
UNIT 7 POLYMERS

Structure

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7.1 INTRODUCTION

Polymers are all around us. They are important materials used in every sphere of life. Both natural and synthetic polymers have become an integral part of our daily life.

In this unit, we will first highlight the importance of polymers. Then, we would focus on classification of polymers into various types such as **addition** and **condensation** polymers depending upon the process involved in their formation. Here, some examples of both these categories of polymers would be discussed along with their structures and uses. This would be followed by discussion on the properties of polymers. Finally, we would consider various types of natural and synthetic rubbers.

Objectives

After studying this unit, you should be able to

- highlight the importance of polymers in our daily life,
- define the terms polymer and monomer,
- differentiate between a natural and a synthetic polymer,
- give examples of addition polymers,
- write the mechanism of free radical, cationic and anionic polymerizations,
- explain the classification of polymers as isotactic, syndiotactic and atactic,
- define copolymers and give their examples,
- describe condensation polymers with examples,
- explain important properties of polymers,
- differentiate between natural and synthetic rubber on the basis of their structures, and
- discuss vulcanization and its importance.

7.2 IMPORTANCE OF POLYMERS

A **polymer** is a large molecule consisting of many smaller repeating units called **monomers** which are bonded together. **Natural polymers** have been all along with us. They are biopolymers such as DNA, cellulose, proteins etc. But today when we refer to polymers, we generally mean **synthetic organic polymers**. The first synthetic polymer was made accidentally in 1838 when vinyl chloride was polymerized. In 1839, polystyrene, another polymer, was made. And today, we live in the world of polymers. In less than 200 years, so many polymers have been synthesized which exhibit a wide variety of properties and find diverse applications. We wear *nylon* and *polyester* clothes, use *polythene* carry bags, walk on *polystyrene* carpets, use moulded luggage and drive automobiles in which many parts are made of polymers. Nevertheless, we use telephone instruments, pens, computers, mobile phones, moulded furniture, electrical fittings, toys, raincoats, umbrellas, packaging materials, all of which are made up of polymeric materials.

In the field of medicine also, artificial limbs, artificial hearts, stitching thread etc. are made from polymers. In space technology, the spacecrafts, rocket parts and other equipment use polymers in one form or other. Polymeric protective coatings, paints, adhesives etc. have become our routine requirements.

In addition to above, we use many plastic household items, melamine kitchenware, shoes, PET bottles and containers, CDs, floppies, air conditioners, coolers, heaters etc. which are all made using polymers.

7.3 TYPES OF POLYMERS

Polymers can be classified in many ways. According to their *mode of formation*, polymers can be divided into two major classes – **addition polymers** and **condensation polymers**. Let us now study them in detail.

7.3.1 Addition Polymers

These polymers result from the addition of one monomer at a time to the growing polymer chain. Thus, they are also known as **chain growth polymers**. The monomers are usually the molecules of alkenes. Some important addition polymers are given in Table 7.1.

Addition polymers can be obtained by free radical, carbocation or carbanion intermediates depending upon the type of monomer and the initiator used for polymerization. Let us now study about them in detail.

(a) Free-radical Polymerization

It involves the polymerization of a suitable alkene in the presence of a free radical initiator such as benzoyl peroxide. Polymerization of ethylene is such an example. It occurs at high temperature (100-250°C) and high pressure (1000-3000 atm). The overall reaction involves three steps – viz, *chain initiation*, *chain propagation* and *chain termination*.

Table 7.1 : Addition Polymers

Sl. No.	Monomer	Polymer	Repeating Unit	Uses
1	$\text{H}_2\text{C} = \text{CH}_2$ (ethylene)	Polyethylene (polythene)	$[\text{CH}_2 - \text{CH}_2]_n$	Bottles, containers, films, packaging
2	$\begin{array}{c} \text{H} \\ \\ \text{C} = \text{C} - \text{CH}_3 \\ \quad \\ \text{H} \quad \text{H} \end{array}$ (propylene)	Polypropylene	$\begin{array}{c} \text{CH}_3 \\ \\ [\text{CH}_2 - \text{CH}]_n \end{array}$	Plastics, carpet fibres, ropes
3		Polystyrene		Plastics, foam, insulation, molded articles
4	$\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ (vinyl chloride)	Polyvinyl chloride (PVC)	$\begin{array}{c} \text{Cl} \\ \\ [\text{CH}_2 - \text{CH}]_n \end{array}$	Insulation, vinyl plastics, films, PVC pipes
5	$\begin{array}{c} \text{H} \quad \text{CN} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ (acrylonitrile)	Polyacrylonitrile	$\begin{array}{c} \text{CN} \\ \\ [\text{CH}_2 - \text{CH}]_n \end{array}$	Fibres, orlon
6	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$ (tetrafluoroethylene)	Polytetrafluoroethylene	$[\text{CF}_2 - \text{CF}_2]_n$	Teflon, coatings, plastics
7	$\text{H}_2\text{C} = \text{CHOCOCH}_3$ (vinyl acetate)	Polyvinylacetate	$\begin{array}{c} \text{OCOCH}_3 \\ \\ [\text{CH}_2 - \text{CH}]_n \end{array}$	Paints, adhesives

(i) *Chain Initiation*

The free radical initiator, benzoyl peroxide undergoes homolytic cleavage of O – O bond to give benzyloxy free radicals as shown below :

The benzyloxy free radical so generated attacks the alkene to yield an alkyl radical.

(ii) *Chain Propagation*

The alkyl radical in turn adds to another molecule of the alkene to give another radical. This step is repeated many times and the polymeric chain is thus obtained.

(iii) *Chain Termination*

When two such chains as obtained above combine together, then there is a termination of the growing chain. This is shown below :

Such a type of chain termination is one possibility. Chain termination can also occur when the polymeric chain combines with other free radicals present in the system.

Similarly, we can write the steps of polymerization for various monomers given in Table 7.1.

The polyethylene obtained under the conditions mentioned above is called *low-density polyethylene*. It is normally used for making polyethene carry bags.

Low-density polyethylene is soft and can be made into thin films because it has a highly branched structure. The branching of a chain occurs when a hydrogen radical is obstructed from the middle of a chain by the free radical end of a chain. This is illustrated in Figure 7.1.

(b) **Cationic Polymerization**

The mechanism of cationic-polymerization is similar to that of free radical polymerization but it involves a carbocation intermediate instead of a free radical. A **carbocation** is a species having a positively charged carbon atom. Cationic polymerization requires the use of strong protic or Lewis acid catalyst. BF_3 is one such Lewis acid catalyst. The cationic polymerization is shown in Figure 7.2.

Figure 7.1 : Branching of a Polymer Chain by Hydrogen Abstraction

Initiation Steps : The catalyst protonates the monomer, starting the chain.

Propagation Step : Another molecule of monomer adds to the chain.

Figure 7.2 : Cationic Polymerization of Isobutylene

Note that a tertiary carbocation is formed as an intermediate in the cationic polymerization. The tertiary carbocations being very stable facilitate the effective polymerization.

Styrene can also undergo cationic polymerization as stable benzylic carbocation is obtained as an intermediate in this case.

Cationic polymerization is favoured when the monomer contains electron donating groups which stabilize the intermediate carbocations.

(c) Anionic Polymerization

You can now easily say that the anionic polymerization would be favoured by the presence of electron withdrawing groups in the monomer. The examples of such groups are $>C=O$, $-CN$, $-NO_2$ etc.

The anionic polymerization is initiated by reagents such as organolithium ($R-Li$) or Grignard reagent ($R-MgX$). These reagents give carbanion which attacks the monomer to yield a stable anion. The stable anion so produced in turn attacks another monomer and thus the chain grows. This is shown in Figure 7.3.

Initiation Step : The initiator adds to the monomer to form an anion.

Propagation Step : Another molecule of monomer adds to the chain.

Figure 7.3 : Anionic Polymerization of Acrylonitrile

‘Superglue’ is a polymer of methyl α - cyanoacrylate whose one drop can support very large weights and has excellent adhesive properties.

Methyl α - cyanoacrylate $\left(\begin{array}{c} \text{H} \cdot \\ \cdot \\ \text{H} \cdot \end{array} \text{C} = \text{C} \cdot \begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array} \begin{array}{c} \text{COOCH}_3 \\ \cdot \\ \text{CN} \end{array} \right)$ can easily undergo

anionic polymerization in presence of trace amounts of water or bases (OH^-).

Stereochemistry of Polymers

When we talk about polymerization of substituted alkenes ($\text{H}_2\text{C} = \text{CHR}$) where R represents different substituents, the resulting polymer can have a variety of structures and thereby very different properties depending upon the position of R groups on the polymeric backbone. Three such possible arrangements of R groups are shown in Figure 7.4.

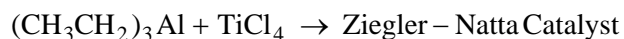
When the R substituents are present on the *same* side of the polymeric backbone, then the polymer is called **isotactic polymer**. In Greek, *iso* means **same** and *tactic* means **order**.

When the R substituents are present in *alternate* position on the polymeric backbone, then the polymer is called **syndiotactic** polymer. **Syndiotactic** in Greek stands for **alternating order**.

Figure 7.4 : Isotactic, Syndiotactic and Atactic Polymers

Lastly, when R groups are *randomly* distributed on either side of the polymeric chain, then the polymer is known as **atactic** polymer. **Atactic** in Greek stands for *no order*.

It is possible to synthesize isotactic, syndiotactic and atactic polymers with the help of Ziegler-Natta catalysts. In 1953, Karl Ziegler and Giulio Natta discovered catalysts which are complexes of organometallic compounds and a titanium compound.



Karl Ziegler

Giulio Natta (1903 – 1979)

Another advantage of Ziegler-Natta catalysts was that they produced linear polymers with almost no branching.

The discovery of Ziegler-Natta catalysts revolutionized the growth of polymer industry in just ten years. In 1963, Ziegler and Natta received Nobel prize for their work.

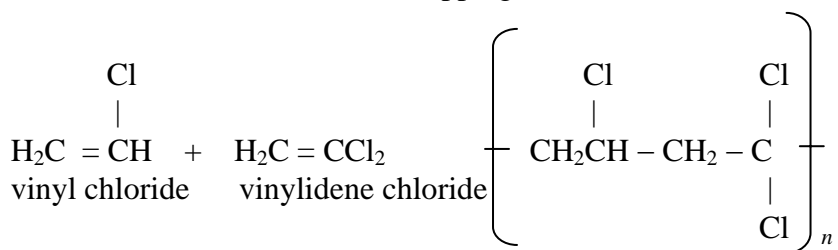
It is worthwhile mentioning here that *high density polyethylene* containing 4,000-7,000 monomer units could be synthesized using Ziegler-Natta catalysts. High molecular weight polyethylenes containing 10,000-18,000 monomer units were used in making pipes and large containers.

In contrast to low density polyethylene which you have studied before, high density polyethylene is strong and heat resistant. It is used for making moulded household items and squeeze bottle for ketchups etc.

Copolymers

So far we were discussing polymers containing identical monomer units. They are also known as **homopolymers**. However, polymers can also be prepared using two or more different monomers. These are called **copolymers**.

Saran is a copolymer of vinyl chloride (20%) and vinylidene chloride (80%). It is used as a film for wrapping food.

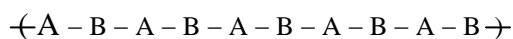


The properties of copolymers are different from the homopolymers of their constituent monomers. Thus, copolymerization of various monomers gives copolymers having diverse properties. Some examples of copolymers are listed in Table 7.2.

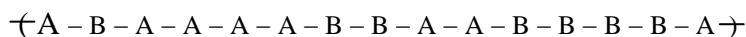
Table 7.2 : Some Copolymers and their Uses

Sl. No.	Monomers	Structure	Trade Name	Uses
1	Styrene (25%) 1, 3 – Butadiene (75%)	$H_2C = CHC_6H_5$ $H_2C = CHCH = CH_2$	SBR (Styrene-butadiene rubber)	Rubber articles tyres
2	Acrylonitrile 1, 3 – Butadiene	$H_2C = CHCN$ $H_2C = CHCH = CH_2$	Nitrile rubber	Adhesives, gasoline hoses
3	Isobutylene, Isoprene	$H_2C = C(CH_3)_2$ $H_2C = C(CH_3)CH = CH_2$	Butyl rubber	Inner tubes
4	Hexafluoropropene vinylidene fluoride	$F_2C = CFCF_3$ $H_2C = CF_2$	Viton	Seals, gaskets
5	Acrylonitrile 1, 3 – Butadiene styrene	$H_2C = CHCN$ $H_2C = CH = CH = CH_2$ $H_2C = CHC_6H_5$	ABS	Pipes, bumpers, crash helmets, other heavy impact materials

Depending upon the arrangement of monomers in a copolymer, it can be called as an **alternating copolymer** or a **random copolymer** as shown below :



Alternating Copolymer



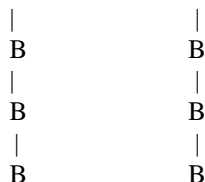
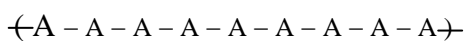
Random Copolymer

Here, A and B denote two different monomers.

There are two other types of copolymers viz., **block copolymers** and **graft copolymers** as shown below :



Block Copolymer



Graft Copolymer

You can see above that in a *block copolymer*, there are alternate blocks of two monomer units whereas in a *graft copolymer*, branches of one monomer are grafted on the polymer chain of another monomer. A visual depiction of these classes of polymers is shown below :

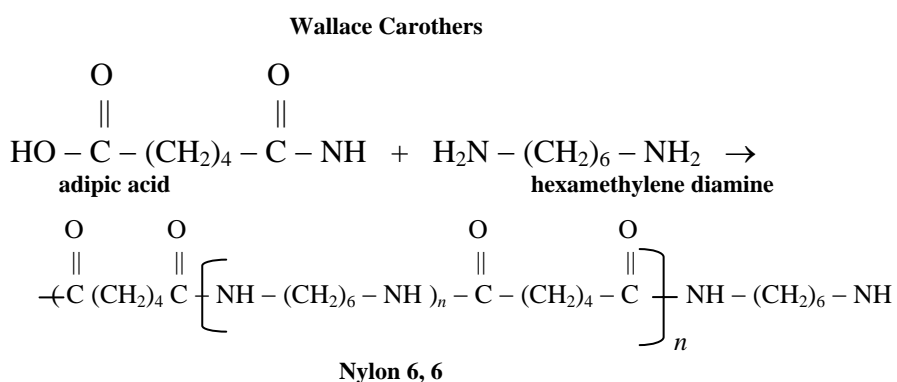
7.3.2 Condensation Polymers

Condensation polymers results as a condensation of two monomer units with the elimination of a small molecule such as NH_3 or H_2O . The polymerization involves the formation of **ester** or **amide** linkages between the monomers. Since each condensation process is a separate step, this type of polymerization is also known as **step-growth polymerization**. Let us now consider some examples of condensation polymers.

(i) **Nylon**

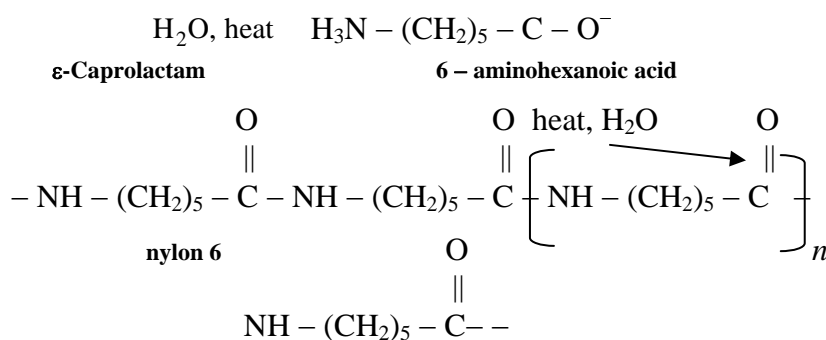
Nylon was discovered by Wallace Carothers of DuPont Company in 1938. It is a polyamide.

When a six carbon dicarboxylic acid (adipic acid) is condensed with a six carbon diamine (hexamethylene diamine), Nylon 6, 6 is obtained.



Nylon can also be synthesized from a single monomer called ϵ -caprolactum. When ϵ -caprolactum is heated in the presence of trace amounts of water, it hydrolyses to give 6-aminohexanoic acid as shown below :





Further heating of 6-aminohexanoic acid leads to the condensation and polymerization yielding nylon 6 in the molten state which can be made into fibres and threads. Nylon is used for making nylon clothings, flexible fibres for ropes and tyre cord.

(ii) Polyesters

Polyesters can be obtained by the condensation of a dicarboxylic acid with a diol. For example, when we condense terephthalic acid with ethylene glycol, we get a polyester called poly ethylene terephthalate (PET), also called as *Dacron*.

Dacron Polyester

Dacron fibres are used for making fabrics and tyre cords. When blow-moulded, in the form of PET plastics, we get a range of plastic bottles and containers for households.

Polyester fibres in general are used for making wrinkle-free fabrics. They are very strong fibres and the clothes made from them are very durable and long-lasting without requiring much maintenance.

It would also be interesting here to know that the suture thread used for surgical stitches is a polymer called poly (ϵ -caprolactone) which is obtained from the polymerization of ϵ -caprolactone. This polymer is a bio-absorbable polyester.

SAQ 1

- What is the difference between addition and condensation polymers?
- What are the three types of addition polymerization?
- Give two examples of addition polymers.
- Differentiate between isotactic, syndiotactic and atactic polymers on the basis of their structure.
- What is a copolymer? Explain with the help of an example.

- (f) Give one example of a condensation polymer and explain its preparation.
- (g) What is PET? Give its important uses.

7.4 PROPERTIES OF POLYMERS

Polymers are not very-very different from other similar molecules as far as their reactions are concerned. The difference is really in their physical properties because of their large size as compared to other small organic molecules. The van der Waals forces between large polymers are larger as compared to those present in the small organic molecules.

Polymers generally do not form proper crystals characteristics of other organic compounds but there are certain microscopic crystalline regions in the polymer which are called **crystallites** (Figure 7.5). Crystallites are highly ordered portions where the polymer chain is held together by van der Waals forces.

Figure 7.5 : Crystallites in Polymer

Low density polyethylene has very small crystallites because of branched chains which cannot be packed together in a regular way. On the other hand, high density polyethylene having linear structure has more crystallites because the polymeric chain can pack more easily in it. Thus, high density polyethylene shows a higher degree of crystallinity and is stronger, denser and more rigid than the low density polyethylene.

When polymers of high crystallinity are heated, the crystalline regions melt at the **melt transition temperature**, T_m to give an amorphous material.

Non-crystalline amorphous polymers such as plexiglass (polymethyl methacrylate) on heating become soft and flexible at a temperature known as **glass transition temperature** T_g .

A highly crystalline polymer becomes flexible and mouldable above T_g . Since it is mouldable (called plastic), it is known as **thermoplastic**. The thermoplastics have high T_g . They can be moulded into toys, household items, beads, etc.

Thermoplastics lack cross linking and hence their chains can slip over one-another on melting. Polystyrene and Plexiglass are non-crystalline *amorphous thermoplastics*.

Usually **plasticizers** such as dibutyl phthalate are added to thermoplastics to *avoid* them from becoming brittle at room temperature.

dibutyl phthalate

A plasticizer dissolves in the polymers and allows the slipping of chains over one-another by reducing the attraction between them. Their addition makes the material flexible.

In contrast to thermoplastics, **thermosetting** polymers are highly cross-linked in nature and on heating they set into a hard mass. Bakelite is one such polymer. It is used for making moulded parts, switches, coatings, adhesives, etc. It is made from phenol and formaldehyde and has the following structure.

Bakelite

In the next section, you will study about another class of polymers called elastomers of which rubber is one example.

SAQ 2

- (a) Which one of the two – low density polyethylene or high density polyethylene – is stronger and why?
- (b) What are melt transition and glass transition temperatures?
- (c) What is Plexiglass?
- (d) What is the role of plasticizers?
- (e) What is the difference between thermoplastic and thermosetting polymers?

7.5 MOULDING OF PLASTICS

An important step in the manufacture of any plastic product is the moulding or fabrication of plastic to give the articles of desired shapes. Various methods are used for fabrication depending upon the type of plastic used :

Extrusion

It is used for continuous moulding of thermoplastic materials into articles of uniform cross section like filaments, tubes, pipes, rods, cables etc. It is done by an extrusion machine consisting of an extruder and a die.

Compression Moulding

It is the oldest method of moulding and it is still widely used. The polymer is placed in one half (female half) of the mould and the 'male half' is pressed to it with pressure. The polymer is simultaneously heated. The moulded article is taken out by opening the mould parts.

Injection Moulding

This method is used for making thermoplastic materials having intricate shapes.

A definite quantity of the polymer is fed into a heated cylinder where it is injected at a controlled rate under pressure into a relatively cold mould where it solidifies. Pressure is then released and the article is expelled from the open mould. This method can be used for bottle manufacture.

Casting

It is used both for thermoplastic and thermosetting polymers. The components are added to a mould in the required amount. After packing, the mould is closed and simultaneously both temperature and pressure are increased. In case of thermoplastics, cooling is done before releasing the pressure while for thermosettings, first pressure is released and then cooling is done. Casting is used for making cylinders, gears, handles etc.

7.6 RUBBER

Natural rubber is obtained from *latex* which is a white fluid oozing from cuts of bark of *Hevea brasiliensis* commonly known as rubber tree. The term rubber was used by Joseph Priestley.

Natural rubber is a polymer of *isoprene*. The IUPAC name of isoprene is 2-methyl - 1, 3 - butadiene.

Many isoprene units are linked in *cis* fashion in natural rubber to each other as shown below.

cis - 1, - 4 Polyisoprene

On an average, there are about 5000 monomers linked to each other. The *cis* geometry gives to a kinky structure to the chains which can be stretched by applying force. When the force is removed, the original shape is restored. The crude rubber is very soft and tacky and hence could not be used as such for applications requiring strength and durability.

Natural rubber can be made tough and more elastic by a process called **vulcanization**. It was accidentally discovered by Charles Goodyear in 1839 when he dropped a mixture of natural rubber and sulphur on a stove. He found that the rubber become strong and elastic.

Vulcanization causes cross-linking of polymeric chains as shown in Figure 7.6.

Figure 7.6 : Vulcanization of Rubber

The formation of cross links prohibits the sliding of chains over one another which gives hardness to the material. It also improves the resistance to wear and abrasion.

Different quantities of rubber can be obtained by varying the amount of sulphur : soft and stretchy rubber used for making rubber bands and inner tubes is obtained by adding 1-3% sulphur. Rubber containing 3-10% sulphur is flexible and hard and is used for making tyres.

Natural rubber can also be synthesized using Ziegler-Natta catalysts.

Gutta-percha is an isomer of rubber. It also occurs naturally and it can also be synthesized. It has all *trans* double bonds as shown below.

Gutta-percha

Gutta-percha is more brittle and harder than the natural rubber.

Neoprene is another synthetic rubber obtained by the polymerization of chloroprene.

It has excellent weather resistance and is used for making gloves, industrial hoses etc.

SAQ 3

- (a) What is the monomer of natural rubber? Explain vulcanization.
- (b) What is gutta-percha?
- (c) How is neoprene prepared?
- (d) What are Ziegler Natta catalysts?
- (e) Explain vulcanization.

7.7 SUMMARY

In this unit, you have learnt that

- Polymers have unique importance in our daily lives.
- Polymers can be classified as addition or condensation polymers.
- Addition polymerization could occur via free radical, cationic or anionic intermediates. Depending upon their stereochemistry, polymers can be classified as isotactic, syndiotactic or atactic polymers.

- Copolymers contain two or more different monomers.
- Nylon and polyesters are important condensation polymers.
- Depending upon their thermal behaviour, polymers can be classified as thermoplastics or thermosettings.
- Natural rubber is a polymer of isoprene.
- Neoprene and gutta percha are examples of synthetic elastomers.

7.8 ANSWERS TO SAQs

SAQ 1

- Addition polymers arise as a result of addition of one monomer at a time to the growing polymer chain whereas condensation polymers form by condensation of two monomer units with the elimination of a small molecule.
- Free radical, cationic and anionic polymerization.
- Polystyrene, PVC or any other.
- Isotactic – side groups on same side of chain.
Syndiotactic – side groups on alternating sides of chain.
Atactic – side groups on random sides of chain.
- Copolymer – polymer formed by two different monomers. Suitable example given.
- Nylon or polyester explained.
- Polyethylene terephthalate used as follows :
 - making fabrics and tyre cords
 - making plastic bottles and containers

SAQ 2

- High density polythene because of linear structure with more crystallites leading to easy packing of the chains.
- Melt transition temperature – The temperature at which crystallites of polymer of high crystallinity melt.
Glass transition temperature – The temperature at which non-crystalline amorphous polymers become soft and flexible.
- Plexiglass is a non-crystalline amorphous thermoplastic.
- Plasticizers are added to thermoplastics to avoid them from becoming brittle at room temperature.
- Thermoplastic – Polymers which become flexible and mouldable on heating.
Thermosetting – Cross linked polymes which set into a hard mass on heating.

SAQ 3

- (a) Isoprene
- (b) Trans polymer of isoprene.
- (c) By polymerization of chloroprene.
- (d) Catalysts which are complexes of organometallic compounds and a titanium compound. These are used for producing polymers of different stereochemistry.
- (e) Process of treating natural rubber with sulphur to form cross-linking in the polymer. It makes rubber tough and more elastic.