylacrylate respectively.

4. In the case of polyethylene terephthalate the presence of aromatic rings in the chain backbone increases the inflexibility of the chains and T_g value is high (69°C).



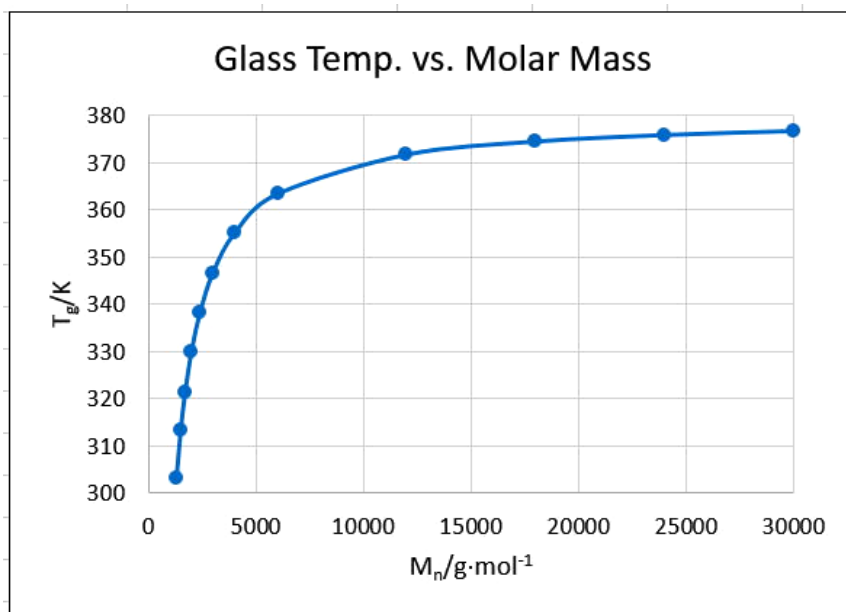
Glass transition temperature and molecular weight

The glass transition temperature of a polymer is influenced by its molecular weight at least up to a value of 20000. Beyond this the effect of the molecular weight is not pronounced. The following two mathematical relationships have been established between the two.

$$T_g = T_g^\infty - \frac{K}{M_n}$$

$$\frac{1}{T_g} = \frac{1}{T_g^\infty} - \frac{A}{M_n}$$

Where T_g^∞ is the glass transition temperature at infinite molecular weight, K and A are arbitrary constants.



Now let us see how the molecular weight can effect the T_g values. We know that the polymeric chains made of hundreds of monomeric units. Now the chain segments that are away from the chain ends have a restricted mobility whereas the two ends segments containing chain ends have more freedom for motion. For a given weight of polymer a low molecular weight sample will have more chain end segments than a high molecular weight sample. The larger the number of chain end segments, the larger will be the effective segmental motion. Thus the T_g will be lower for low molecular weight polymers.

Glass transition temperature and melting points.

Many attempts have been made to study the relationship between the glass transition temperatures and melting point. Based on experimental observations, T_g and T_m (in degree Kelvin) have been shown to be related as.

$$T_g = \frac{1}{2}T_m \text{ (for symmetrical polymers)}$$

$$T_g = \frac{2}{3}T_m \text{ (for unsymmetrical polymers)}$$

A combined version of these two equations, irrespective of molecular symmetry can be shown

$$\frac{1}{2} < \frac{T_g}{T_m} < \frac{2}{3}$$

Effect of chemical structure

The effect of the nature of the chain repeat unit on T_g are pronounced as it is related to intermolecular forces, chain stiffness and symmetry. Probably the most important factor among these is hindrance to free rotation along the polymer chain due to the presence of bulky side groups. The effect can be visualized by comparing the glass transition temperature of the following polymers.

Polybutadiene $-85\text{ }^\circ\text{C}$

Styrene-butadiene copolymer $-55\text{ }^\circ\text{C}$

Polystyrene $+100\text{ }^\circ\text{C}$

Poly(methyl styrene) $+150\text{ }^\circ\text{C}$