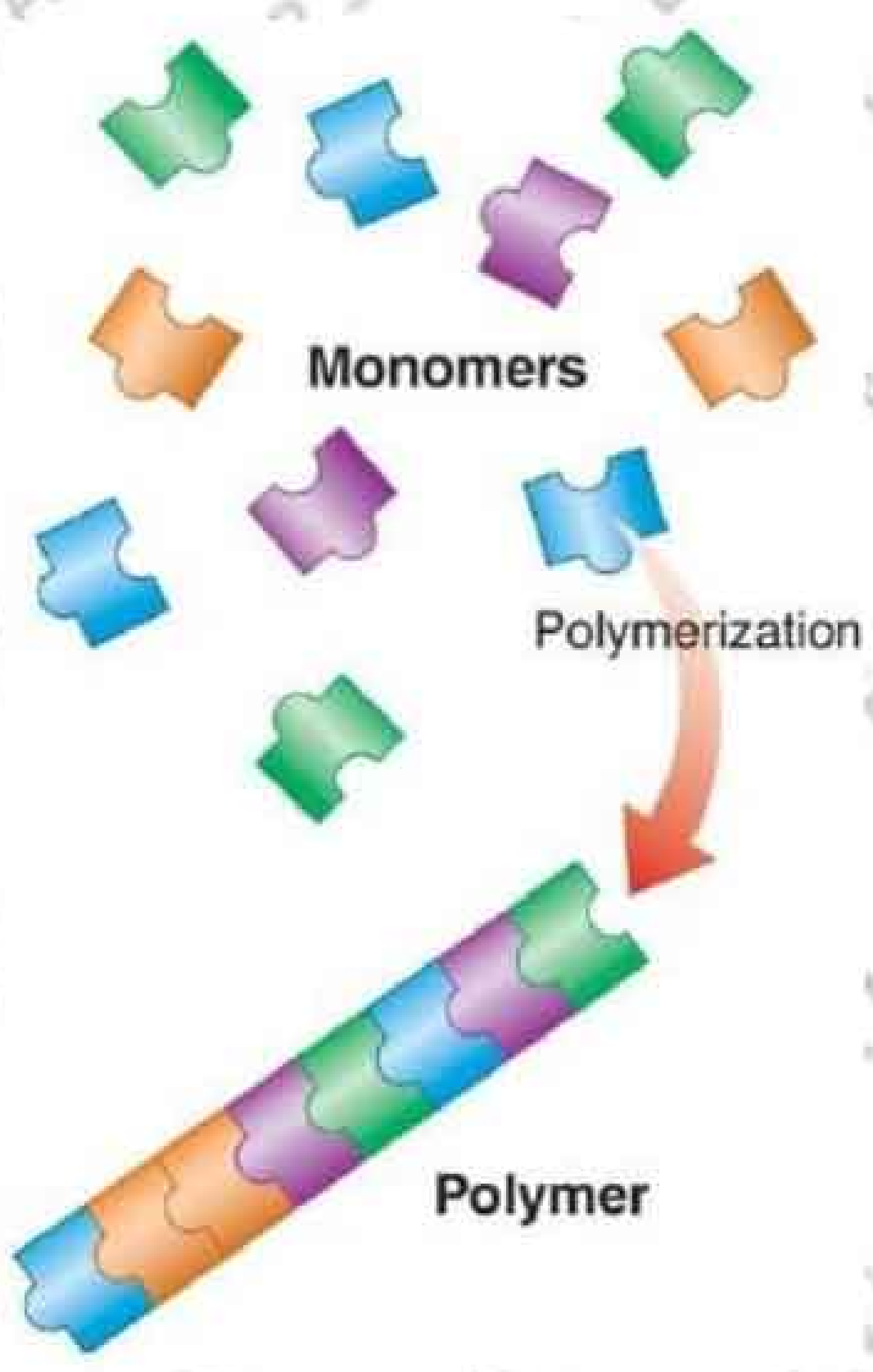
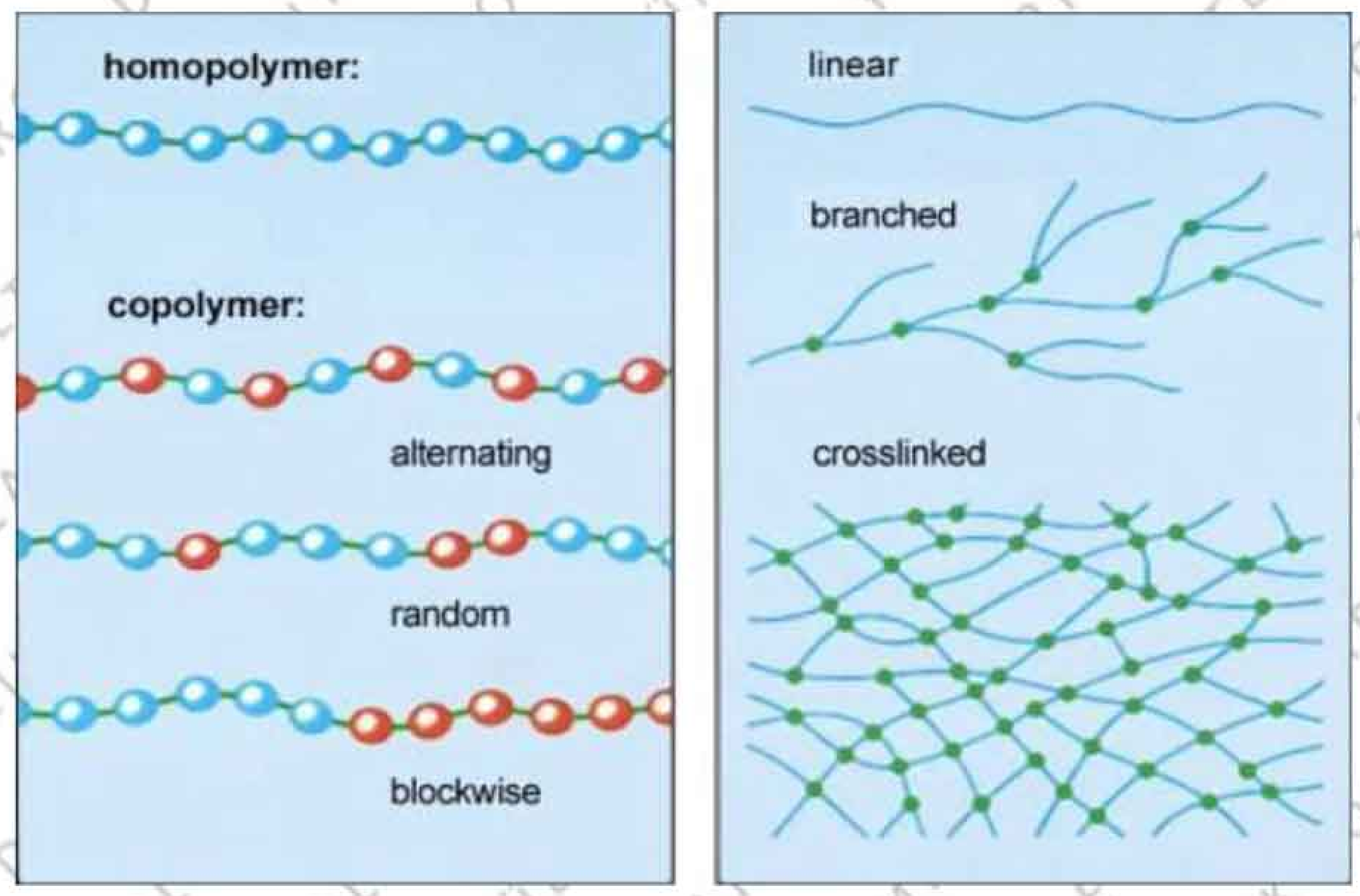
POLYMERS

High polymers, also known as macromolecules, are large molecules of colloidal dimensions (10^{-3} to 10^{-6} mm in diameter) having high molecular weight (10,000 to millions). Small molecules called monomers undergo polymerization reaction (with this reaction, monomers join together) and form macromolecules. The examples of polymeric materials are **resins, plastics and rubbers**.

Polymerization may be defined as the **union of two smaller molecules** of similar or different types with or without elimination of water resulting in the formation of new **C-C linkages**. The mechanism by which polymerization takes place may be **addition or condensation**. A monomer for polymerization should be bi-, or polyfunctional, i.e., it must contain **two or more functional groups**. Some of the other functional groups are hydroxyl acid, amino acid, di-amino acid, di-acids, di- or polyalcohols. The structures depend on the functionability of monomers.

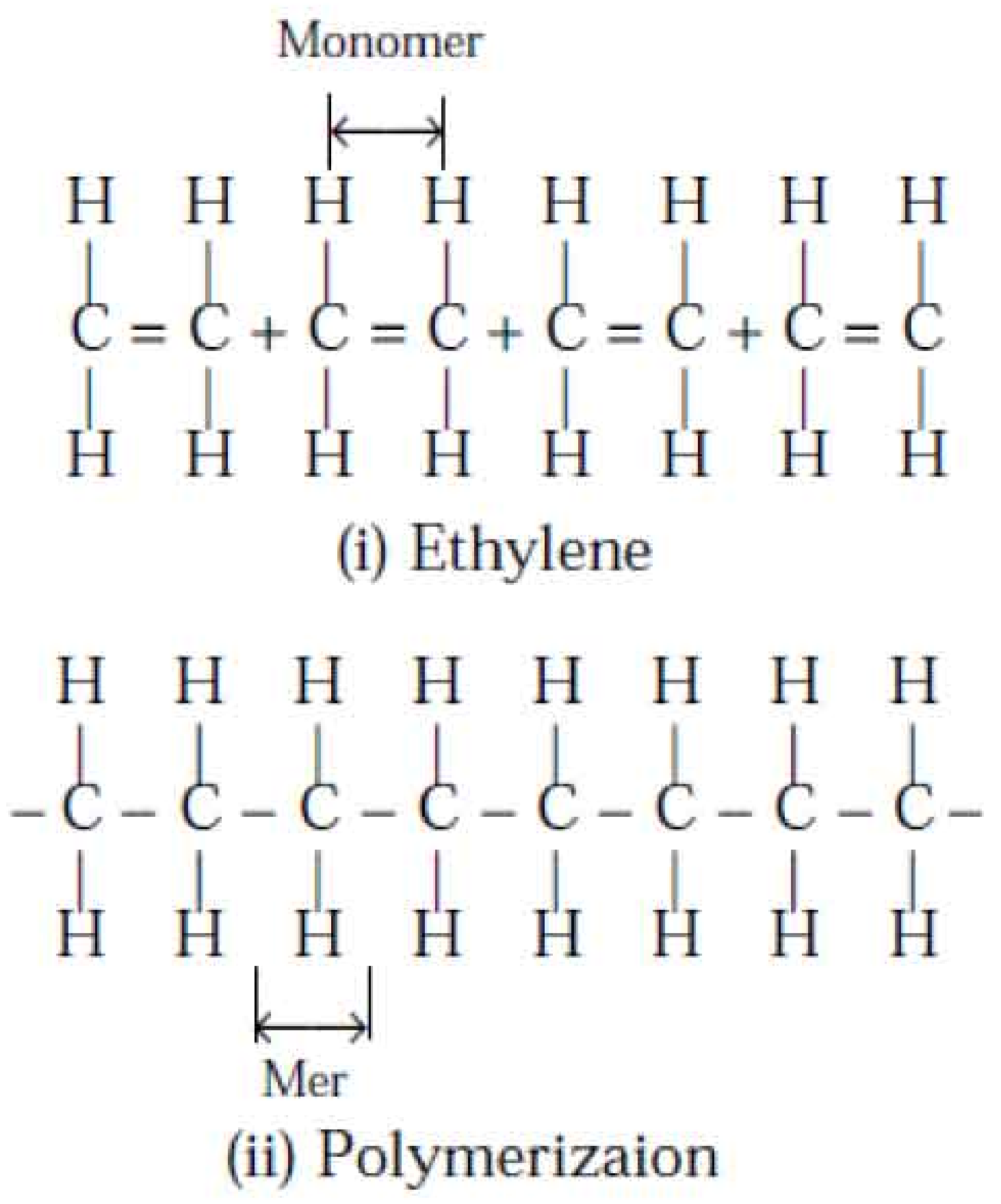


In case of a bi-functional monomer there will be two reactive groups at its ends. These groups may align side by side to form a **straight chain like molecule**. The monomer units are linked by primary covalent bonds and the different chains are held together by secondary force of molecular attraction. However, during the chain growth side chains may also develop leading to **branched chain molecules**. In case of poly-functional groups the monomer molecules are connected to each other by covalent bonds and form a **three-dimensional network**.

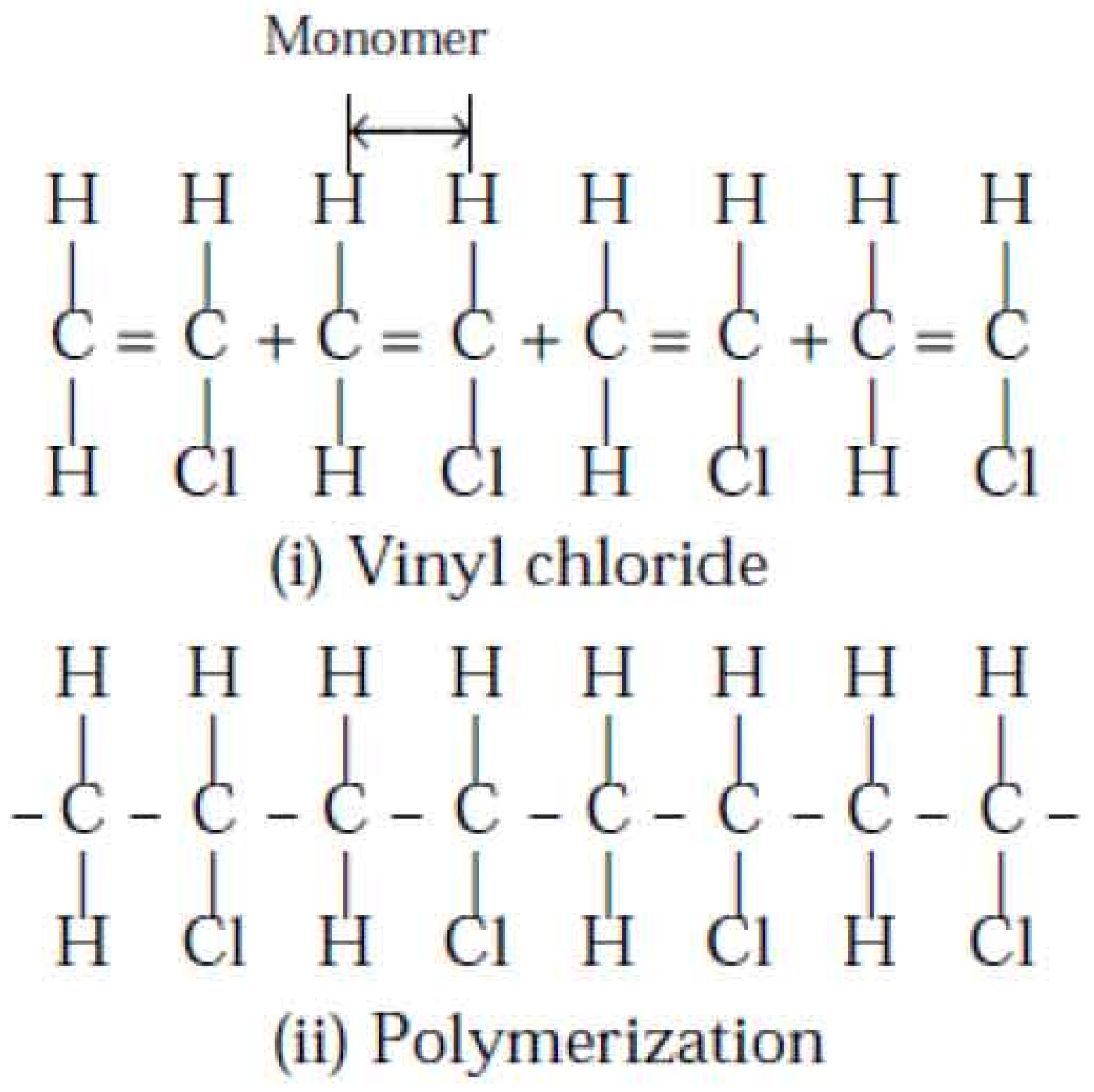


Addition polymerization may be defined as a reaction that yields a product which is an exact multiple of the original monomeric molecule. Such a monomeric molecule usually contains one or more double bonds, which by intermolecular rearrangement may make the molecule bi-functional.

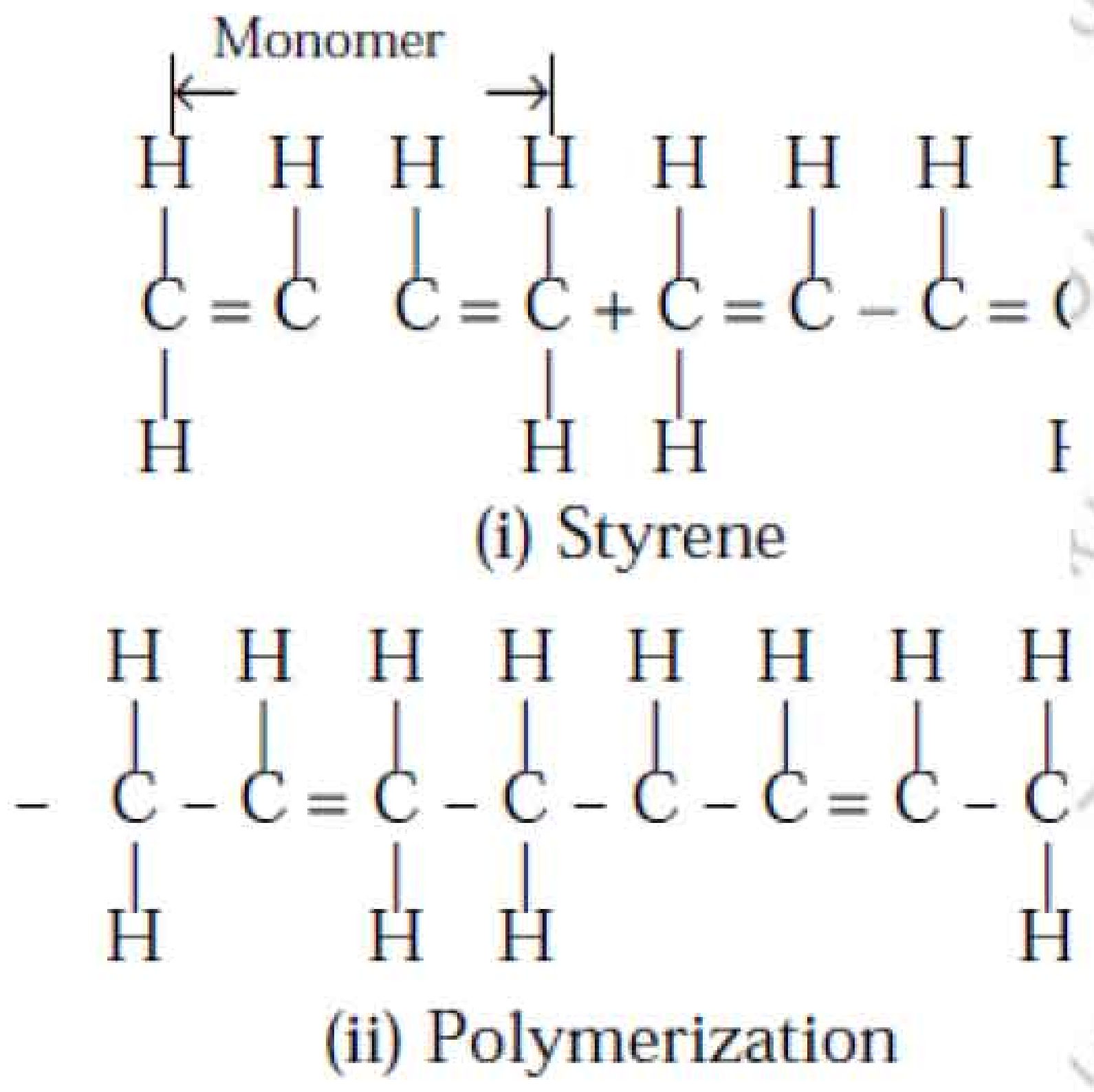
Figure below shows ethylene, vinyl chloride and styrene polymerizations. One of their double bond is transferred to form a bond with the adjacent monomer and the resultant products serve the prototype for addition polymerization. The addition polymerization reactions can take place only by the application of heat, light, pressure, or catalyst.



polymerization of ethylene



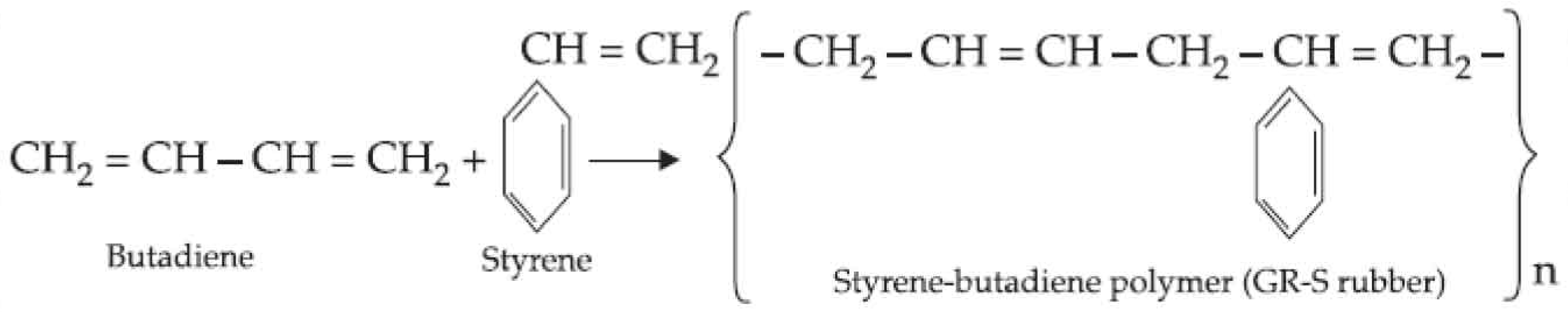
polymerization of vinyl chloride



polymerization of styrene

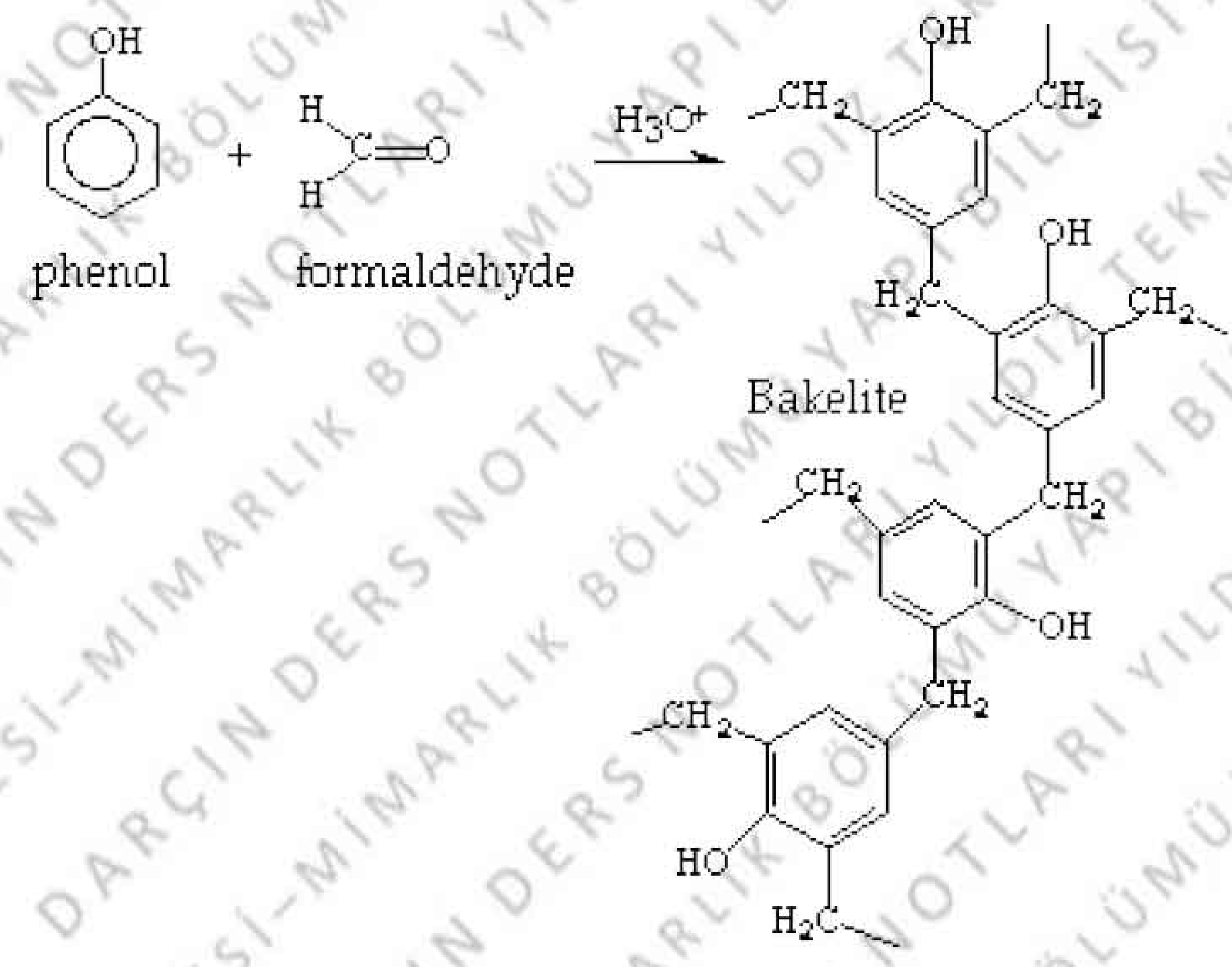
(polyethylene) (polyvinyl chloride) (polystyrene)

Co-polymerization is a type of addition polymerization where simultaneous polymerization of two or more chemically different monomers takes place resulting in the formation of a polymer containing both monomers linked in one chain.

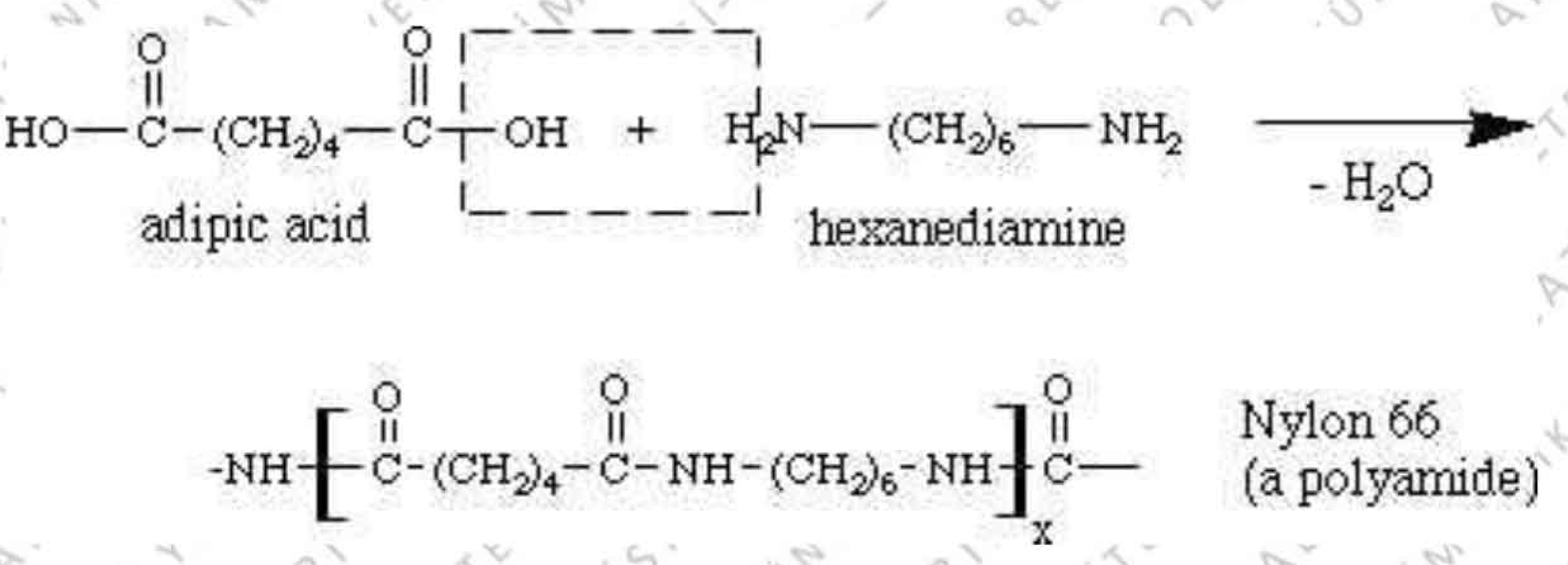


polymerization of styrene-butadiene

Condensation polymerization can be defined as the reaction between functional monomer molecules leading to the formation of a polymer with the elimination of some small molecules such as water, HCl, etc. The most common is nylon formed from hexamethylene diamine and adipic acid. Phenol formaldehyde resin (bakelite) is another example.



polymerization of bakelite

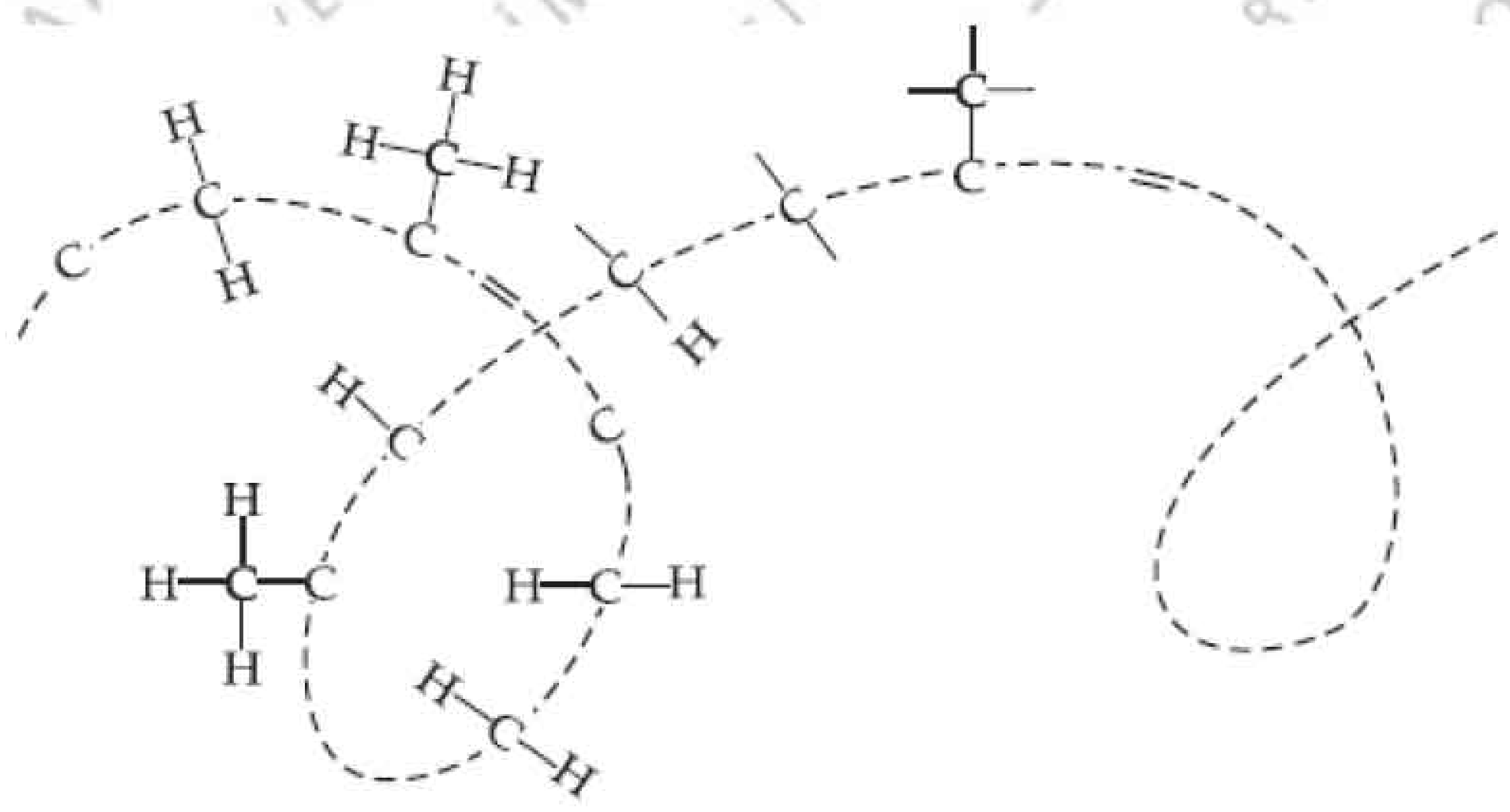


polymerization of nylon

Depolymerization, also known as degradation, may occur when used for extended period of time with steam as in the case of urea-formaldehyde plastic or due to thermal variations disrupting the intermolecular bonds within the molecules haftaya yeni şifreler gelecek ☺ of plastic formed at high temperatures. Depolymerization is used to its advantage for cracking petroleum into highly combustible products, light molecules charring of carbohydrates (toast) and of cellulose (charcoal).

Rubbers

Rubbers, also known as elastomers, are high polymers having the unique property of undergoing **large deformations under load** and **returning to their original shape and dimension** on its removal owing to lengthening and shortening of the springs of polymeric chains (elastomer molecule is not straight chained but is in the form of **coil**).



coiled elastomeric chain of natural rubber (polyisoprene)

The unstretched rubber molecule is amorphous. In stretching, the macromolecules in it get partially aligned with respect to one another causing crystallization. Consequently the material gets stiffened due to increased attractive forces between the molecules. On releasing the stress the chain regains its original coiled state and the material again becomes amorphous.

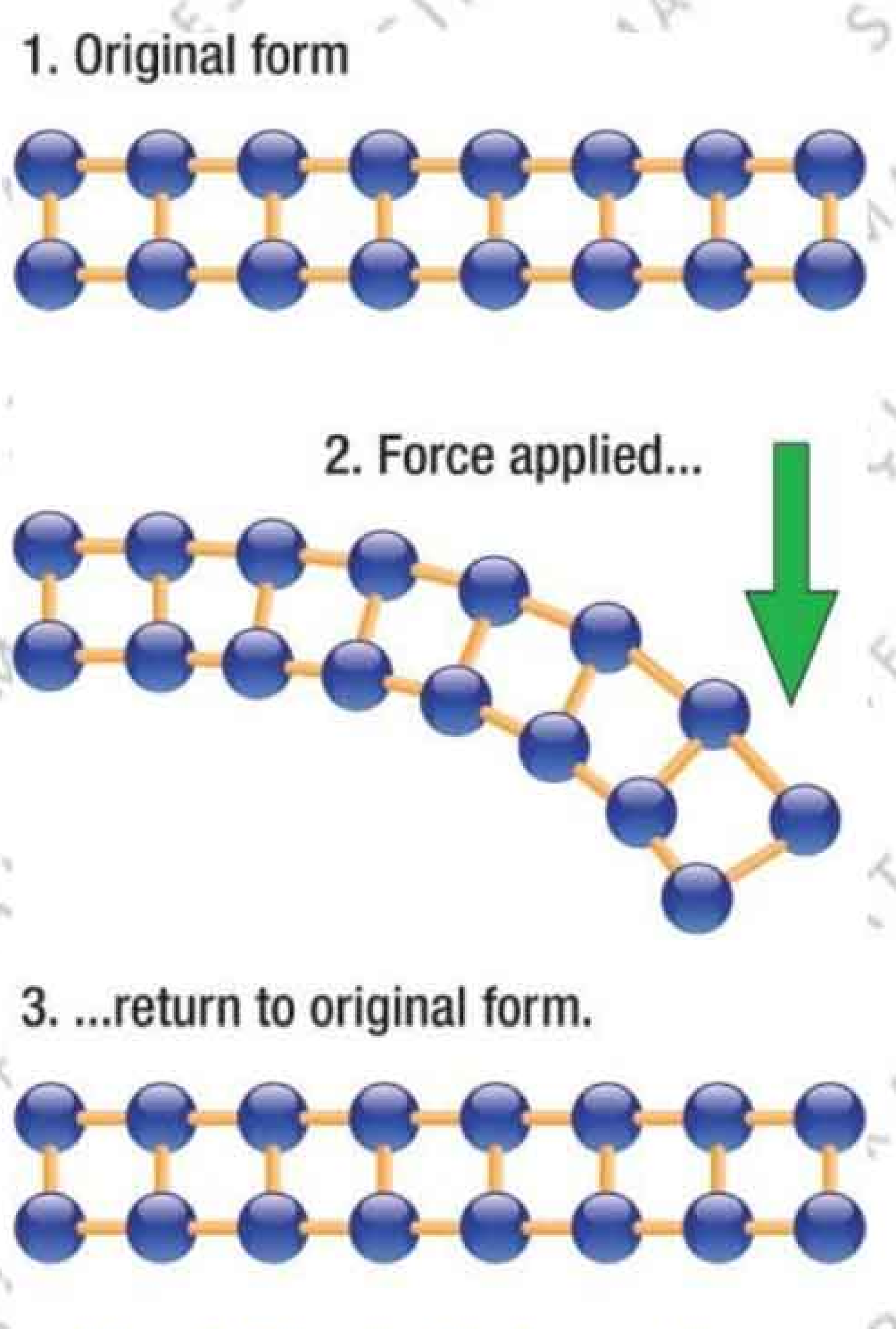
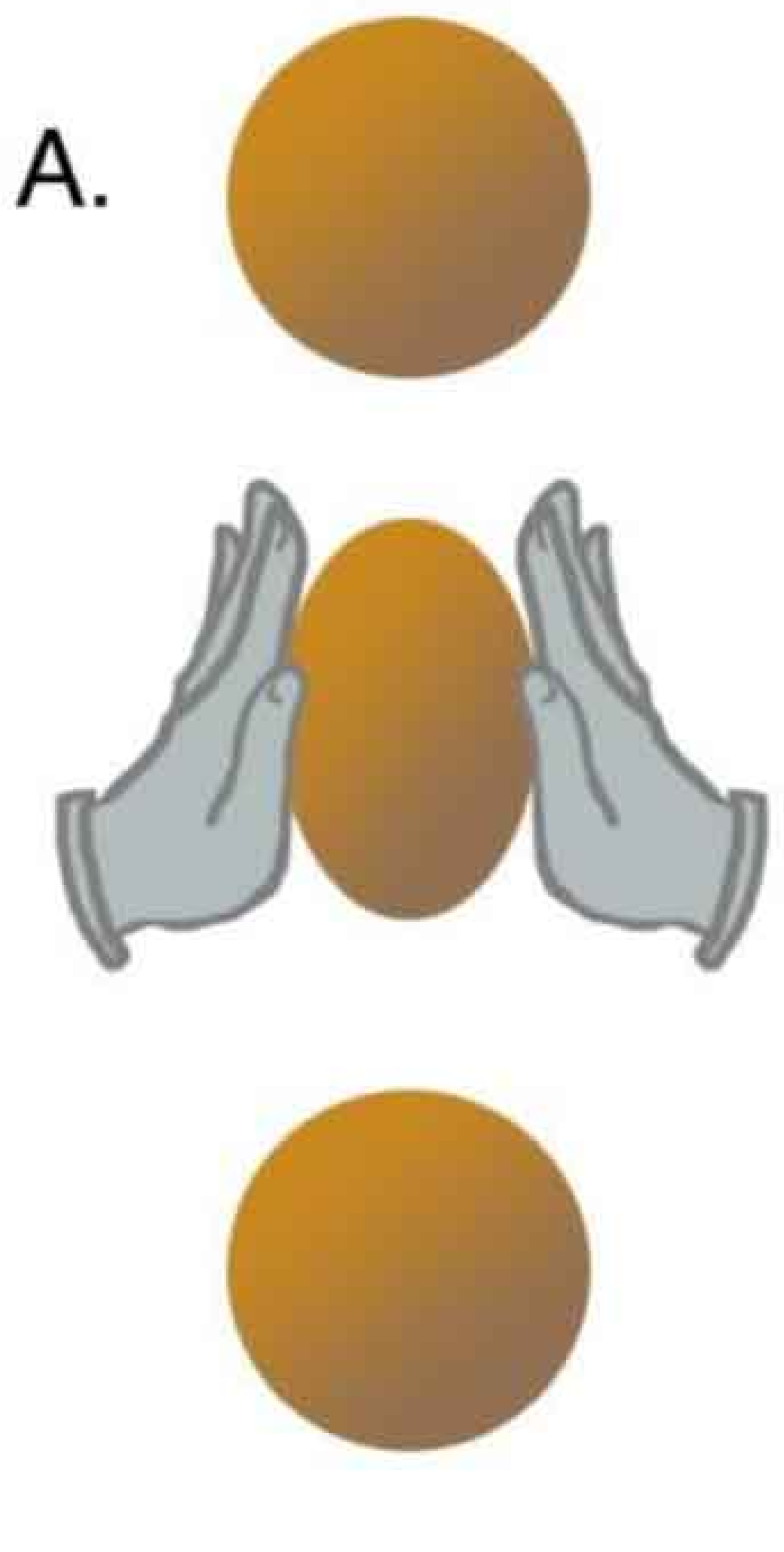


Fig. 4 Elastic Deformation



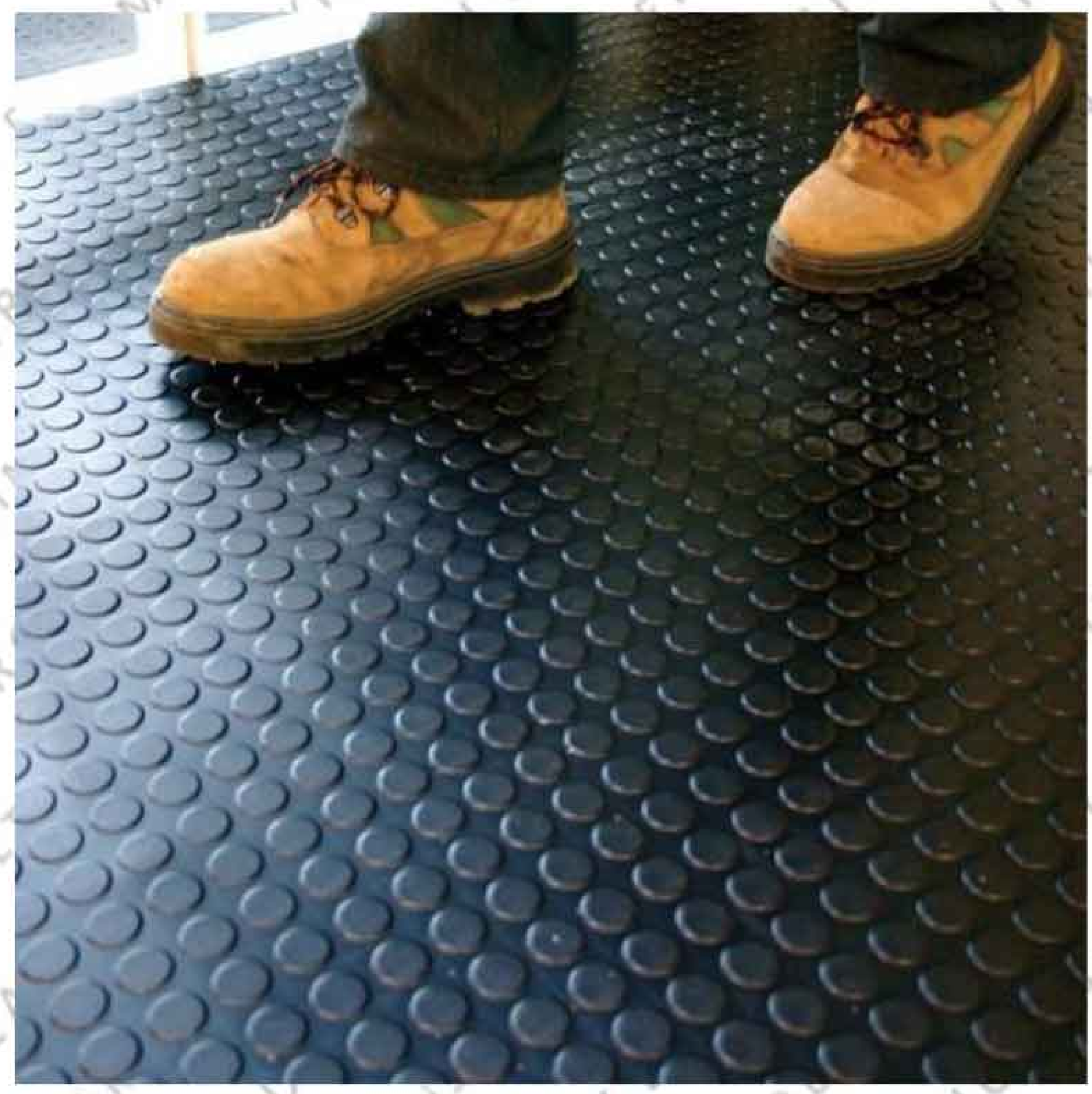
Rubber can be classified as natural, synthetic and rubber like plastic.

natural rubber consists of basic material latex, dispersion of isoprene, which polymerizes to form long coiled chain of polyisoperene. It is made from the **sap** occurring in cells of the various parts of the plants such as have a brasiliansis and gauyile. The latex is obtained by making **incisions** in the bark of the rubber tree, allowing the **sap to flow out**. It is collected and diluted to contain 15–20% of rubber and then strained to remove any dirt. Thereafter the rubber is **coagulated** by adding **acetic or formic acid.** The coagulated rubber is then treated to produce **crude rubber** known as crepe rubber and smoked rubber which is further processed, milled and vulcanized to produce commercial rubber.

synthetic rubber is based on the model of natural rubber and thermoplastic vinyl high polymers. The possible number of synthetic rubbers is unlimited. It is so because all straight-chain polymers can be made to specific requirements to produce rubber like properties. However, the cheap price and easy availability of natural rubber has suppressed the demand of synthetic rubber.

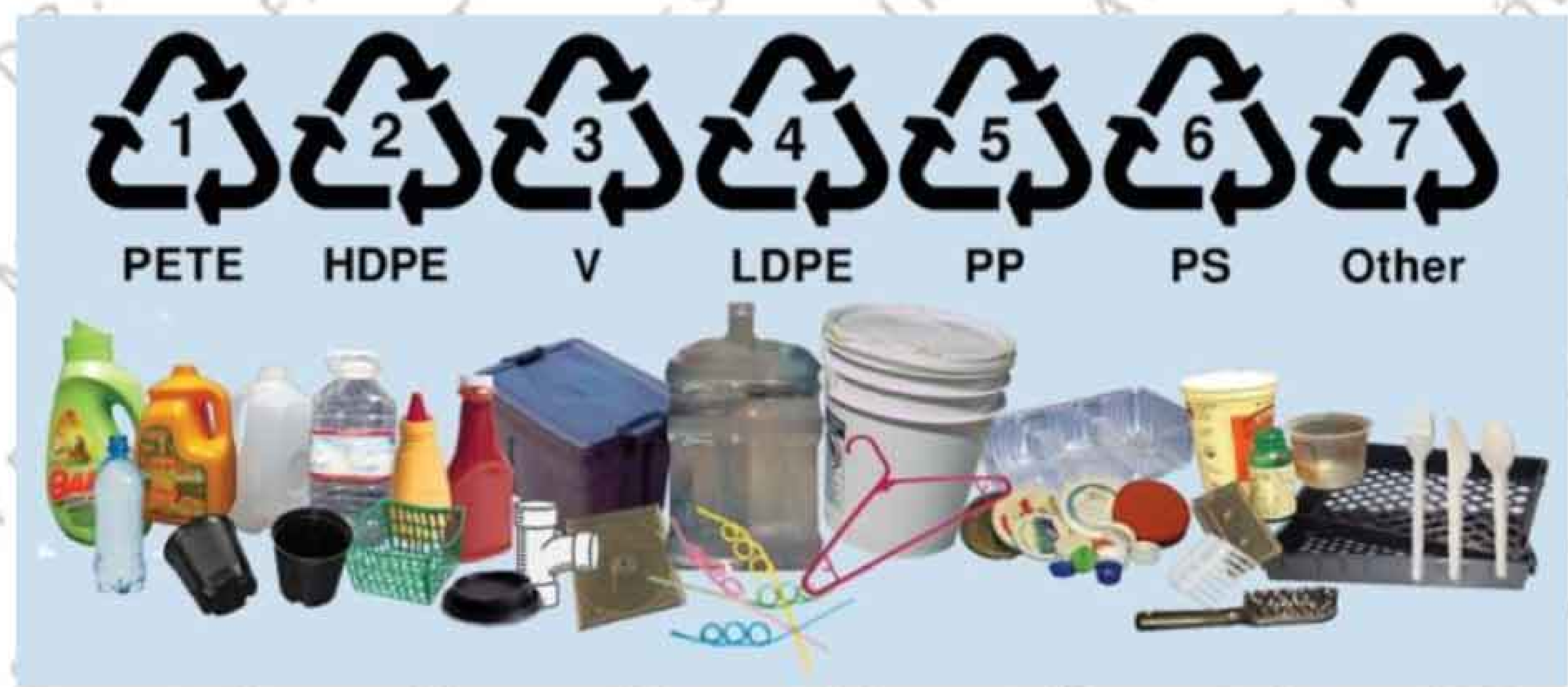
The crude rubber is elastic. In cold weather it is elastic whereas soft and sticky in hot weather. These defects are removed by vulcanization. Softeners and plasticizers such as vegetable oils, wax and rosin oil are added to natural or synthetic rubber to enhance tenacity and adhesion; vulcanizing agents such as sulfur (0.15–32%) which combines chemically at the double bonds of different rubber springs and thus enhance stiffness. The vulcanization process is however, slow and the product is porous, lacks sufficient strength and deteriorates on prolonged exposure to atmosphere. To overcome these short comings some additives are added prior to vulcanization. These additives are classified as accelerators, reinforcing pigments, softeners and antioxidants according to the functions they perform. Accelerators like benzthiozole shorten the time required for vulcanization; antioxidants like complex amines are added to check the tendency of natural rubber to perish due to oxidation; reinforcing fillers such as carbon black are added to give strength and rigidity to the tires. Plasticizers such as stearic acid, resins and fatty oils are sometime incorporated in rubber composition. Antioxidants or age resistors decrease the rate of deterioration and prolong the life of the rubber.

Rubber is the most suitable material for conveyer belts, linings for tanks. Tires, gaskets, mountings, hoses, insulating coatings and toys, phenolaldehyde resin with waste rubber is used to make flooring tiles. Like cyclised rubber chlorinated rubber, is a modified form of natural rubber, most widely used in the production of protective coatings and adhesives. Rubber hydrochloride, on processing can produce thin films of wrapping and packages. Rubber is also being used increasingly in the manufacture of foam rubber, which is used in upholstery and furniture.



Plastics

Plastics are made from **resin** with or without **fillers, plasticizers and pigments**. These are organic materials of high molecular weight which can be molded to any desired form when subjected to heat and pressure in the presence of a catalyst. Plastics are classified as **thermoplastic**, and **thermosetting**.



The **thermoplastic** variety softens on heating and hardens on cooling, i.e., their hardness is a temporary property subjected to change with rise or fall of temperature and can be brought again to plastic stage on heating. These are formed by addition polymerization and have long chain molecular structure. They can be remolded, for use, as many times as required. Examples are **material resins** (rosin, kopal, amber, shellac), **cellulose derivatives** (cellulose acetate, cellulose nitrate, nitrocellulose or celluloid, cellulose acetate-butyrate); **polythenic or vinyl resin** (polyethylene, polyvinyl chloride, polyvinyl acetate, vinyl chloride = vinyl acetate,

poly vinylidene chloride, polystyrene, polymethyl methyacrylate or lucite or plexiglass and polytetrafluoroethylene), **polyamides** (Nylon 6:6, Nylon 6 and Nylon 11).

Thermosetting plastic cannot be reused. They require great pressure and momentary heat during molding and finally get hardened on cooling. The chemical reaction in this process cannot be reversed. Once solidified they cannot be softened. Compared to thermoplastics, they are hard, strong and more brittle. The important thermosetting resins are phenolic resins or phenoplasts (bakelite), amino resins, polyester resins, epoxy resins and silicon resins.

Constituents of Plastics

The constituents of plastics are resin, plasticizer, filler, pigment and dye, lubricant and catalyst.

resin: acts as binder for holding different constituents together. Thermosetting resins are usually supplied as linear polymer of a comparatively low molecular weight being fusible and moldable.

plasticizer: modifies plastic to impart desirable combination of strength, flexibility and toughness. Plasticizers, which are mostly liquids, are usually organic compounds or resins possessing very low vapor pressure. Their addition is particularly necessary when the softening temperature of a resin is too high. Plasticizer is supposed to neutralize a part of the intermolecular force of attraction between macromolecules of resins. Consequently the polymeric macromolecules of resin move with greater freedom, thereby increasing the plasticity and flexibility of the compounded material. However, tensile strength and chemical resistance is reduced. Some of the examples of plasticizers are vegetable oils (non-drying type),

camphor, esters of stearic and oleic acids, tricresyl phosphate, tributyl phosphate, tetrabutyl phosphate and triphenyl phosphate.

filler: is added up to 50 % of the molding mixture to increase the hardness, tensile strength, bond, opacity, finish and workability besides reducing the cost, shrinkage on setting, and brittleness of the final product. Some of the fillers are wood flour, mica, diatomaceous earth, saw dust, ground cork, paper pulp, corn husk, carbon black, cotton fiber, metallic oxides, metal powder (Al, Cu, Pb).

mica powder

pigment: is added to achieve desired color of the plastic and should be resistant to the action of sunlight.

lubricant: is used to make the molding of plastic easier to prevent sticking of materials to the mould for a flawless finish. The examples are stearates, oleates and soaps.

sodium stearates (major component of soap)

catalyst: is added only in the case of thermosetting plastics to accelerate the polymerization of fusible resin during molding operation into cross-linked infusible form.

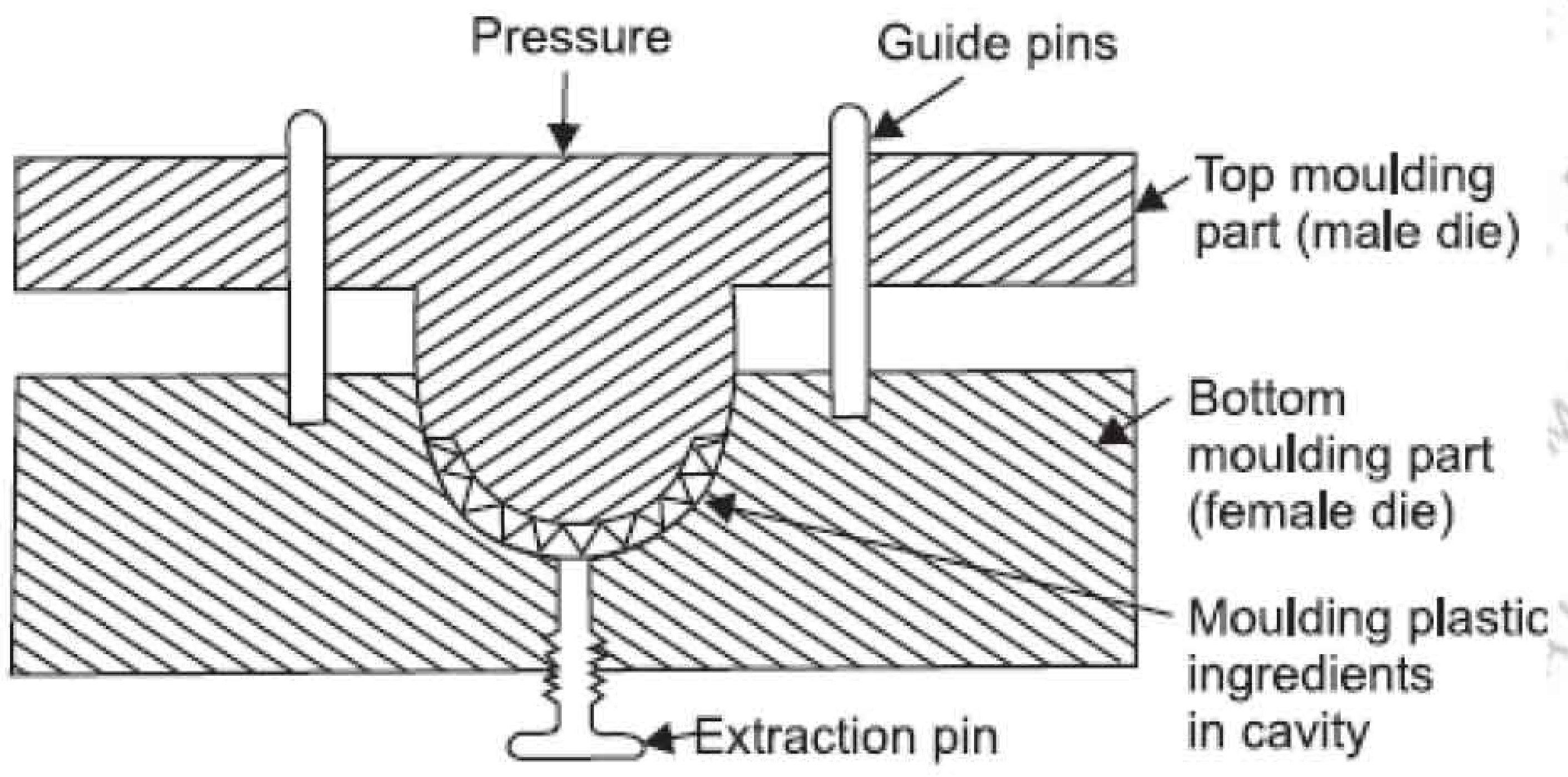
blowing agent: Sodium bicarbonate and ammonium carbonate are sometimes added to plastics to produce porous products.

sodium bicarbonate (baking soda)

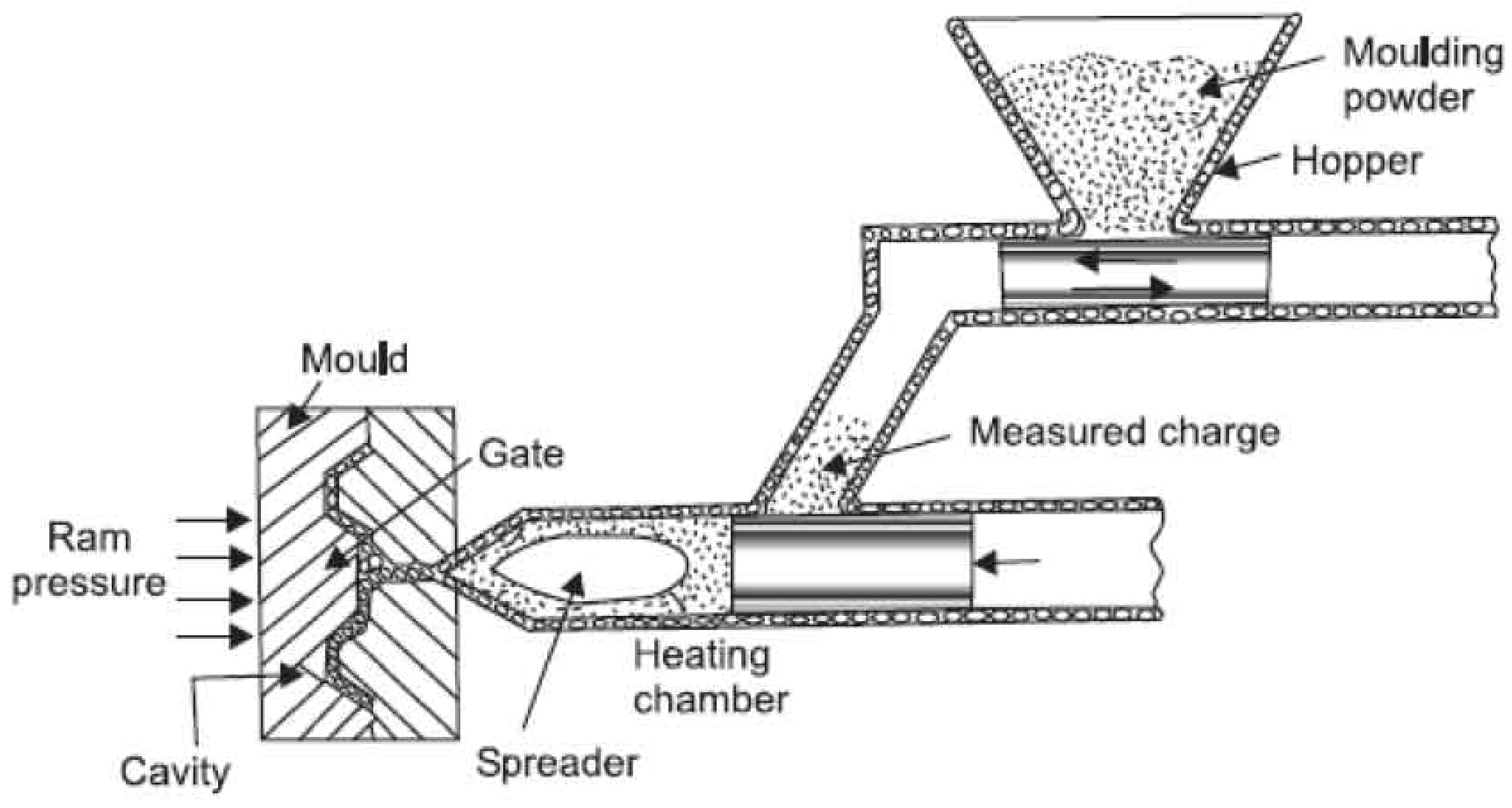
Fabrication of Plastic Products

The method used for fabrication of commercial articles from plastics depends primarily on the type, resin used, shape, size and thickness of the articles. Main production methods are molding, casting and lamination.

compression molding: can be employed both for the thermoplastics and thermosetting plastics. The fluidized material is filled in the mould cavity by hydraulic pressure. There is an arrangement to heat the plastic if desired. Temperature and pressure is applied till the chemical reaction is complete. Finally curing is done by heating (thermosetting plastics) or by cooling (thermoplastics). After curing is complete, mould is opened and molded material is taken out.



injection molding: is best suited for the molding of thermoplastic materials. The plastic powder is fed into a cylinder from a hopper where it is heated. The resin melts in the heating zone from where it is sent to the mould cavity through nozzle. The mould is kept cold to allow the hot plastic to cure and acquire the shape.



extrusion molding: is used for continuous molding of thermoplastic materials into articles of uniform cross-section such as tubes, rods, strips, electric cables, etc. The thermoplastic material is heated to plastic state and is pushed to a die by a screw conveyer. As the extruder rotates it has a mixing, smearing, and frictional heating action which changes the dry granular charge into a soft plastic mass before it reaches the end of the screw. Here the plastic mass by air jets.

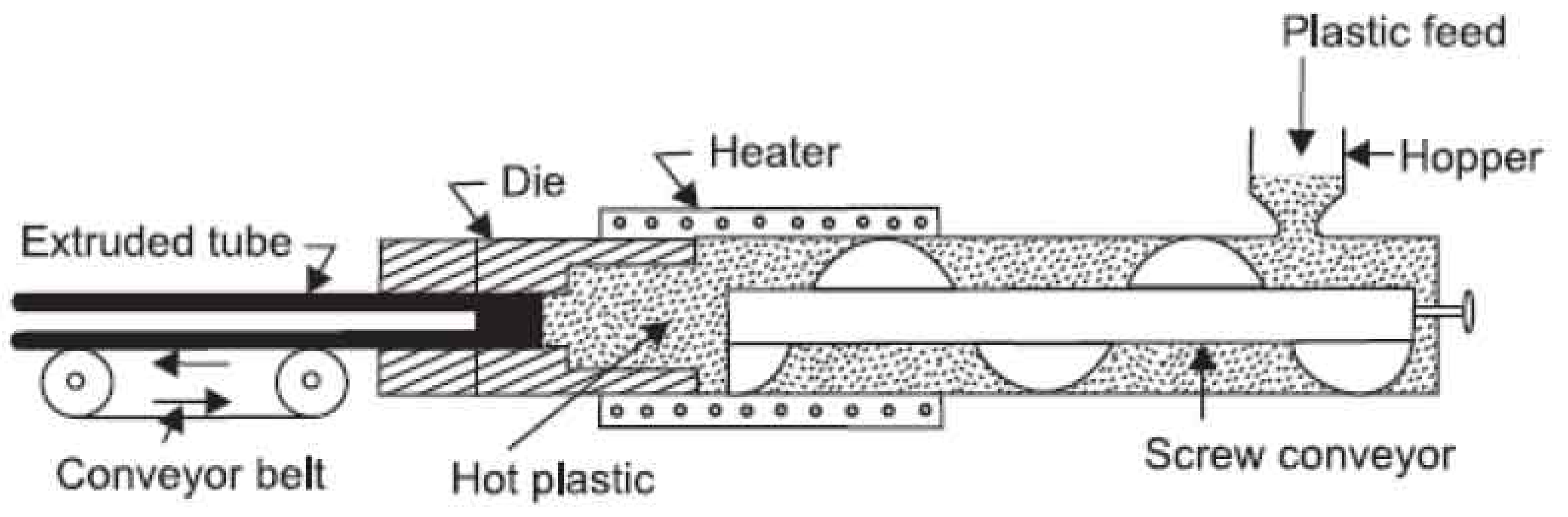


Fig. 16.14 Moulding of Tube by Horizontal Extrusion Moulding

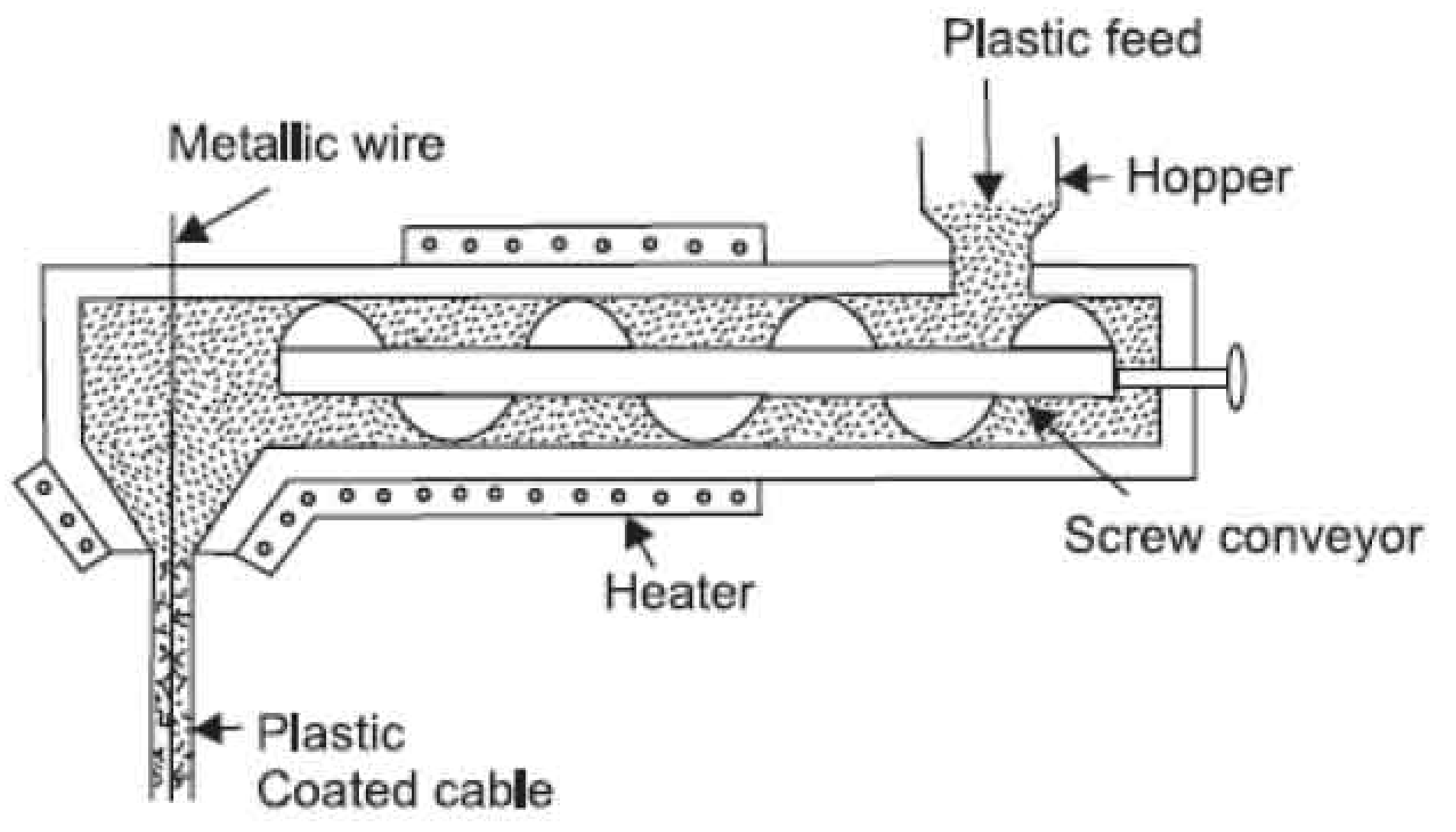


Fig. 16.15 Moulding of Cable by Vertical Extrusion Moulding

casting: The plastics are molded without application of pressure. The resin is melted and poured into mould. The casting of plastics is similar to that of cast iron. Since the cast plastic is not so smooth just after casting, they are polished. This method is most suited to the plastics formed form cellulose acetate and cellulose nitrate.

lamination: Thin sheets of cloth are impregnated with thermosetting resin. These lamins are then pressed by a hydraulic press. Under temperature and pressure the lamins are bonded together to form one sheet. The laminated plastics exhibit improved mechanical and electrical properties. The thickness of laminated plastics ranges between 0.13 mm–15 mm. Vinyl resin is most suitable for lamination.

Properties of Plastics

- Can be produced in any desired shape or size and have high tensile and compressive strengths.

- Easy to work upon.
- Light in weight and a few varieties are glossy like glass.
- Not attacked by insects and fungi.
- Available in desired color and texture.
- Require a little maintenance.
- Good electrical insulators and have low thermal conductivity.
- Shock absorbing material.
- Can be sawn, drilled and punched and welded easily.
- High strength to weight ratio.
- High resistance to weathering conditions.
- Corrosion resistant.
- Painting or polishing of the surface is not required.
- Some varieties are as hard as steel.
- Withstands moisture, oil and grease well.
- High coefficient of thermal expansion (about ten times of steel).
- Deterioration under prolonged exposure to sun’s ultra violet rays.
- Low manufacturing cost, hence cheap.

BITUMEN

Bitumen is a non-crystalline solid or viscous material derived from petroleum, by natural or refinery process and substantially soluble in carbon disulphide. It is asphalt in solid state and mineral tar in semi fluid state. Bitumen is brown or black in color. Its main constituents are petrolene (a yellowish oily substance, an excess of which makes bitumen to melt at low temperature) and asphaltene (hard black substance, an excess of which makes bitumen brittle and non-plastic). It contains carbon 87 %, hydrogen 11 % and oxygen 2 %.

Bitumen is not affected by light, air or water individually, but in combination they can make it brittle, porous and susceptible to oxidation forming blisters and cracks. It becomes soft at temperatures between 30°–100° C (no sharp melting point), and therefore must be protected from exposure to heat. It is insoluble in water and fairly resistant to most acids. Although bitumen is combustible, composite products, such as mastic asphalt, are not readily ignited.

Classification

based on source: Bitumens are classed as natural and petroleum bitumens.

natural bitumen: Pure natural bitumen occurs rarely. Limestones, sandstones and soils impregnated with bitumen are frequently found. It originates from the accumulation of petroleum in the top layers of earth crust through migration, filling pores and cavities of rocks, under the action of high temperature and pressure.