

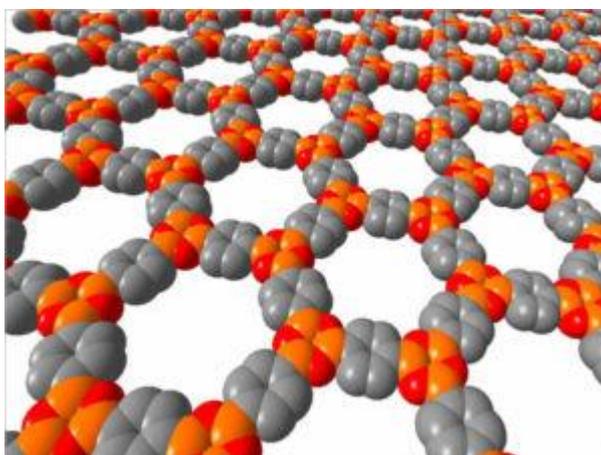
# Polymer Chemistry

## Classification of Polymers

Look around and you will see Polymers are everywhere. From the plastic bottle, you carry to school, to the silicone rubber tips on your favourite earphones. The nylon and polyester in your sneakers. Not only inanimate objects, many proteins in your body are polymers. So let us now look into the classification of polymers.

## Polymers

The word “Polymer” is derived from two Greek words, ‘Poly’ that means many (numerous) and ‘Mer’ which means units. In basic terms, a polymer is a long-chain molecule that is composed of a large number of *repeating units* of identical structure. These identical structures, we understand as a unit made up of two or more molecules, join together to form a long chain.



Simply stated, a polymer is a long-chain molecule that is composed of a large number of *repeating units* of identical structure. Those monomers can be simple — just an atom or two or three — or they might be complicated ring-shaped structures containing a dozen or more atoms.

## Classification of polymers

Since Polymers are numerous in number with different behaviours and can be naturally found or synthetically created, they can be classified in various ways. The following below are some basic ways in which we classify polymers:

### 1] Classification Based on Source

The first classification of polymers is based on their source of origin, Let's take a look.

#### (i) Natural polymers

The easiest way to classify polymers is their source of origin. Natural polymers are polymers which occur in nature and are existing in natural sources like plants and animals. Some common examples are Proteins (which are found in humans and animals alike), Cellulose and Starch (which are found in plants) or Rubber (which we harvest from the latex of a tropical plant).

## **(ii) Synthetic polymers**

Synthetic polymers are polymers which humans can artificially create/synthesize in a lab. These are commercially produced by industries for human necessities. Some commonly produced polymers which we use day to day are Polyethylene (a mass-produced plastic which we use in packaging) or Nylon Fibers (commonly used in our clothes, fishing nets etc.)

## **(iii) Semi-Synthetic polymers**

Semi-Synthetic polymers are polymers obtained by making modification in natural polymers artificially in a lab. These polymers formed by chemical reaction (in a controlled environment) and are of commercial importance. Example: Vulcanized Rubber (Sulphur is used in cross bonding the polymer chains found in natural rubber) Cellulose acetate (rayon) etc.

Learn different types of Polymerization here.

## 2] Classification Based on Structure of Polymers

Classification of polymers based on their structure can be of three types:

### **(i) Linear polymers:**

These polymers are similar in structure to a long straight chain which identical links connected to each other. The monomers in these are linked together to form a long chain. These polymers have high melting points and are of higher density. A common example of this is PVC (Poly-vinyl chloride). This polymer is largely used for making electric cables and pipes.

### **(ii) Branch chain polymers:**

As the title describes, the structure of these polymers is like branches originating at random points from a single linear chain. Monomers join together to form a long straight chain with some branched chains of different lengths. As a result of these branches, the polymers are not closely packed together. They are of low density having low melting points. Low-density polyethene (LDPE) used in plastic bags and general purpose containers is a common example

### **(iii) Crosslinked or Network polymers:**

In this type of polymers, monomers are linked together to form a three-dimensional network. The monomers contain strong covalent bonds as they are composed of bi-functional and tri-functional in nature. These polymers are brittle and hard. ex:- Bakelite (used in electrical insulators), Melamine etc.

## 3] Based on Mode of Polymerisation

Polymerization is the process by which monomer molecules are reacted together in a chemical reaction to form a polymer chain (or three-dimensional networks). Based on the type of polymerization, polymers can be classified as:

### **i) Addition polymers:**

These type of polymers are formed by the repeated addition of monomer molecules. The polymer is formed by polymerization of monomers with double or triple bonds (unsaturated compounds). Note, in this process, there is no elimination of small molecules like water or alcohol etc (no by-product of the process). Addition polymers always have their empirical formulas same as their monomers. Example: ethene  $n(\text{CH}_2=\text{CH}_2)$  to polyethene  $-(\text{CH}_2-\text{CH}_2)_n-$ .

### **ii) Condensation polymers:**

These polymers are formed by the combination of monomers, with the elimination of small molecules like water, alcohol etc. The monomers in these types of condensation reactions are bi-functional or tri-functional in nature. A common example is the polymerization of Hexamethylenediamine and adipic acid. to give Nylon – 66, where molecules of water are eliminated in the process.

Read about Polymers of Commercial Importance.

## 4] Classification Based on Molecular Forces

*Intramolecular forces* are the *forces* that hold atoms together within a *molecule*. In Polymers, strong covalent bonds join atoms to each other in individual polymer molecules. *Intermolecular forces* (between the molecules) attract polymer molecules towards each other.

Note that the properties exhibited by solid materials like polymers depend largely on the strength of the forces between these molecules. Using this, Polymers can be classified into 4 types:

### **i) Elastomers:**

Elastomers are rubber-like solid polymers, that are elastic in nature. When we say elastic, we basically mean that the polymer can be easily stretched by applying a little force.

The most common example of this can be seen in rubber bands(or hair bands). Applying a little stress elongates the band. The polymer chains are held by the weakest intermolecular forces, hence allowing the polymer to be stretched. But as you notice removing that stress also results in the rubber band taking up its original form. This happens as we introduce crosslinks between the polymer chains which help it in retracting to its original position, and taking its original form. Our car tyres are made of Vulcanized rubber. This is when we introduce sulphur to cross bond the polymer chains.

### **ii) Thermoplastics:**

Thermoplastic polymers are long-chain polymers in which inter-molecules forces (Van der Waal's forces) hold the polymer chains together. These polymers when heated are softened (thick fluid like) and hardened when they are allowed to cool down, forming a hard mass. They do not contain any cross bond and can easily be shaped by heating and using moulds. A common example is Polystyrene or PVC (which is used in making pipes).

### iii) Thermosetting:

Thermosetting plastics are polymers which are semi-fluid in nature with low molecular masses. When heated, they start cross-linking between polymer chains, hence becoming hard and infusible. They form a three-dimensional structure on the application of heat. This reaction is irreversible in nature. The most common example of a thermosetting polymer is that of Bakelite, which is used in making electrical insulation.

### iv) Fibres:

In the classification of polymers, these are a class of polymers which are a thread like in nature, and can easily be woven. They have strong inter-molecular forces between the chains giving them less elasticity and high tensile strength. The intermolecular forces may be hydrogen bonds or dipole-dipole interaction. Fibres have sharp and high melting points. A common example is that of Nylon-66, which is used in carpets and apparels.

The above was the general ways to classify polymers. Another category of polymers is that of Biopolymers. Biopolymers are polymers which are obtained from living organisms. They are biodegradable and have a very well defined structure. Various biomolecules like carbohydrates and proteins are a part of the category.

### Solved Example for You

Q: Which of these polymers occur naturally?

- a. Starch and nylon
- b. Cellulose and Starch
- c. Proteins and PVC
- d. Nylon and Proteins

Sol: The correct option is "B". On the basis of classification of polymers based on their sources, we know that Nylon and PVC are synthetic polymers. While starch and cellulose are naturally occurring polymers.

### Nomenclature

The terms polymer and macromolecule do not mean the same thing. A polymer is a substance composed of macromolecules. The latter usually have a range of molar masses (unit  $\text{g mol}^{-1}$ ), the distributions of which are indicated by dispersity ( $\mathcal{D}$ ). It is defined as the ratio of the mass-average molar mass ( $M_m$ ) to the number-average molar mass ( $M_n$ ) i.e.  $\mathcal{D} = M_m/M_n$ . Symbols for physical quantities or variables are in italic font but those representing units or labels are in roman font.

Polymer nomenclature usually applies to idealized representations meaning minor structural irregularities are ignored. A polymer can be named in one of two ways. Source-based nomenclature can be used when the monomer can be identified. Alternatively, more explicit structure-based nomenclature can be used when the polymer structure is proven. Where there is no confusion, some traditional names are also acceptable.

Whatever method is used, all polymer names have the prefix *poly*, followed by enclosing marks around the rest of the name. The marks are used in the order:  $\{[( )]\}$ . Locants indicate

the position of structural features, e.g., poly(4-chlorostyrene). If the name is one word and has no locants, then the enclosing marks are not essential, but they should be used when there might be confusion, e.g., poly(chlorostyrene) is a polymer whereas polychlorostyrene might be a small, multi-substituted molecule. End-groups are described with  $\alpha$ - and  $\omega$ -, e.g.,  $\alpha$ -chloro- $\omega$ -hydroxy-polystyrene.

## Homopolymers

Homopolymers are named using the name of the real or assumed monomer (the ‘source’) from which it is derived, e.g., poly(methyl methacrylate). Monomers can be named using IUPAC recommendations, or well-established traditional names. Should ambiguity arise, class names can be added.

polyalkylene:vinyloxirane (left) and polyether:vinyloxirane (right)

For example, the source-based name poly(vinyloxirane) could correspond to either of the structures shown. To clarify, the polymer is named using the polymer class name followed by a colon and the name of the monomer, i.e., class name:monomer name. Thus on the left and right, respectively, are polyalkylene:vinyloxirane and polyether:vinyloxirane.

## Copolymers

The structure of a copolymer can be described using the most appropriate of the connectives shown in Table 1. These are written in italic font.

Copolymer	Qualifier	Example
unspecified	<i>co</i> (C)	poly(styrene- <i>co</i> -isoprene)
statistical	<i>stat</i> (C)	poly[isoprene- <i>stat</i> -(methyl methacrylate)]
random	<i>ran</i> (C)	poly[(methyl methacrylate)- <i>ran</i> -(butyl acrylate)]
alternating	<i>alt</i> (C)	poly[styrene- <i>alt</i> -(maleic anhydride)]
periodic	<i>per</i> (C)	poly[styrene- <i>per</i> -isoprene- <i>per</i> -(4-vinylpyridine)]
block	<i>block</i> (C)	poly(buta-1,3-diene)- <i>block</i> -poly(ethene- <i>co</i> -propene)
graft <sup>a</sup>	<i>graft</i> (C)	polystyrene- <i>graft</i> -poly(ethylene oxide)

<sup>a</sup>The first name is that of the main chain.

## Non-linear polymers

Non-linear polymers and copolymers, and polymer assemblies are named using the italicized qualifiers in Table 2. The qualifier, such as *branch*, is used as a prefix (P) when naming a (co)polymer, or as a connective (C), e.g., *comb*, between two polymer names.

(Co)polymer	Qualifier	Example
blend	<i>blend</i> (C)	poly(3-hexylthiophene)- <i>blend</i> -polystyrene
comb	<i>comb</i> (C)	polystyrene- <i>comb</i> -polyisoprene
complex	<i>compl</i> (C)	poly(2,3-dihydrothieno[3,4- <i>b</i> ][1,4]dioxine)- <i>compl</i> - poly(vinylbenzenesulfonic acid) <sup>a</sup>
cyclic	<i>cyclo</i> (P)	<i>cyclo</i> -polystyrene- <i>graft</i> -polyethylene
branch	<i>branch</i> (P)	<i>branch</i> -poly[(1,4-divinylbenzene)- <i>stat</i> -styrene]
network	<i>net</i> (C or P)	( <i>net</i> -polystyrene)- <i>ipn</i> -[ <i>net</i> -poly(methyl acrylate)]
interpenetrating network	<i>ipn</i> (C)	( <i>net</i> -polystyrene)- <i>ipn</i> -[ <i>net</i> -poly(methyl acrylate)]
semi-interpenetrating polymer network	<i>sipn</i> (C)	( <i>net</i> -polystyrene)- <i>sipn</i> -polyisoprene
star	<i>star</i> (P)	<i>star</i> -polyisoprene

<sup>a</sup>In accordance with IUPAC organic nomenclature, square brackets indicate the nature of the locant sites in fused ring systems.<sup>[8]</sup>

## Polymer Chemistry: Intermolecular Forces

The intermolecular forces for polymers are the same as for small molecules. Because polymer molecules are so large, though, the magnitude of their intermolecular forces can vastly exceed those between small molecules. The presence of strong intermolecular forces is one of the main factors leading to the unique physical properties of polymers.

### *Dispersion Forces*

Dispersion forces are due to instantaneous dipoles that form as the charge clouds in the molecules fluctuate. Dispersion forces, the weakest of the intermolecular forces, are present in all polymers. They are the only forces possible for nonpolar polymers such as polyethylene.

Dispersion forces depend on the polarizability of a molecule. Larger molecules generally are more polarizable, so large polymers with high molecular weights can have significant

dispersion forces. Ultra high molecular weight polyethylene (UHMWPE), which has a molecular weight in excess of 3,000,000 g/mole, is used to make bulletproof vests.

### *Dipole-Dipole Forces*

Dipole-dipole forces result from the attraction between polar groups, such as those in polyesters and vinyl polymers with chlorine pendant groups.

### *Hydrogen Bonding*

Hydrogen bonding can take place when the polymer molecule contains -OH or -NH groups. Hydrogen bonding is the strongest of the intermolecular forces. Polymers such as poly(vinyl alcohol) and polyamides are hydrogen bonded.

### **Texture of polymers:**

Polymer is on a size level larger than the crystallite but smaller than the spherulite. It is based on the data from x-ray diagrams at small angles, combined with crystallite dimensions measured from wide-angle x-ray patterns. The width of these elementary fibrils is proportional to the width of the crystallites. The amount of regularity of crystallite positions along an elementary fibril and the length of the repeat period are both variable; they depend on the manner of original nucleation and the thermal treatment after nucleation. The length of the long period is a function of the length of the crystallites. These elementary fibrils can pack closely to form a higher state of ordered texture. The amount of close packing is variable; it is optimal after a relaxation treatment.

What are 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 ethene or 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 of the 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 comprise of 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 bioplastics and those made from petroleum as they are said to be non-biodegradable.

Types of Synthetic Polymers with Examples-

There are various synthetic polymers developed so far. Let us study in brief about few of the synthetic polymers used in everyday life-

- Nylon-
  - 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.

Polyvinyl Chloride –

- Polyvinyl Chloride or PVC is third-most majorly produced plastics coming after polypropylene and polyethylene. This PVC is used for construction purposes as it is known to be stronger and cheaper than other alternatives like copper or iron. PVC is also used in the clothing, electrical cable insulation including many other applications replacing rubber.

Low-Density Polyethylene–

- The Low-Density Polyethylene polymers are the most common kind of synthetic polymers, which are widely used in households. LDPE is a kind of thermoplastic which is prepared from the monomer called ethylene.

Polypropylene–

- Polypropylene also called as polypropene is a kind of thermoplastic synthetic polymer which is used in variety of applications such as packaging, labeling, stationery, textiles, plastics and in reusable containers, laboratory equipments and etc.

Some of the other examples includes Thermoplastic Polyurethane, Teflon, Polystyrene, High Density Polyethylene, Neoprene, etc.

Uses of Synthetic Polymers

Some of the uses are given below-

1. The polymer called Polyethylene is used in plastic bags and film wraps.
2. Polyethylene is utilized in the bottles, electrical insulation, toys, etc
3. Polyvinyl Chloride( PVC) is used in siding, pipes, flooring purposes.
4. The synthetic polymer Polystyrene is used in cabinets and in packaging.
5. Polyvinyl acetate is used in adhesives and latex paints.

There are two basic types of **polymerization**, chain-reaction (or addition) and step-reaction (or condensation) **polymerization**. One of the most common types of **polymer** reactions is chain-reaction (addition) **polymerization**. This type of **polymerization** is a three step **process** involving two chemical entities

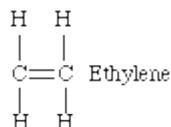
### **Polymerization Reactions**

The chemical reaction in which high molecular mass molecules are formed from monomers is known as polymerization. There are two basic types of polymerization, chain-reaction (or addition) and step-reaction (or condensation) **polymerization**.

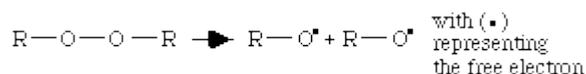
i) Chain-Reaction Polymerization

One of the most common types of polymer reactions is chain-reaction (addition) polymerization. This type of polymerization is a three step process involving two chemical entities. The first, known simply as a monomer, can be regarded as one link in a polymer chain. It initially exists as simple units. In nearly all cases, the monomers have at least one

carbon-carbon double bond. Ethylene is one example of a monomer used to make a common polymer.



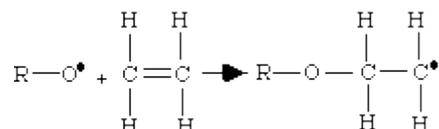
The other chemical reactant is a catalyst. In chain-reaction polymerization, the catalyst can be a free-radical peroxide added in relatively low concentrations. A free-radical is a chemical component that contains a free electron that forms a covalent bond with an electron on another molecule. The formation of a free radical from an organic peroxide is shown below:



In this chemical reaction, two free radicals have been formed from the one molecule of  $\text{R}_2\text{O}_2$ . Now that all the chemical components have been identified, we can begin to look at the polymerization process.

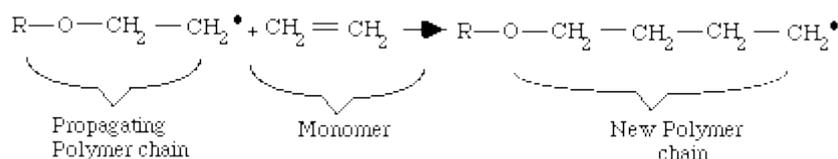
### Step 1: Initiation

The first step in the chain-reaction polymerization process, initiation, occurs when the free-radical catalyst reacts with a double bonded carbon monomer, beginning the polymer chain. The double carbon bond breaks apart, the monomer bonds to the free radical, and the free electron is transferred to the outside carbon atom in this reaction.



### Step 2: Propagation

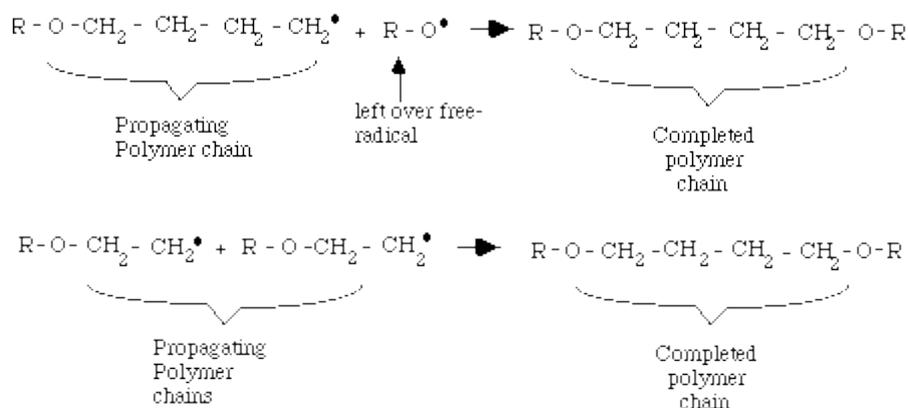
The next step in the process, propagation, is a repetitive operation in which the physical chain of the polymer is formed. The double bond of successive monomers is opened up when the monomer is reacted to the reactive polymer chain. The free electron is successively passed down the line of the chain to the outside carbon atom.



This reaction is able to occur continuously because the energy in the chemical system is lowered as the chain grows. Thermodynamically speaking, the sum of the energies of the polymer is less than the sum of the energies of the individual monomers. Simply put, the single bonds in the polymeric chain are more stable than the double bonds of the monomer.

### Step 3: Termination

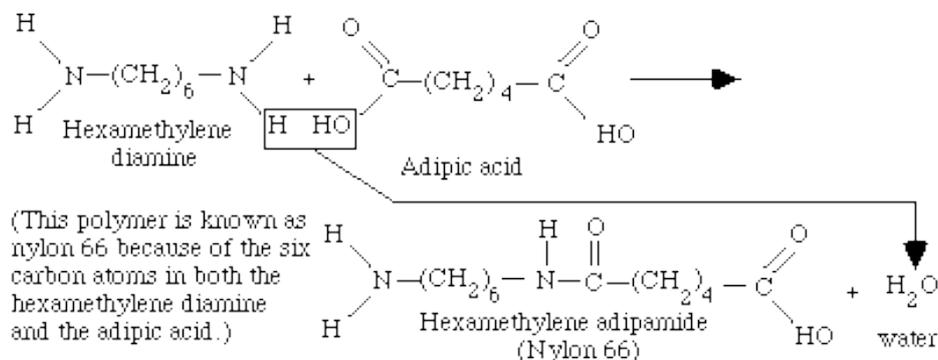
Termination occurs when another free radical (R-O $\cdot$ ), left over from the original splitting of the organic peroxide, meets the end of the growing chain. This free-radical terminates the chain by linking with the last CH<sub>2</sub> $\cdot$  component of the polymer chain. This reaction produces a complete polymer chain. Termination can also occur when two unfinished chains bond together. Both termination types are diagrammed below. Other types of termination are also possible.



This exothermic reaction occurs extremely fast, forming individual chains of polyethylene often in less than 0.1 second. The polymers created have relatively high molecular weights. It is not unusual for branches or cross-links with other chains to occur along the main chain.

### ii) Step-Reaction Polymerization

Step-reaction (condensation) polymerization is another common type of polymerization. This polymerization method typically produces polymers of lower molecular weight than chain reactions and requires higher temperatures to occur. Unlike addition polymerization, step-wise reactions involve two different types of di-functional monomers or end groups that react with one another, forming a chain. Condensation polymerization also produces a small molecular by-product (water, HCl, etc.). Below is an example of the formation of Nylon 66, a common polymeric clothing material, involving one each of two monomers, hexamethylene diamine and adipic acid, reacting to form a dimer of Nylon 66.



At this point, the polymer could grow in either direction by bonding to another molecule of hexamethylene diamine or adipic acid, or to another dimer. As the chain grows, the short chain molecules are called oligomers. This reaction process can, theoretically, continue until no further monomers and reactive end groups are available. The process, however, is relatively slow and can take up to several hours or days. Typically this process breeds linear

chains that are strung out without any cross-linking or branching, unless a tri-functional monomer is added.

According to IUPAC, the functionality of a monomer is defined as the number of bonds that a monomer's repeating unit forms in a polymer with other monomers. Thus in the case of a functionality of  $f=2$  a linear polymer is formed by polymerizing (a thermoplastic). Monomers with a functionality  $f \geq 3$  lead to a branching point, which can lead to cross-linked polymers (a thermosetting polymer). Mono-functional monomers do not exist as such molecules lead to a chain termination.

From the average functionality of the used monomers the reaching of the gel point can be calculated as a function of reaction progress. Side reactions may increase or decrease the functionality.

However, IUPAC definition and the use of the term in organic chemistry differ with respect to the functionality of a double bond. In polymer chemistry, a double bond possesses a functionality of two (because two points of contact for further polymer chains are present, on each of the two adjacent carbon atoms), while in organic chemistry the double bond is a functional group and thus has a functionality of one.

**The degree of polymerization, or DP,** is the number of monomeric units in a macromolecule or polymer or oligomer molecule.

For a homopolymer, there is only one type of monomeric unit and the *number-average* degree of polymerization is given by, where  $M_n$  is the number-average molecular weight and  $M_0$  is the molecular weight of the monomer unit. For most industrial purposes, degrees of polymerization in the thousands or tens of thousands are desired. This number does not reflect the variation in molecule size of the polymer that typically occurs; it only represents the mean number of monomeric units.

Some authors, however, define DP as the number of repeat units, where for copolymers the repeat unit may not be identical to the monomeric unit. For example, in nylon-6,6, the repeat unit contains the two monomeric units  $\text{—NH(CH}_2\text{)}_6\text{NH—}$  and  $\text{—OC(CH}_2\text{)}_4\text{CO—}$ , so that a chain of 1000 monomeric units corresponds to 500 repeat units. The degree of polymerization or chain length is then 1000 by the first (IUPAC) definition, but 500 by the second.

### **Glass Transition Temperature (T<sub>g</sub>) Vs Melting Temperature (T<sub>m</sub>)**

At the molecular level, at T<sub>g</sub>, the chains in amorphous (i.e., disordered) regions of the polymer gain enough thermal energy to begin sliding past one another at a noticeable rate. The temperature where entire chain movement occurs is called the melting point (T<sub>m</sub>) and is greater than the T<sub>g</sub>. Glass Transition is a property of the amorphous region while melting is the property of crystalline region

1. Below T<sub>g</sub>, there exists disordered amorphous solid where chain motion is frozen and molecules start wiggling around above T<sub>g</sub>. The more immobile the chain, the higher the value of T<sub>g</sub>.
2. While, below T<sub>m</sub> it is an ordered crystalline solid which becomes disordered melt above T<sub>m</sub>  
The operating temperature of polymers is defined by transition temperatures.

## Factors Affecting Tg

### Chemical Structure

- **Molecular Weight** – In straight chain polymers, increase in MW leads to decrease in chain end concentration resulting in decreases free volume at end group region – and increase in Tg
- **Molecular Structure** - Insertion of bulky, inflexible side group increases Tg of material due to decrease in mobility,
- **Chemical cross-linking** - Increase in cross-linking decreases mobility leads to decrease in free volume and increase in Tg
- **Polar groups** - Presence of polar groups increases intermolecular forces; inter chain attraction and cohesion leading to decrease in free volume resulting in increase in Tg.

### Addition of Plasticizers

Addition of plasticizer increases the free volume in polymer structure (Plasticizer gets in between the polymer chains and spaces them apart from each other). This results in polymer chains sliding past each other more easily. As a result, the polymer chains can move around at lower temperatures resulting in decrease in Tg of a polymer

### Water or moisture content

Increase in moisture content leads formation of hydrogen bonds with polymeric chains increasing the distance between polymeric chains. And, hence increases the free volume and decreases Tg.

### Effect of entropy and enthalpy

The value of entropy for amorphous material is higher and low for crystalline material. If value of entropy is high, then value of Tg is also high. Pressure and free volume increase in pressure of surrounding leads to decrease in free volume and ultimately high Tg.

Other factors like branching, alkyl chain length, bond interaction, flexibility of polymer chain, film thickness etc. also have significant impact on glass transition temperature of polymers.

Find commercial grades matching your thermal properties target using "**Property Search - Glass Transition Temperature**" filter in Omnexus Plastics Database.