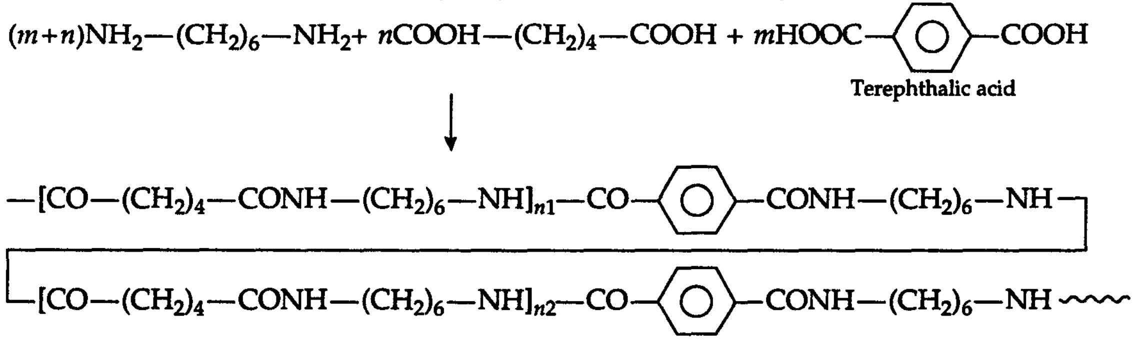
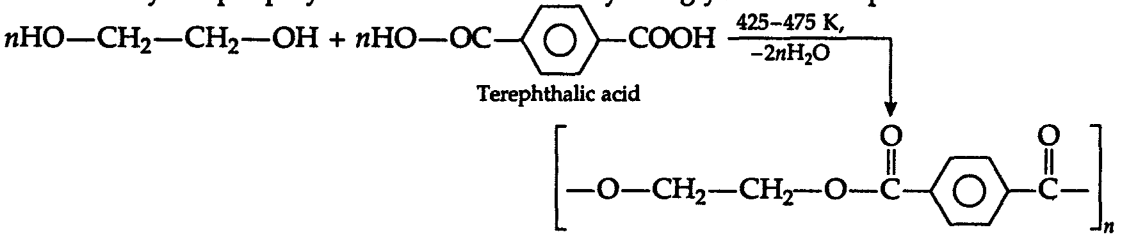
Nylon 66 is a tough and crystalline material, which has very low melting point 270°C. If the melting point of this polyamide has to be increased, the terephthalic acid is used to mix in the reaction mixture.

In this case, the copolycondensation reaction is involved and produces a copolymer polyamide with high melting point, and increased crystallinity. This product contains the aromatic nucleus, rather than purely aliphatic chains all through the chain backbone as :



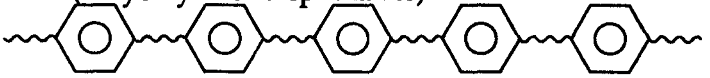
Similarly simple polyester is made from ethylene glycol and terephthalic acid as :



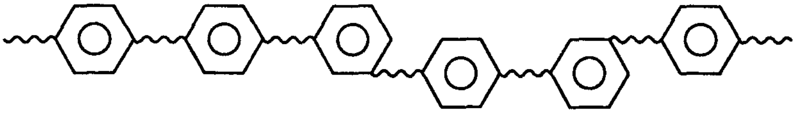
Polyethylene glycol terephthalate

The polyethylene glycol terephthalate is a highly crystalline and rigid copolymer, which is difficult to process due to the presence of a large number of para linked aromatic rings in its chain backbone. When a small amount of dimethyl isophthalate is mixed into the reaction mixture, it forms a copolymer or mixed polyester which consists of para linkages along with meta linkages in the structure. This mixed polyester also contains reduced chain rigidity and crystallinity.

Simple polyester (Polyethylene terephthalate)



Mixed polyester (Polyethylene terephthalate + dimethyl isophthalate)



(where ∿∿ = —COO—CH$_2$—CH$_2$—OCO—)

◆ TYPES OF COPOLYMERS

The copolymerisation involves two monomers. A variety of structures can be obtained even in the simplest case of copolymers. The five important types of existing copolymers are as :

(i) Statistical copolymers : When irregular propagation of monomers, A and B takes place the two units enter the chain in a statistical fashion, thus the statistical copolymers are formed. The most commonly encountered structure of this type is—

—(ABBAAAABAABBBA)—

(ii) Alternating copolymers : When equimolar quantities of two monomers are distributed in a regular alternating manner in the chain, the alternating copolymer is formed. For example

—(ABABABA)—

Many of the step-growth polymers are formed by the condensation of two (A – A), (B – B) type monomers. They could be considered as alternating copolymers but these are commonly treated as homopolymers with the repeat unit corresponding to the dimeric residue.

(iii) Block copolymers : The copolymers may also contain long sequences of one monomer joined to another sequence or block of the second. This produces a linear copolymer of form AA ~ AABBB ~ B, *i.e.*, an {A} {B} block, but other combinations are also **possible as :**

A B di block

A B A Tri block

B A B Tri block

Alternating block

Tappered block

Fig. 8. Block copolymers.

(iv) Graft polymer : This is a non-linear or branched block copolymer which is formed by attaching chains of one monomer to the main chain of another homopolymer.

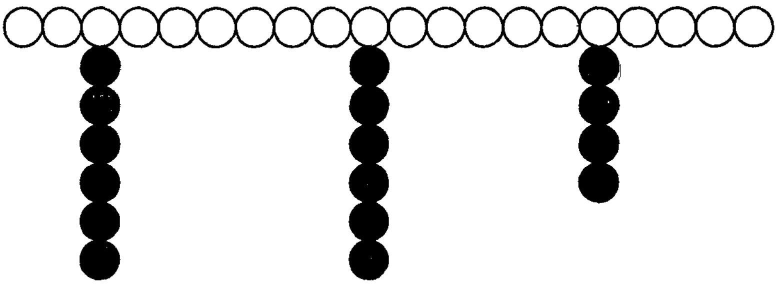
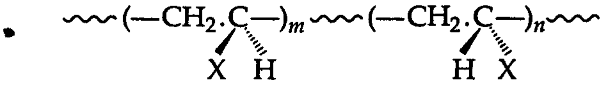


Fig. 9. Graft copolymer.

(v) Stereoblock copolymers : Stereoblock copolymer consists of very special structure which is formed from one monomer where the distinguishing feature is the tacticity of each block, *i.e.*,.



$$\sim(-CH_2.\underset{X\quad H}{C}-)_m\sim(-CH_2.\underset{H\quad X}{C}-)_n\sim$$

The block and graft copolymers possess the properties of both homopolymers, whereas the random and alternating structures have characteristics which are more of a compromise between the extremes.

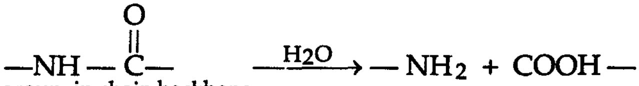
POLYMER REACTIONS

A polymer molecule contains functional groups which are not very much different in behaviour from those of a simple organic molecule. On the basis of the chemical nature of the functional groups, they can undergo a variety of reactions and form a polymer structure with entirely new properties and applications. Because of this reason, various interesting reactions are available with polymer molecules. Some of them are discussed as :

HYDROLYSIS

Hydrolysis proceeds in the presence of acids or alkalies. Polymers containing amide, ester and acetal groups can be easily hydrolysed.

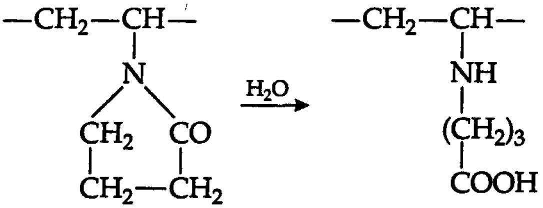
When these functional groups present in the backbone of the polymer chain, the hydrolysis degraded the chain as follows :



$$-NH-\overset{\overset{O}{\|}}{C}- \xrightarrow{H_2O} -NH_2 + COOH-$$

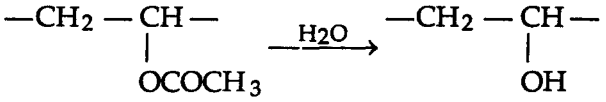
Amide group in chain backbone

Contrary to this, when these groups are present in the side chain of the polymer nolecule, hydrolysis causes only to a change of functional group and not any chain degradation as shown below :



Polyvinyl pyrrolidone

Another example of degradation of side chain is an polymer having ester linkage, which can be easily hydrolysed in presence of an alkali as :



$$-CH_2-\underset{\underset{OCOCH_3}{|}}{CH}- \xrightarrow{H_2O} -CH_2-\underset{\underset{OH}{|}}{CH}-$$

Polyvinyl acetate

Polyvinyl alochol

In hydrolysis reactions, the chemical composition of the polymer repeat unit is changed, but its degree of polymerisation remains same.