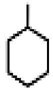
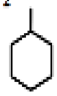
Basic concepts of polymer science

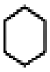
(1) Polymer: It is a large molecule built up by the repetition of small, simple chemical units. In some cases the repetition is linear, much as a chain is built up from its links. In other cases chains are branched or interconnected to form three dimensional networks. The repeat unit of polymer is usually equivalent or nearly equivalent to the monomer, or starting material from which the polymer is formed. The repeat unit of poly (vinyl chloride) is—CH2CHCl—; its monomer is vinyl chloride, CH2 = CHCl Table below
The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerization (DP). The DP is also defined as the number of repetitions of mers in a polymer chain. Mathematically,

$$DP = \frac{molecular\ weight\ of\ polymer}{molecular\ weight\ of\ single\ monomer}$$

The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the DP.
As an example, poly (vinyl chloride), a polymer of DP 1000 has a molecular weight of 63_1000 = 63,000. Most high polymers useful for plastics, rubbers, or fibres have molecular weights between 10,000 and 1,000,000. The molecular weight increases with the size of the molecule. The molecules having low DP are called oligomers الاولغيمرات, the oligo meaning few. Usually, the term polymer is used for macromolecule, i.e. alarge size molecule.

Table 17.3 Some linear high polymers, their monomers and their repeat units

Polymer	*Monomer*	*Repeat unit*
Polyethylene	$CH_2 = CH_2$	$—CH_2CH_2—$
Poly (vinyl chloride)	$CH_2 = CHCl$	$—CH_2CHCl$
Polyisobutylene	$CH_2 = C(CH_3)_2$	$—CH_2—C(CH_3)_2—$
Polystyrene[1]	$CH_2 = CH$ 	$—CH_2—CH—$ 
Poly caprolactan (6-nylon)	$H—N(H)(CH_2)_5C(=O)—OH$	$—N(H)(CH_2)_5C(=O)—$
Polyisoprene (natural rubber)	$CH_2 = CH—C(CH_3)=CH_2$	$—CH_2CH = C(CH_3)—CH_2—$

1.  represents benezene ring, double bonds being omitted

When DP attains a critical value or the length of a polymer chain **attains** تحرز a **sufficient** كافي length, the properties of polymer starts to appear. With the increase in **DP**, the properties of a polymer become more and more **prominent**بارز, i.e. polymer size increases. Although, the molecular weight for most of the polymers ranges between 8,000 to 150,000 but higher molecular weights in the range of 108 are also in existence.

For example, C2H4 (ethylene) is a gas, its oligomers having DP in the range 3 to 20 are liquids. With the increase in DP their viscosity goes on increasing. The polymers of ethylene (C2H4) with DP in the range 25 to 40 are like gases and with DP in the range 50 to 60, they are like **waxes** شمع . When DP **increases less than 350**, **ethylene polymers become resins**. The effect of DP on softening temperature is shown in Fig. 17.9. From figure it is obvious that with the increase in DP, the softening temperature also increases, but when DP increases less than 1000, the rise in softening temperature is small.

The tensile strength increases with the molecular weight or DP. The viscosity also increases tensile strength rapidly in the initial stages but viscosity increases when molecular weight is large. **Impact strength also increases** with the increase in molecular weight (Fig. 17.10). Polymers with higher molecular weights **possess superior mechanical properties تمتلك خصائص ميكانيكية فائقة** but the fabrication becomes difficult due to higher viscosities. One has to make a **compromise حل وسط** between properties and processability for commercial range.

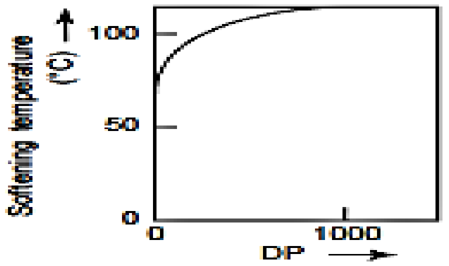


Fig. 17.9

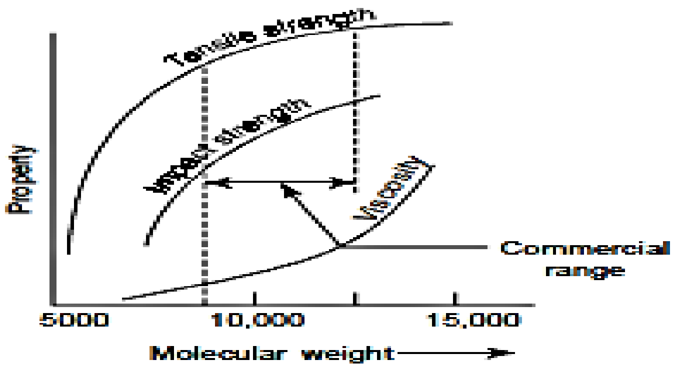


Fig. 17.10

(2) Polymerization Process: Polymerization, or the joining of large unit molecules called monomers, **utilizes يستخدم** the valence of the partially filled outer shell of the carbon atom (carbon has a valence of 4) to join smaller units together to form larger chains of molecules. Oxygen, sulphur, silicon, or nitrogen can be used to replace the carbon atom.

Two conditions must be met for polymerization to occur:

(i) a molecule must have at least two locations that have unsatisfiedغير مستقرة او مشبعة bonds, which will easily join with other molecules. This requirement means starting with a molecule that has a double bond, such as carbon. Because the carbon molecule has a double bond, each bond is a pair of shared electrons. If one of the bonds between the carbon atoms opens up, a single bond exists, leaving the other two electrons to share with other atoms. If another carbon atom passes by that has opened up its double bond, the two can join to form a chain. This procedure continues, producing a polymer chain, and is called **polymerization**. The process continues as long as the second condition is met.

(2)The second condition necessary for polymerization is that after each reaction, at least two open locations must remain. Many chains form within polymers. These chains form threads that entwine themselves around each other for strength.

Polymers can be strengthened by cross-linking. Cross linking occurs when the double bonds between atoms within a chain are broken and these atoms or molecules form, or link up, with **neighbouring atoms**الذرات المتجاورة. This linkage provides additional strength to the chain and reduces the slippage that occurs between molecules.

Slippage occurs when the polymer threads slide past each other when subjected to a load.

The properties of polymers also depend on the structure as well as the composition of the molecule. Two molecules with the same composition may form two different-configurations having different properties, such as propyl (1-propanol) and isopropyl (2-propanol) alcohol. These variations are called isomers.

Polymerization takes place through addition polymerization, copolymerization, or condensation polymerization.

In the polymerization process, a large unit molecule, the monomer, is added to another monomer to form a large chain, the polymer (referring to many parts), which has a number of repeated units, mers. Mers are the smallest units recognizable in the chain. The degree of polymerization is the number of repeating units that have identical structures within the chain formed by the polymer. Addition polymerization involves only one type of mer. Figure shows polymerization by addition.

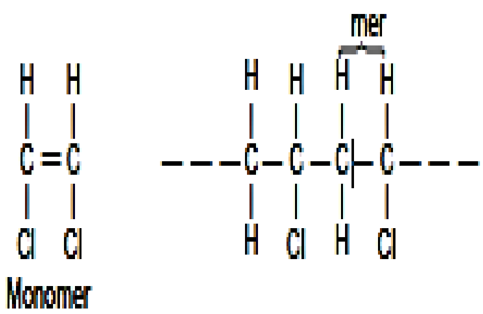


Fig. 17.11 Addition polymerization

In copolymerization, more than one molecule makes up the mer. Acrylonitride-butadiene-styrene (ABS) is an example of a copolymer. Figure 17.12 shows the copolymerization process for ABS polymers.

Condensation polymerization involves the chemical reaction of two or more chemicals to form a new molecule. This chemical reaction produces a condensate or nonpolymerizable by product, usually water. A

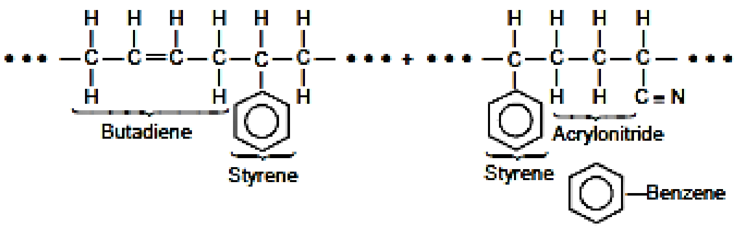


Fig. 17.12 Copolymerization

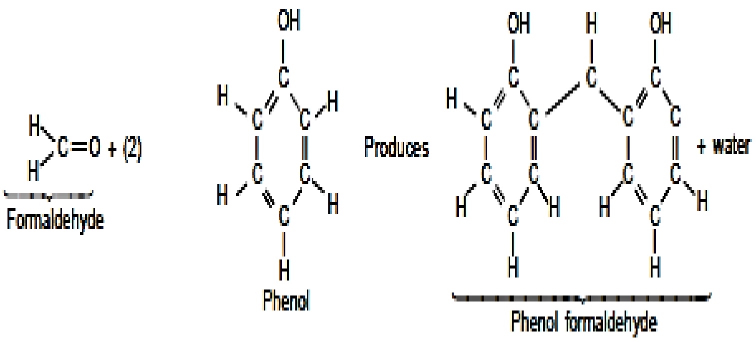


Fig 17.13 Condensation polymerization

catalyst is often required to start and maintain the reaction. It can also be used to control the reaction rate.
With some exceptions, polymers made in chain reactions often contain only carbon atoms in the main chain (homochain polymers), whereas polymers made in step reactions may have other atoms, originating in the monomer functional groups, as part of the chain (heterochain polymers).

(3) Molecular weight and its Distribution: In both chain and stepwise تدريجي polymerization, the length of a chain is determined by purely random events. In step reactions, the chain length is determined by the local availability of reactive groups at the ends of the growing chains. In radical polymerization, chain length is determined by the time during which the chain grows before it diffuses into the vicinity of a second free radical and the two react. In either case, the polymeric product contains molecules having many different chain lengths.
Extremely, large molecular weights (sometimes 'molecular mass', molar mass', and 'relative molar mass' are also used) are reported in polymers with very long chains. During the polymerization process in which these large macromolecules are synthesized from smaller molecules, not all polymer chains will grow to the same length; this results in a distribution of chain lengths or molecular weights. Normally, an average molecular weight is specified, which may be determined by the measurement of various physical properties, e.g. viscosity and osmotic pressure.
Average molecular weight can be defined through several ways. One can obtain the number average molecular weight M n by dividing the chains into a series

of size ranges and thus determining the number of fraction of chains within each size range. One can express this number average molecular weight as