

## 1

## Organic Polymers: Past and the Present

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### 1.1 Introduction and History of Polymers

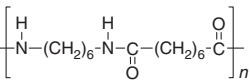
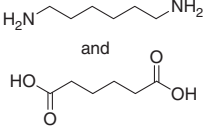
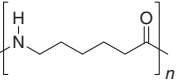

The word polymer is derived from the Greek word “polumeros” where “Polus” means “many” and “meros” means “units.” Henceforth polymers can be defined as the complex and giant molecules or “**macromolecules**” which are supposed to form by the combination of many small repeating molecules called monomers. Examples of some commercially important polymers and their practical applications have been highlighted in Table 1.1. The most practical distinguishing feature of polymer from its monomer is its huge difference in physical, chemical, and mechanical properties after the polymerization process occurs (Dorel 2008). For example, ethene is a gas but when they combine with each other via the polymerization process, a new class of compound, i.e., polyethene, is formed which differs from its monomer in terms of many physicochemical properties. Monomers being smaller have low molecular weight, while polymers being much larger have very high molecular weight. Compared to simple organic molecules, polymers aren't composed of identical molecules; hence, a polymer sample generally comprises chains of different lengths, which is why their molecular weight is always expressed as an average molecular weight. For instance, the HDPE (high-density polyethylene) molecules are all long-chain carbon chains, but the lengths generally vary by thousands of monomer units. Depending on the type of monomeric units, polymers may be of different types such as homopolymers where all the repeating units (RUs) are same and co-polymers which can be made up of two or more monomer species. For example, in case of homopolymers such as polythene the monomer unit is ethylene, in polyvinylchloride (PVC) the monomer unit is vinyl chloride. Important examples of co-polymers include polyethylene-vinyl acetate (PEVA), nitrile rubber, and acrylonitrile butadiene styrene (ABS) which are formed by the combination of more than one monomer.

Based on the type of backbone chain and composition, polymeric materials are classified into two types, viz. organic polymers and inorganic polymers

**Table 1.1** Some commercially important polymers and their uses.

Name of polymer and structure	Monomer	Practical applications
Polythene $\left[ \begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right]_n$	Ethene $\begin{array}{c} \text{H} \quad \text{H} \\ \backslash \quad / \\ \text{C} = \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$	Electrical insulators, packing of materials
Polystyrene $\left[ \begin{array}{c} \text{Ph} \quad \text{H} \\   \quad   \\ \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right]_n$	Styrene $\begin{array}{c} \text{---} \text{C} = \text{C} \\   \quad \backslash \\ \text{H} \quad \text{Ph} \end{array}$	As insulator, wrapping material, for construction of toys
Polyvinyl chloride $\left[ \begin{array}{c} \text{Cl} \quad \text{H} \\   \quad   \\ \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad   \\ \text{H} \quad \text{H} \end{array} \right]_n$	Vinyl chloride $\begin{array}{c} \text{H} \quad \text{Cl} \\ \backslash \quad / \\ \text{C} = \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{H} \end{array}$	In the manufacture of raincoats, handbags
Polytetrafluoroethylene (Teflon) $\left[ \begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad   \\ \text{F} \quad \text{F} \end{array} \right]_n$	Tetrafluoroethene $\begin{array}{c} \text{F} \quad \text{F} \\ \backslash \quad / \\ \text{C} = \text{C} \\ / \quad \backslash \\ \text{F} \quad \text{F} \end{array}$	As lubricant insulator in the manufacture of semiconductors, non-stick coating in kitchen cookware and medical devices
Polyacrylonitrile (PAN) $\left[ \begin{array}{c} \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad \backslash \\ \text{H} \quad \text{CN} \end{array} \right]_n$	Acrylonitrile $\begin{array}{c} \text{N} \equiv \text{C} \\ \backslash \quad / \\ \text{C} = \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{---} \end{array}$	In construction of synthetic fibers and wools
Styrene butadiene rubber (SBS) or Buna-S rubber $\left[ \begin{array}{c} \text{---} \text{C} = \text{C} \text{---} \text{C} \text{---} \text{C} \text{---} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{Ph} \end{array} \right]_n$	1,3-Butadiene and styrene $\begin{array}{c} \text{---} \text{C} = \text{C} \text{---} \text{C} = \text{C} \text{---} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \quad \text{and} \quad \begin{array}{c} \text{---} \text{C} = \text{C} \\   \quad \backslash \\ \text{H} \quad \text{Ph} \end{array}$	For making of automobile tires and footwear, etc.
Terylene (Dacron), polyester $\left[ \text{---} \text{O} \text{---} \text{C} \text{---} \text{C} \text{---} \text{O} \text{---} \text{C} \text{---} \text{C} \text{---} \right]_n$	Ethylene glycol and terephthalic acid $\begin{array}{c} \text{HO} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{OH} \end{array} \quad \text{and} \quad \begin{array}{c} \text{HO} \text{---} \text{C} \text{---} \text{C}_6\text{H}_4 \text{---} \text{C} \text{---} \text{OH} \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	For making fibers, safety belts, plastic bottles, hard wear clothes like dresses

Table 1.1 (Continued)

Name of polymer and structure	Monomer	Practical applications
Nylon-6,6 	Hexamethylenediamine and adipic acid 	In making brushes, synthetic fibers, water-resistant machine parts
Nylon-6 	Caprolactum 	For manufacture of carpets, tire cords, seat belts, parachutes, ropes, etc.

(Currell and Frazer 1969; Gowarikar et al. 2022). Basically, organic polymers are made of carbon-carbon backbone skeleton (Peng et al. 2017), while inorganic polymers do not have carbon-carbon skeleton, rather they have a skeleton like Si-Si for polysilanes, Si-O for polysiloxanes, Si-N for polysilazanes, S-S for polysulfides, B-N for polyborazylenes, and S-N for polythiazyls (Seth 2020; Indra and Shrray 2015).

Cellulose is one of the most abundant organic polymers on Earth, and it is a linear polymer of as many as 10,000 dextro-glucose units joined with each other. Starch, belonging to carbohydrates, can be found in grains and potatoes. Starch is a polymer, also known as a polysaccharide because it is made from glucose as monosaccharide. Starch molecules include two types of glucose polymers, amylose and amylopectin. Amylopectin, being a major starch component, is found in many plants. Amylose belongs to a linear-chain polymer having around two hundred glucose molecules per molecule.

Based on the existence and method of formation, organic polymers may be further categorized as natural or synthetic, and interestingly both of them find equal attention in our day-to-day life. Natural organic polymers can be found in nature or living system and important examples of natural organic polymers include proteins or polypeptides, polynucleotides like DNA and RNA (DNA is a double-stranded polynucleotide chain, while RNA is a single-chain structure of polynucleotides), silk, wool, cellulose, natural rubber. Synthetic polymers are man-made polymers which are being synthesized in the industry or laboratory. Important examples of synthetic polymers include polyethylene (both low-density polyethylene – LDPE and high-density polyethylene – HDPE), polypropene (PP), polyacrylonitrile (PAN), polyaniline (PANI), polystyrene (PS), polyvinylchloride (PVC), tetrafluoroethene (Teflon), polyacetylene, nylon, thermoplastic polyurethane (TPU), and Bakelite. Most of the synthetic polymers possess enhanced lifetime and improved mechanical

properties. However due to the absence of a functional group in most of them, they do not have some important physical and chemical properties which limit their synthetic utility in many practical applications. To address this problem post-synthetic functionalization and further modification of polymers have been done in recent times to achieve multinational properties.

During the fifteenth century, Christopher Columbus was involved in the discovery of rubber by isolating it from trees, and later Joseph Priestly observed that the material is helpful for erasing pencil marks on paper. This observation launched the rubber industry. Combining the latex of rubber tree with the morning glory plant juice in various proportions helped to achieve rubber's distinct properties for designing selective products like bouncing balls, various kinds of rubber bands, etc. To gain the advantages and properties of both natural and synthetic polymers, researchers across the globe were always in search for the development of improved semi-synthetic organic polymers. For example, vulcanization of rubber was introduced for enhancing the quality of natural rubber where a small amount of sulfur is added as a cross-linking agent which can enhance the quality and stability of rubber. Vulcanized rubber is comparatively stronger, elastic, more resistant to abrasion and temperature change, and most importantly inert with respect to chemicals and electric current as compared to untreated natural rubber (Brown and Poon 2005).

Likewise, natural resources polymeric materials like cellulose and proteins have been extensively used for making improved polymers via copolymerization techniques.

Henri Braconnot's Braconnot, Christian Schönbein, and coworkers in 1830s first developed the derivatives of cellulose for constructing novel semi-synthetic materials, known as celluloid and cellulose acetate. Later the term "polymer" was introduced in 1833 by Jöns Jakob Berzelius, even though Berzelius could not provide significant contribution for the development of modern polymer science.

In 1909, Leo Baekeland developed Bakelite from cheap and readily available chemicals such as phenol and formaldehyde which opened the door of emerging technology for designing many innovative polymeric products (Baekeland 1909; Wallace 1945).

In spite of the noteworthy developments in polymer synthesis, the molecular nature of polymers was not clear until the concept was introduced by Hermann Staudinger in the year 1922. Earlier formation of polymers was explained via aggregation theory proposed by Thomas Graham in 1861. According to Graham, cellulose and other polymers were supposed to have colloidal nature where aggregation of small molecules having smaller molecular masses was joined by some unknown intermolecular force. Later, Hermann Staudinger first anticipated that polymers consist of long chains of atoms held together by some covalent bonds. Staudinger, for his immense contribution in providing concepts to understand about polymeric structure, was awarded the Nobel Prize in Chemistry in the year 1953.

During the period of World War II there had been an increased demand of natural polymers such as silk and rubber. But due to their limited supply, alternative synthetic polymers such as nylon were introduced to meet the essential requirements.

Then, the invention of advanced polymeric materials like Kevlar and Teflon became eye-catching to launch the robust polymer industry.

The most important properties of a reactant to be a monomer or to take part in polymerization reaction are (i) presence of reactive functional group and (ii) the minimum requirement of bifunctionality. Depending upon the nature of functionality, for example, bi- or tri-functionality, the polymers may be designed as chain polymers, blocked or cross-linked polymers, respectively. For the synthesis of polymers, various methods such as addition polymerization, condensation polymerization, and co-ordination polymerization have been employed. In most of the synthetic procedures use of catalyst, initiator, application of high pressure and temperatures are the important requirements to assist rapid polymerization process.

Due to the great demand of polymeric materials in day-to-day life, many researchers across the globe are working in this field, and hence Nobel Prize has been awarded to many scientists for the development of this particular field. Karl Ziegler (1898–1973) and Giulio Natta (1903–1979) independently developed catalysts which smoothly assist polymerization under ambient condition with high stereospecificity to furnish isotactic polypropylene (i-PP) and HDPE. In the year 1963, Giulio Natta and Karl Ziegler were jointly awarded Nobel Prize in Chemistry for their immense contributions in the area of polymer science. Next, Flory was awarded Nobel Prize in Chemistry in 1974 for his important contribution in both theoretical and experimental development of polymer science. In the year 2000, Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa were jointly awarded Nobel Prize in Chemistry for their work on conductive polymers which provide significant contributions in the advancement of molecular electronics. John Bennett Fenn, Koichi Tanaka, and Kurt Wüthrich were awarded Nobel Prize in Chemistry in the year 2002 for their innovative methods in identification and structural analysis of biological macromolecules. Robert Grubbs, Richard Schrock, and Yves Chauvin were awarded Nobel Prize in Chemistry in the year 2005 for the development of olefin metathesis also known as ring-opening metathesis polymerization reaction (ROMP). The use of Ru-based Grub's catalyst for polymerization gained significant popularity in recent past. Some of the major breakthroughs that evolved during the development of polymer science have been depicted in Table 1.2.

Even though polymeric materials have important applications, their non-biodegradability always poses a threat to the surroundings. For example, polyethylene compounds cannot be broken down by the bacteria present in the soil, and due to constant accumulation of these materials soil and water pollution arises. To solve this particular problem, extensive study is going on around the world for the development of biodegradable polymers which are also considered as green polymers. One important example of biodegradable polymers is poly  $\beta$ -hydroxybutyrate-co- $\beta$ -hydroxy valerate (PHBV) which can be prepared by the combination of 3-hydroxy butanoic acid and 3-hydroxy pentanoic acid.

Recently polymer matrix composites (PMCs) have been introduced which possess a wide range of potential applications (Tewatia et al. 2017; Ramakrishna et al. 2001). PMCs are polymers reinforced with additives such as glass fibers, carbon fibers, carbon nanofibers, graphene, and carbon nanotubes. They have been

**Table 1.2** Major breakthroughs in the history and discovery of polymer science.

Year	Name of the scientists and contribution
1833	Berzelius for the introduction of the polymer terminology
1839	Edward Simon for the synthesis of polystyrene
1859	A.V. Lourenço and Charles Adolphe Wurtz for the production of polyethylene glycol
1900	Hermann Staudinger (Father of Modern Polymer Science) for providing the idea about the structure of polymers (long-chain molecules), awarded Nobel Prize award in 1953
1938	W.H. Carothers for the synthesis of nylon which laid the foundation of the synthetic fiber industry
1963	Giulio Natta and Karl Ziegler awarded Nobel Prize in Chemistry for the metathesis ring-opening polymerization reaction
1974	Paul Flory awarded Nobel Prize in Chemistry for providing significant contributions in the area of experimental and theoretical polymer research
1984	Bruce Merrifield for the development of solid-phase protein synthesis awarded Nobel Prize in Chemistry
2000	Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa awarded Nobel Prize in Chemistry for the discovery and development of electrically conductive polymers
2002	John Bennett Fenn, Koichi Tanaka, and Kurt Wüthrich for identification and structure analysis of biological macromolecules, awarded Nobel Prize in Chemistry
2005	Grubbs and coworkers awarded Nobel Prize in Chemistry for the introduction of metathesis tactics which provided significant advancement in synthetic chemistry

widely employed because of the magical enhancements of mechanical, thermal, and electrical properties associated with this special type of material. Presently, researchers are looking for intelligent polymers which are specially designed materials that can extend the scope of polymer science.

## 1.2 Classification of Organic Polymers

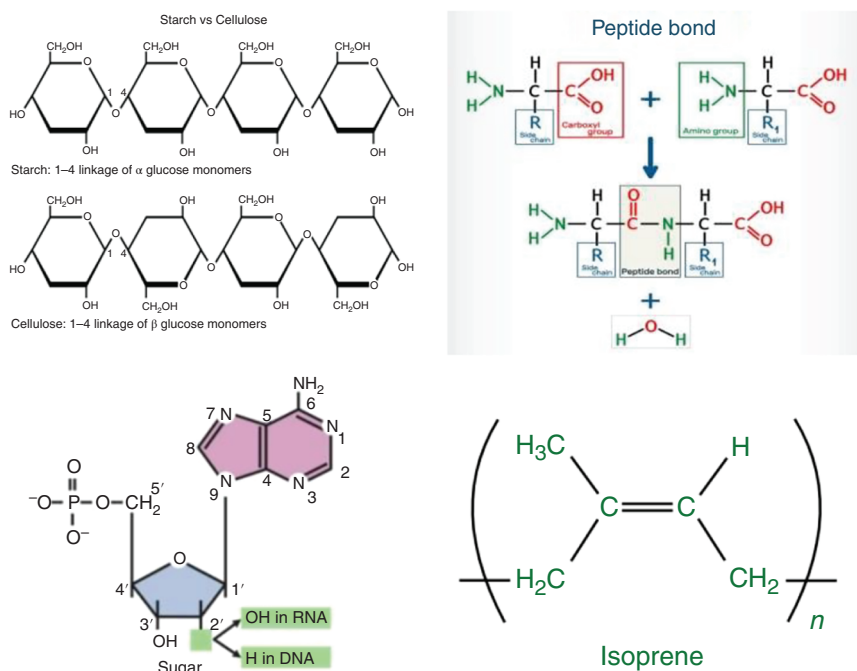
Polymers are divided primarily into organic polymers and inorganic polymers based on the nature of backbone chain. Primarily, organic polymers are made up of carbon backbone structures, while inorganic polymers do not have carbon atoms in their backbone. Organic polymers are suitable for several applications because of their simple structures and biodegradable nature, which make them environmentally friendly. Nevertheless hybrid polymers like “silicones,” which are organosilicon polymers or polysiloxanes, are also well known because of their potential industrial applicability. Silicones found wide applications because of the presence of strong

carbon-silicon (C—Si) bonds. The formation takes place in a few steps, starting from the alkylation/arylation of a silicon tetrachloride and finally resulting in silicones,  $R_2(SiO)_n$ . Here “R” represents an alkyl/aryl group. Silicones found commercial applications mainly under three category namely fluids, elastomers, and resins (Zielecka et al. 2002).

It is well known that most of the polymers are built up via two organic-chemistry-based mechanisms. One is addition/chain and the another is condensation/step-growth polymerization mechanism. Both of these mechanisms involve a combination of small monomers or repeating units. The mechanism of polymer formation results in either addition or chain polymers. Apart from this, polymers are broadly classified based on their source, structure, molecular forces operating, and thermal behavior (Kariduraganavar et al. 2014).

(a) Originally polymers were classified as either “natural or synthetic polymers.” Natural polymers occur naturally, whereas synthetic polymers can be synthesized artificially. Natural polymers are obtained from animals and plants. A few examples include

(i) *Proteins*: Wool and natural silk are protein-based products. Proteins are the building blocks of animal cells. The proteins are formed by the repetition of  $\alpha$ -amino acids (Figure 1.1).



**Figure 1.1** Building blocks of a few natural polymers. Source: Adapted from [https://d1hj4to4g9ba46.cloudfront.net/questions/1536297\\_1144437\\_ans\\_9129a4f3e7f84e03932353ae379c21a0.png](https://d1hj4to4g9ba46.cloudfront.net/questions/1536297_1144437_ans_9129a4f3e7f84e03932353ae379c21a0.png).

- (ii) *Carbohydrate polysaccharides*: Repetition of smaller monosaccharides like “glucose” leads to the formation of macromolecules like cellulose and starch, which constructs the plant cell. These biological molecules also supply energy to animal cells (Figure 1.1).
- (iii) *Nucleic acids*: “RNA” and “DNA” are the bio-polymers formed by the repetition of nucleotides. These are the primary constituents of all living cells (Figure 1.1).
- (iv) *Natural rubber*: This is a well-known plant-extracted component. It is present in the latex of rubber plant. It is also known as *cis*-polyisoprene, which is a polymer of isoprene. However the *trans*-isomer is known as “gutta-percha” (Figure 1.1).

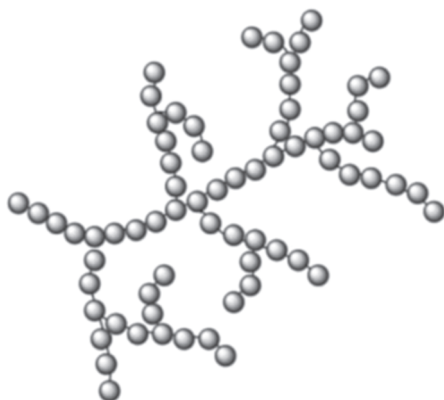
On the other hand, most of the daily-use polymers are synthetic ones. This covers a series of polyvinyl-based chain polymers like “polyvinylchloride” and functional-group-based condensed polymers like “polyethyleneterephthalate.” A few examples are PVC, polyethylene, polystyrene, Teflon, synthetic rubber, nylon-6, and nylon-66. Most of these are organic polymers. Moreover “semi-synthetic polymers” also do exist. These are obtained by chemical modification of natural polymers. For example, one of the important materials, cellulose diacetate, is synthesized from cellulose by reacting with acetic anhydride in the presence of sulfuric acid (Kamide 2005). It is formed by the acetylation reaction. Some of the hydrogen atoms in cellulose are substituted by acetyl ( $-\text{COCH}_3$ ) groups.

- (b) Polymers are divided into three structural categories, namely, linear, branched, and cross-linked polymers.
  - (i) Linear polymers are long straight-chain molecules with highly ordered structures. Importantly, the randomness is comparatively less as the monomers are linked together in linear fashion. Because of the linear arrangement their structure is densely packed. Some of the characteristics, like high densities, melting temperatures, and mechanical strengths, are the result of this. Polyester and polyethylene belong to this category.

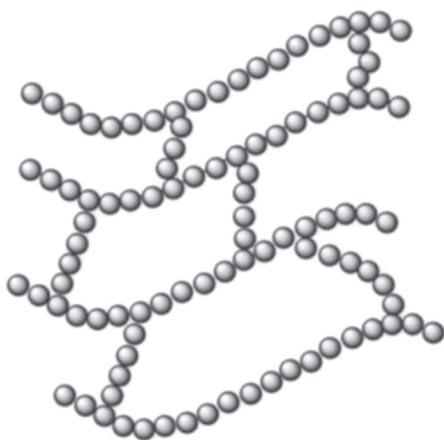


- (ii) Branched one possesses secondary polymer chains connected to a primary backbone, resulting in a branching-tree-like structure. The chains are less well packed due to branching, which results in much lower melting temperatures, densities, and mechanical strengths (Abuzreda 2023). Branch-chain polymers can be created via condensation or addition polymerization methods. Examples include amylopectin, glycogen, LDPE, and any rubbers that have been vulcanized.



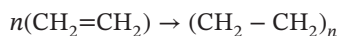


- (iii) Network or more specifically the cross-linked polymers are formed by connecting two or more chains by cross-linking agents. The initially formed linear polymeric chains are joined together to form a three-dimensional network structure. The chain linkages give these polymers their hard, stiff, and brittle characteristics. Condensation polymers are invariably cross-linked polymers. A group of cross-linked polymers is known as resins.



- (c) Depending upon the mechanism of formation, polymers are classified into addition and condensation polymers. Addition or chain reaction polymers are formed by successive addition of monomers (small molecules). The linked monomers are called “repeating units” (RUs). The RUs are joined predominantly by covalent bonds. Their mechanism of formation is primarily dependent upon the three steps: initiation, propagation, and termination. The propagation step is responsible for getting high-molecular-weight polymers. The molecular weight is an important property in polymer characterization. “Polyethylene” is a chain polymer formed by the repetition of ethylene

monomers.



Alternatively, condensation reaction between monomers bearing typical functional groups like hydroxyl ( $-\text{OH}$ ), carboxyl ( $-\text{COOH}$ ), ester ( $-\text{COOR}$ ), and amide ( $-\text{CONH}_2$ ) results in the formation of condensed polymers. During condensation reaction some small molecules like water or mineral acids are released from the monomers by condensation. Polymerization proceeds by successive formation of dimers, trimers, and tetramers. However the extent of polymerization between them is important for having a high-molecular-weight condensation polymer (Kariduraganavar et al. 2014). Nylon-6,6 is a common example of condensation polymer. It is formed by the condensation of hexamethylene diamine,  $\text{NH}_2-(\text{CH}_2)_6-\text{NH}_2$ , and adipic acid,  $\text{COOH}-(\text{CH}_2)_4-\text{COOH}$ . The reaction takes place between a diamine and a dibasic acid. The two monomers are linked by a peptide bond as shown in Figure 1.1. One of the advantages here is that no initiator is required for the reaction.

- (d) Elastomers and fibers are two subcategories of polymers that are determined by the molecular forces between individual chains.

An elastomer is plastic and its polymeric chains are bounded by very weak van der Waal forces. Because of such weak operating molecular forces, these polymers are stretchable as well as compressible. They can be reverted back to their earlier form. It is a randomly oriented amorphous polymer. Vulcanized rubber is an elastomer that exhibits cross-linking by sulfur atoms. Such cross-linking prevents the chains from slipping over one another.

However, due to the highly organized geometry and potent intermolecular forces of attraction, fibers possess the highest tensile strength and negligible elasticity. Fibers have a high melting point and low solubility, and are crystalline in nature. Fibers include polymers like cellulose, nylon, wool, and silk (Abuzreda 2023).

- (e) Polymers are divided into thermoplastics and thermosetting plastics based on heat treatment. Interestingly most of organic macromolecules belong to these categories.

Thermoplastics are a type of polymer that softens when heated and may take on any shape when cooled. Thermoplastic polymers can undergo transition from hardness to softness and vice versa. At normal temperature conditions, they are hard. With increase in temperature, hardness decreases and they become soft and viscous. The polymeric chains can slip over one another during heating. When cooled, this material stiffens up after being soft and viscous. Hence depending on temperature, thermoplastic polymers can be molded into various shapes and products. Without affecting the chemical identity and mechanical merits of the plastic, the heating, softening, and cooling procedures can be performed as frequently as needed (Carothers 1929). They have highly ordered crystalline as well as less ordered amorphous regions. Polyethylene, polycarbonate, polypropylene, Teflon, and PVC are a few typical examples.

When thermosetting polymers are heated, they undergo chemical transformation and cross-linking takes place, and when they are cooled, they become permanently hard and infusible. Repeating heat treatment doesn't cause them to soften; instead, they degrade. These polymers undergo setting to only one form during heat treatment. It cannot be converted back to the original form. They become hard on heating and turn into a solid that cannot be re-melted by changing the temperature (Carothers 1929). These polymers set into a solid structure because of the existence of cross-linking. With rise in the degree of cross-linking the rigidity also increases. Upon heating the hardness increases due to extensive cross-linking. Moreover, cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle. Common examples of thermosetting polymers are phenol-formaldehyde resin and urea-formaldehyde resin (Figure 1.2).

- (f) In addition to these, organic polymers also categorized as conducting polymers as they found promising applications in organic light-emitting diode (OLED), semiconductors, and superconductors. Interestingly, the first conducting polymer is an organic polymer, polypyrrole, as reported by Donald Weiss and coworkers in 1960. Polypyrrole is a heterocyclic polymer containing carbon and nitrogen atoms in its rings. Because of the conjugation of electrons in their rings, they can act as conducting polymers. Conductive polymers' most important benefit is their processability, which is mostly attained through dispersion (Saldívar-Guerra and Vivaldo-Lima 2013). Conducting polymers can be further classified into intrinsically conducting polymers, extrinsically conducting polymers or doped polymers.

*Intrinsically conducting polymers:* This class of polymers conducts electricity due to the presence of delocalized electron pairs or conjugated  $\pi$ -bonds in

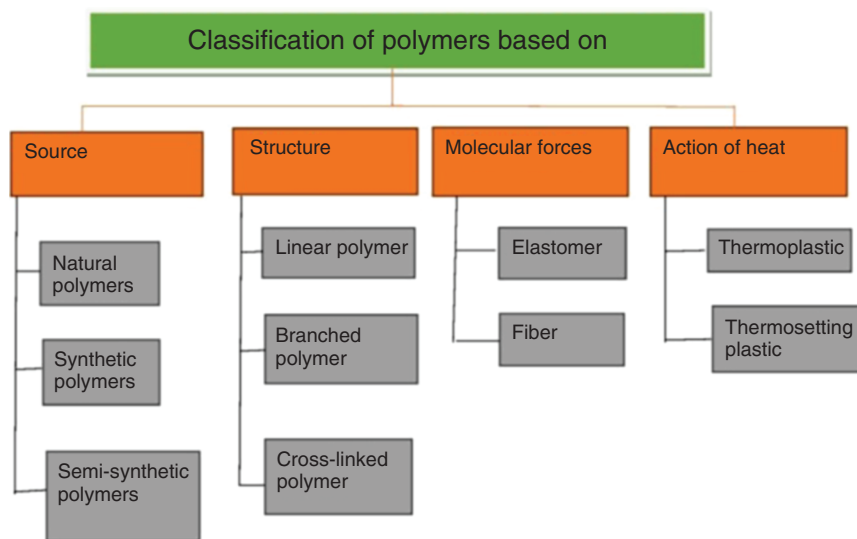


Figure 1.2 General classification of polymers (self-made).

the structural frame. In a polymeric material with an electric field, the delocalized electrons can move across it. Coupled bands, valence bands, and conduction bands are produced as a result of overlapping orbitals.

*Semiconducting or impure polymers:* Doping is a process by which conductivity of materials can be enhanced by adding or doping some impurity. Impurity means certain elements in their chemical form. Doping creates charge carriers in the polymer chain by either oxidation or reduction processes. The common doping processes are *p*-doping and *n*-doping. Both involve creation of positive holes and negative excess electrons by the redox processes.

### 1.3 Synthesis and Properties of Polymers

Polymer can be synthesized by two ways: (i) polymerization of the monomeric units and (ii) chemical modification of monomeric side chain of the polymer. Through the first method molecular weight can be increased, whereas the second method will change the structure of the molecule without molecular weight variation.

The chemical process which converts molecules into polymer macromolecules is known as polymerization. This process is the combination of different reactions which determine the features of the product. The properties of the obtained macromolecules are also dependent on the chemical composition of the starting materials. This chapter will mainly cover the synthesis of polymers by using different polymerization processes. Basically there are two types of polymerization processes: viz. **step growth** or **condensation polymerization** and **addition polymerization**.

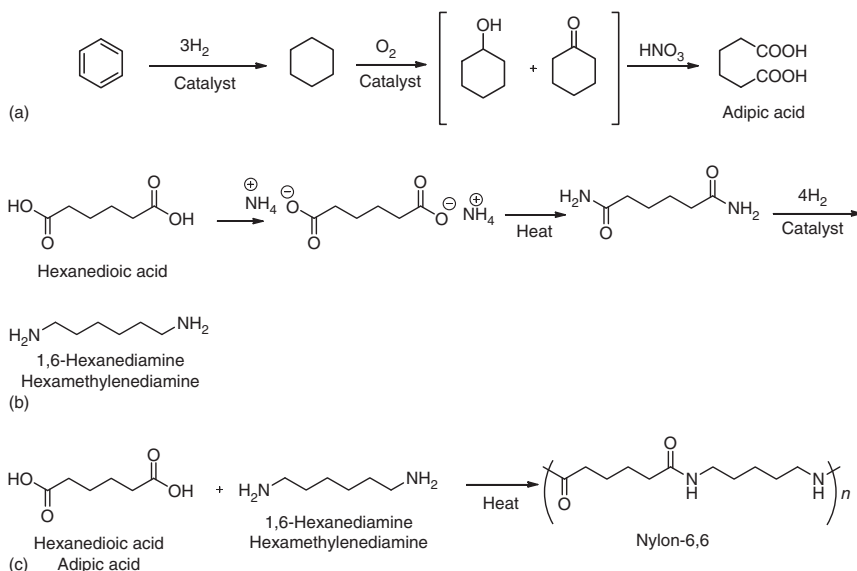
**Step Growth Polymerization** is one type of polymerization process in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers, and eventually long-chain polymers. Through this step growth polymerization, many naturally occurring as well as synthetic polymers can be obtained. For example, polyamides, polyesters, polycarbonates, polyurethanes, epoxy resin, and phenol formaldehyde resin.

#### 1.3.1 Polyamides

Nylon is a generic designation for a family of synthetic polyamides. Nylon, silk-like thermoplastics have significant applications in fabric, fibers, shapes, films, etc. Many synthetic polyamides, including nylon-6,6, nylon-6, nylon-6,10, and nylon-11, are well-known. The synthetic methods of some of the polyamides are discussed below.

#### 1.3.2 Nylon-6,6

Hexamethylene diamine and adipic acid (Hexan-1,6-dioic acid) are co-polymers in it. Benzene, a byproduct of petroleum refining and cracking, is the primary raw material used in the manufacture of nylon-6,6. Adipic acid serves as the precursor once more in the creation of hexamethylene diamine. The synthesis of nylon-6,6 is shown in Scheme 1.1 (Gowarikar et al. 2022).

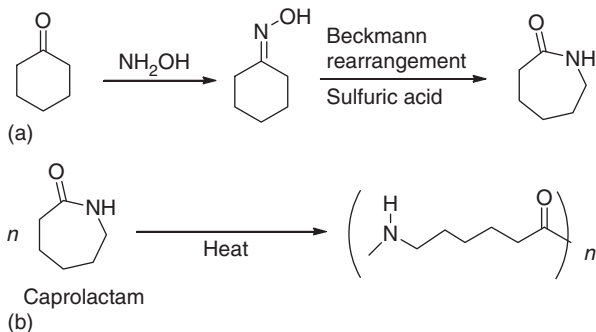


**Scheme 1.1** (a) Synthesis of adipic acid from benzene, (b) synthesis of hexamethylenediamine from adipic acid, and (c) synthesis of nylon-6,6.

During fabrication, nylon fibers are cold-drawn to about four times their original length, which increases crystallinity, tensile strength, and stiffness.

### 1.3.3 Nylon-6

Nylon-6 or polycaprolactam, a semicrystalline polyamide, is synthesized from caprolactam. Fibers, brush bristles, high-impact moldings, and tire cords are all made from nylon-6. The synthesis of nylon-6 is depicted in the Scheme 1.2.



**Scheme 1.2** (a) Synthesis of caprolactam and (b) synthesis of nylon 6.

#### Properties of nylon:

- With their parallel arrangement of molecules and hydrogen bonds holding them together, nylon fibers have a linear structure. Strong intermolecular

forces give these fibers a more crystalline structure and provide them great strength, flexibility, and a high melting point.

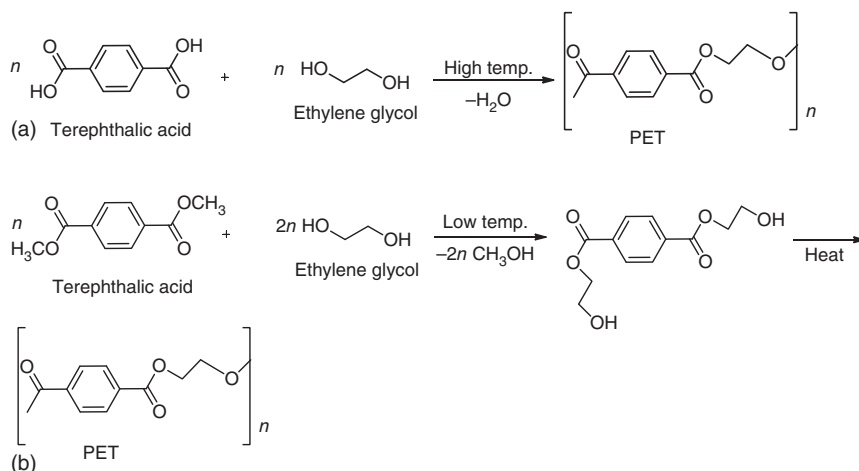
- Nylons are chemically stable and resistant to abrasion.
- The yarn is smooth, long lasting, and can be spun into fabric.
- The fabric can withstand heat and steam and is strong, glossy, moisture-resistant, simple to dye, and retains color.

### 1.3.4 Polyesters

Polyester is a class of polymer in which an ester functional group is present in every repeating unit of the polymer chain. Some polyesters are naturally occurring compounds found in plants and insects, some are synthetic compounds like polybutyrate. But it most frequently refers to a type of substance known as polyethylene terephthalate as a specific material (PET). Biodegradable polyesters include some synthetic as well as some natural varieties; however, the majority of synthetic polyesters are not biodegradable. Synthetic polyester is extensively used in cloth industry.

### 1.3.5 Polyethylene Terephthalate (PET)

The most popular thermoplastic polymer of the polyester family is PET. This is used in clothing fibers, food and liquid storage containers, thermoforming for manufacturing, and in combination with glass fiber for engineering resins (Cann and Connelly 2000). There are two strategies for the synthesis of PET. The first method is the direct reaction between terephthalic acid and ethylene glycol which is mentioned below in Scheme 1.3a. PET is commercially known as Terylene.



**Scheme 1.3** (a) Synthesis of PET by direct method and (b) synthesis of PET by trans esterification method.

This method is a typical Fisher-type esterification reaction where an acid reacts with an alcohol by following the usual mechanism. The second method is the ester

exchange of a diester and a diol. This is a transesterification reaction in which one ester is transformed into another.

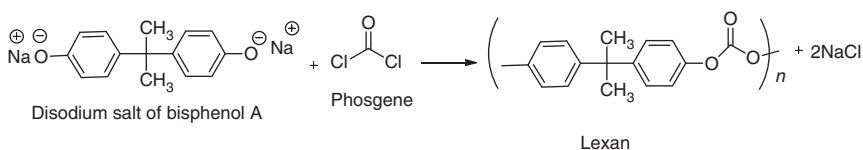
By this method, PET is synthesized by the reaction between dimethylterephthalate and ethylene glycol as shown in Scheme 1.3b (Gowarikar et al. 2022).

#### Terylene's properties:

- It offers excellent mechanical strength and stability in its dimensions.
- It has a very high strength and will only slightly lose strength when wet.
- It is elastic by nature, stable in the temperature range of  $-40$  to  $100^{\circ}\text{C}$ , and has good insulating qualities as well as creep and abrasion resistance.
- It exhibits little water absorption and is resistant to water, diluted acids, salts, aliphatic and aromatic hydrocarbons, and alcohols at room temperature.

### 1.3.6 Polycarbonates

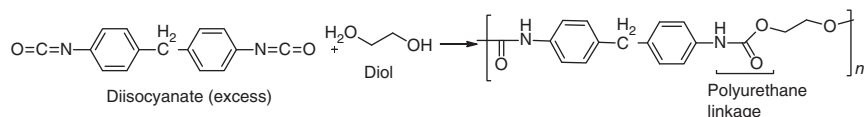
Polycarbonates are a type of thermoplastic polymers featuring a carbonate group in their structure. As this type of polymer can be worked, molded, and thermoformed easily, so it has a variety of applications. The very important polycarbonate Lexan is produced by the reaction of bisphenol A (BPA) and phosgene  $\text{COCl}_2$  in dichloromethane by using phase transfer catalyst as shown in Scheme 1.4. High impact and tensile strength, tough translucent polymer Lexan retains its shape over a wide temperature range. It is utilized in athletic goods like catcher's masks for baseball and hockey as well as bicycle, football, and snowmobile helmets. Moreover, it is employed in the manufacture of safety and unbreakable windows.



**Scheme 1.4** Synthesis of Lexan (Ghosh 2011).

### 1.3.7 Polyurethanes

An immensely versatile class of polymers known as polyurethanes is used in insulators, foams, elastomers, synthetic skins, coatings, adhesives, and other products. Polyurethanes have improved the quality of modern life. The building blocks of polyurethanes alternate between hard urethane units and flexible polyester or polyether units. The more flexible urethane blocks are made from low-MW polyesters or polyethers that include  $-\text{OH}$  groups at the ends of each polymer chain, whereas the rigid urethane blocks are made from a diisocyanate. Dr. Otto Bayer and his coworkers first synthesized polyurethane by simple diisocyanate polyaddition procedures (Janik et al. 2014). It achieved industrial-scale synthesis in 1937, and by the 1950s, it had become a market staple. A urethane linkage distinguishes polyurethanes, and they are easy to synthesize via an addition reaction between alcohol and an isocyanate. The synthesis of polyurethanes is shown in Scheme 1.5.



**Scheme 1.5** Synthesis of a polyurethane.

### 1.3.7.1 Properties of Polyurethanes

Molecular weight between cross-links and the number of segments in a stiff sequence are the key factors affecting polyurethanes' thermal characteristics. Long alkyl chains, aromatic groups, branching and cross-linking, as well as the strength of the secondary bonding forces, all have a significant impact on mechanical qualities like elongation break, rip strength, and tensile strength. The types of polyols and isocyanates that are used to create polyurethane have a significant impact on its chemical characteristics.

Some key properties of polyurethanes are mentioned below:

- Good abrasion resistance
- Good impact resistance
- Good toughness
- Low viscosity
- High elongation
- Good flexibility
- Good tear strength
- Low shrinkage
- Hydrolytically stable

### 1.3.8 Epoxy Resin

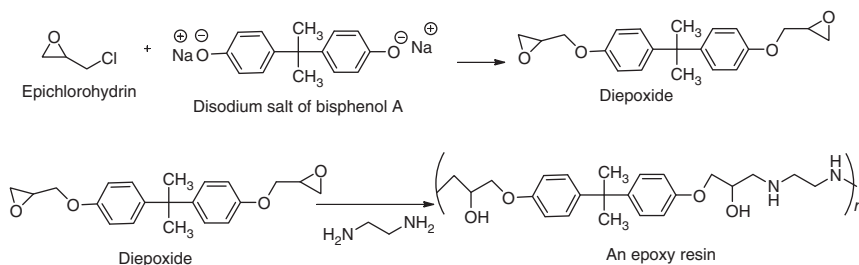
Epoxy resins, a very significant group of thermosetting polymers, are extensively used in aircraft structures because of their low shrinkage and low release of volatiles during curing, high strength, and good durability in hot and moist environments (Januszewski et al. 2021). This type of resins can be produced in different forms ranging from low-viscosity liquids to high-melting solids. The most widely used epoxide monomer, diepoxide, is prepared by the treatment of 1 mol of bisphenol A with 2 mol of epichlorohydrin. This on further reaction with diamine gives the resin. The synthetic route is depicted below in Scheme 1.6.

#### 1.3.8.1 Properties of Epoxy Resin

Epoxyes are compatible with the majority of substrates. They are particularly well suited for composite applications since they have a tendency to moisten surfaces easily. Epoxy resin can also be used to modify some polymers like polyurethane or unsaturated polyesters in order to improve their physical and chemical properties. Some other properties are listed below:

- High strength
- Low shrinkage





**Scheme 1.6** Synthesis of an epoxy resin.

- Effective electric insulation
- Its glass transition temperature ranges from 150 to 220 °C
- Excellent adhesion to various substrates
- Chemical and solvent resistance

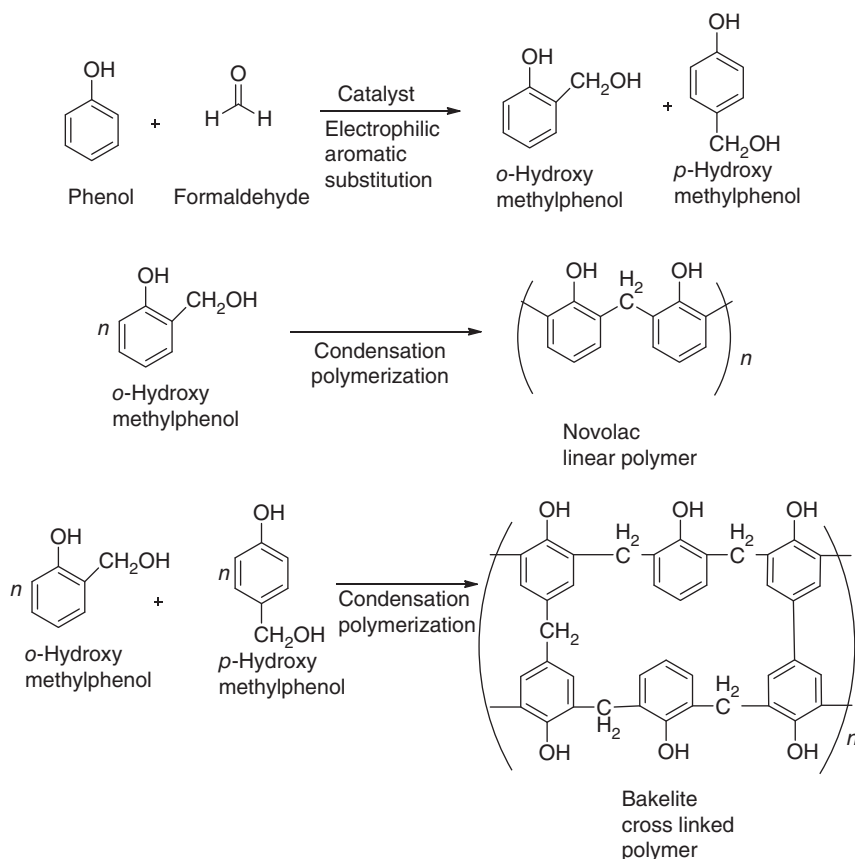
### 1.3.9 Phenol Formaldehyde Resin

The condensation polymer phenol-formaldehyde resins can be synthesized by the polycondensation reaction between phenol and formaldehyde in the presence of acidic or basic catalyst. These are thermosetting polymers. They were the first commercial synthetic resins prepared by Baekeland, an American chemist who gave the name Bakelite. Electrophilic aromatic substitution reaction between phenol and formaldehyde in the presence of a mineral acid like HCl produces *o*-hydroxymethyl phenol and *p*-hydroxymethylphenol, which are the actual monomers. This is the initial stage of the mechanism of polymerization. A linear (straight-chain) polymer known as Novolak is produced when only one type of monomers, such as *o*-hydroxymethylphenol, react together in a head-to-tail fashion. However, if cross-polymerization occurs with a certain amount of polysubstituted phenol, Bakelite – a strongly cross-linked polymer – is produced. The reaction for preparing Bakelite is depicted in Scheme 1.7

#### 1.3.9.1 Properties of Phenol Formaldehyde Resin

Phenol formaldehyde is a synthetic resin made from phenol and formaldehyde. It is thermosetting in nature. It is used to make products such as adhesives, coatings, and molded products. Some of the key properties of phenol-formaldehyde resin are high strength, resistance to chemicals and solvents, low flammability, and good thermal stability. Novolak is a solid and stable resin. It has good solvent and chemical resistance. It is electrically insulated with good dielectric resistance.

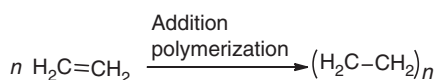
**Chain growth or addition polymerization** is a type of polymerization process which involves adding monomers sequentially that are either unsaturated or have additional reactive functional groups. Carbocations, carbanions, radicals, and organometallic complexes are just a few examples of the reaction intermediates that are produced during this kind of polymerization. This chain growth polymerization proceeds through chain initiation, propagation, and termination steps. The synthesis of some of the important addition polymers is mentioned below.



**Scheme 1.7** Synthesis of phenol formaldehyde resin.

### 1.3.10 Polyethene

Polyethene, a simple and extensively used homopolymer, is synthesized by the addition polymerization of single monomer ethylene. The reaction for preparation of polyethene is shown in Scheme 1.8. Polyethene can also be synthesized by coordination polymerization by using Ziegler–Natta catalyst.

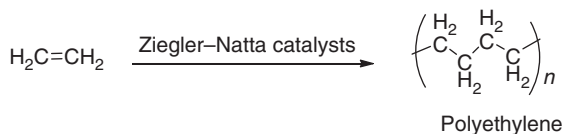


**Scheme 1.8** Synthesis of polyethene.

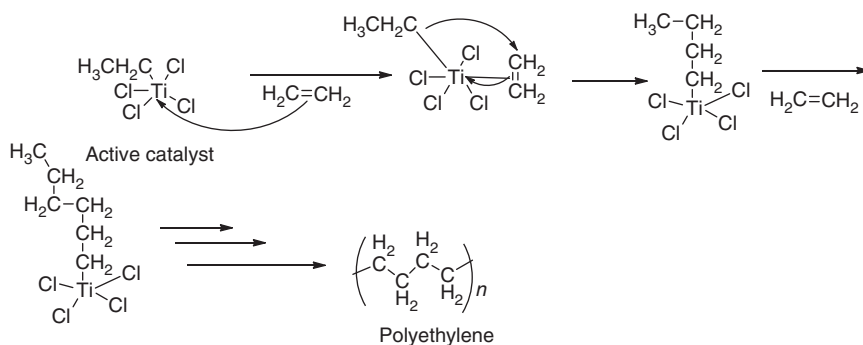
### 1.3.11 Coordination Polymerization

Ziegler–Natta catalysts are used in coordination polymerization. Combination of triethylaluminum and titanium or vanadium tetrachloride is the most used Ziegler–Natta catalyst. This catalyst is highly stereoselective. Polyethene can be

used to explain the mechanism. The ethene monomer produces a  $\pi$ -complex by first attacking the catalyst surface (Ti). It then produces a transition state by partially using its  $\pi$ -electrons and interacting with the alkyl group. In the end, the Ti-alkyl link breaks, leading to the formation of bonds between the monomer and the alkyl group and between the monomer and Ti. Schemes 1.9 and 1.10 describe the process and mechanism of synthesizing polyethylene utilizing Ziegler–Natta catalysts.



**Scheme 1.9** Synthesis of polyethylene by Ziegler–Natta catalysis.



**Scheme 1.10** Mechanism of synthesis of polyethylene by coordination polymerization.

Polyethenes can be broadly categorized into two types

- (i) LDPE
- (ii) HDPE

Very-LDPE is produced using a free radical process at 80–350 °C, high pressures of 1000–3000 atm, and the presence of oxygen or peroxide.

#### Properties:

- It is a transparent waxy substance with superior electrical insulating qualities, a low brittleness temperature, film transparency, and strong impact strength.
- It is chemically inert and has good resistance to acids and alkalis. However, it swells and is permeable to oils.
- It melts in temperature range of 107–120 °C. Its glass transition temperature ( $T_g$ ) value is –120 °C.
- It is flexible over a wide temperature range.

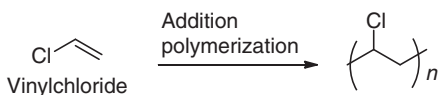
**HDPE** can be prepared by the coordination polymerization using Ziegler–Natta catalyst, but it can also be prepared by the ionic mechanism at low temperatures of 60–70 °C and very low pressures of 6–7. HDPE is a linear polymer with little to no branching.

**Properties:**

- It is opaque and has less impact strength, but better barrier properties than LDPE.
- It has better chemical resistance than LDPE.
- It melts in temperature range of 130–138 °C. Its glass transition temperature is –20 °C.
- It exhibits better stiffness, toughness, tensile strength, and heat resistance.

**1.3.12 Polyvinylchloride**

PVC, a thermoplastic homo-polymer, can be prepared by the addition polymerization of single monomer vinyl chloride. The reaction for preparation of PVC is shown in Scheme 1.11.



**Scheme 1.11** Synthesis of polyvinyl chloride.

PVC can be classified into two classes:

- (a) Unplasticized PVC
- (b) Plasticized PVC

PVC-R or PVC-U, often known as rigid or unplasticized PVC, is a strong, rigid material that is also chemically resistant and naturally flame retardant. To make plasticized polyvinyl chloride (PVC-P) more flexible, several chemical substances known as plasticizers have been added to the polymer.

**Properties:**

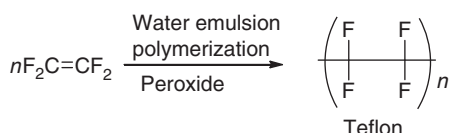
- It is a substance that is chemically inert, colorless, odorless, and very resistant to acids and alkalis. Plasticized PVC is less chemically resistant than unplasticized PVC, nevertheless.
- PVC is now replacing conventional building materials like wood, metal, and concrete because of its versatile properties, including its lightweight nature, durability, and ease of processing. It is also resistant to atmospheric oxygen or oxidation. It also has greater stiffness and rigidity than polyethene.

**1.3.13 Polytetrafluoroethylene (PTFE)**

Polytetrafluoroethylene (PTFE), also known as Teflon, is a homopolymer and its monomer unit is tetrafluoroethylene. It is also a thermoplastic polymer. This is typically synthesized through the use of peroxide or ammonium persulfate as initiators in the emulsion polymerization of tetrafluoroethylene. The procedure for preparing Teflon is depicted in Scheme 1.12.

**Properties:**

- It is a polymer with a high degree of crystallinity (93–98%).
- It is extremely resistant to chemicals.
- Almost none of the solvents can dissolve it, and neither water nor oil can moisten it.
- It has a low coefficient of friction and maintains its slickness over a broad temperature range (−40 to 300 °C).
- It has great temperature stability and is temperature resistant.
- It possesses superb electrical insulating qualities.

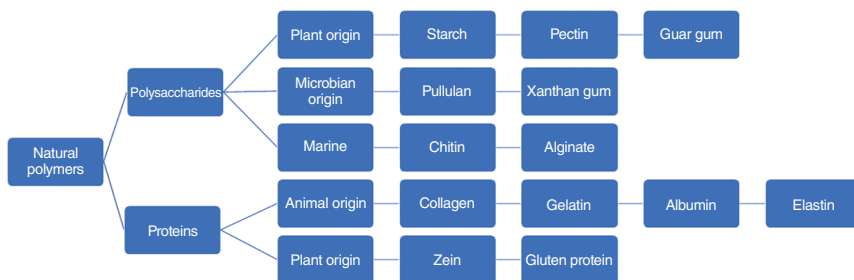
**Scheme 1.12** Synthesis of Teflon.

General applications of organic polymers are discussed in the following section.

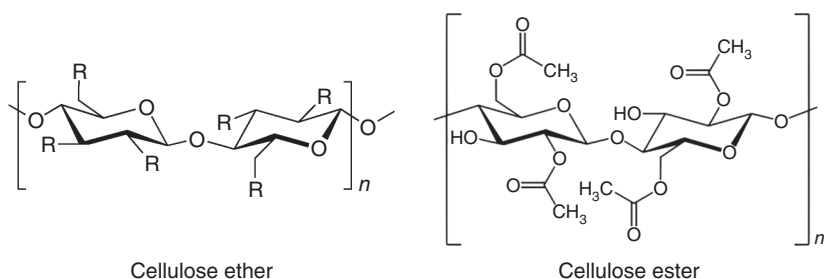
**1.3.14 Application of Natural Polymers**

Organic polymers, either synthetic or natural, are crucial for everyday life. The natural polymers primarily belong to proteins and polysaccharides. Both categories are either plant based or animal based. The existing polysaccharides however are also bacteria based (e.g., Dextran), fungi based (e.g., pullulan), and algae based (e.g., alginate) (McChesney et al. 2007) (Figure 1.3).

Natural polymers are the building blocks of most of the living things providing basic structural materials and participating in vital life processes. For example, the polymers cellulose and starch are the primary construction units of a plant. Natural fibers such as cotton are made up of cellulose. Cellulose is a linear polymer of glucose units, an abundant organic polymer on Earth. Cellulose has gained immense technological importance in recent days. Cellulose as such being water insoluble finds some technological barrier in applications (Guo et al. 1998). So numerous chemical modifications have been carried out upon cellulose, resulting in cellulose derivatives.

**Figure 1.3** A flowchart of natural polymers (self-made).

These derivatives found good industrial importance because of their water-soluble properties. As an example, etherification results in cellulose ethers, which are water soluble in nature. Cellulose ethers are important materials in pharmaceutical industry because of their hydrophilicity and good swelling properties. Apart from this, cellulose and its derivatives are versatile components in many industries such as veterinary foods, wood and paper, fibers and clothes, body care, cosmetics, paint, and coatings (Dumitriu 1996). Cellulose ethers and cellulose esters, which are derivatives of cellulose, exhibit different physicochemical and mechanical properties. Information about a few important semi-synthetic derivatives like methyl cellulose, cellulose nitrates, hydroxypropyl methylcellulose, and ethyl (hydroxyethyl) cellulose is noteworthy to mention here because of their tremendous applications.



The carbohydrate, starch, is a natural polymer formed by the repetition of glucose units. The breakdown of starch in our body releases energy. At the same time, starch is a raw material for bioplastics in industry. Processing of starch with plasticizers can increase its mechanical strength ((Gajre)Kulkarni et al. 2012). In general, starch is an important gradient of food/bakery industry, paper, and textile mills. Polysaccharides are important analogues of cosmetic industries. Starch nanoparticles possess anti-inflammatory properties, which are essential in drug designing.

Natural-polymer-based hydrogels seek research attention for their applications in food industry and agriculture. Hydrogels that can absorb large amount of water can exist either naturally or synthesized. Natural-polymer-loaded drugs find effective treatment of various kinds of diseases. As an example, chitosan-loaded ascorbic acid was found effective against cervical cancer. Polymeric nanoparticles especially derived from natural polymers are mostly used in controlled drug-delivery systems because of their certain pharmaceutically acceptable properties like biocompatibility, bioadhesion capacity, low cost, availability, and lack of toxicity (Pandey and Khuller 2004). The polymeric nanoparticles can act in controlled drug-release systems in addition to drug carriers. Proteins, for example, collagen and gelatin are suitable candidates for development of drug-delivery systems because of their stability under different conditions of pH and ionic strength.

Our food primarily consists of the natural polymers, polysaccharides, and proteins. A small amount of polynucleotides (DNA and RNA) is also involved in the cellular part. Proteins are the source of amino acids in our body and have high water-holding capacity. The creation and stabilization of food structures is

dependent upon the polymers used. Moreover the physiological and biological function of food also relies upon the nature of polymer used. Most of the emulsifiers and stabilizers used in food industry are natural polymers (Adelmann et al. 2012). During food formulation, they stabilize the emulsion droplets and foams. Polymers are also applied as thickeners in food processing to increase the viscosity of the food. A few of the natural polymers can act as gelling agents or can form gels. A gel is a 3D network formed by cross-linking of polymer chains, trapping the water molecules and making them flow resistant. The textural properties of food (such as chewy or creamy) depend on the type and concentration of gel-forming polymers used during food formulation. Interestingly, natural polymers can also develop the bioavailability of vitamins (Guo et al. 1998). Essential nutrients undergo degradation by the action of heat, light, and oxygen. Polymers in this context can protect those by enhancing stability and strength. The antioxidative and antimicrobial functions of certain natural polymers place them in food formulations.

One of the important natural polymers is “natural rubber” that finds enormous application in our daily life. The polymerization of isoprene results in natural rubber. Isoprene is chemically 2-methyl-1,3-butadiene. Its polymerization results in two geometrical isomers. One is “cis” and the other is “trans.” These are chemistry terms. The “cis” isomer is known as “natural rubber” or *cis*-1,4-polyisoprene (Flory 1953). Interestingly one another isomer “neoprene” is a synthetic rubber.

Commonly natural rubber is also known as latex, which is cultivated across the producers. The modern application of natural rubber in refrigeration seals, freon/air conditioning, motor mounts, engine coolants, automotive gaskets, and seals originates from the elastic nature of their molecular chains (Abuzreda 2023).

### 1.3.15 Application of Synthetic Polymers

Synthetic organic polymers are synthesized in laboratories by various chemical modifications. The modification results in different compositions of the polymeric chains. This in turn helps in improvement of the polymeric properties. Properties like tensile strength, gelation, and chain stiffness are important for possible industrial application of synthesized polymers (Flory 1953). They are commonly found in a variety of consumer products. They find technological use as adhesives, fibers, paints, plastics, and rubbers. We have mentioned about cellulose as natural polymer; at the same time cellulose derivatives like hydroxyl propyl methyl cellulose (HPMC), sodium carboxymethyl cellulose fall under synthetic category (Dumitriu 1996). So derivatives of natural polymers belong to synthetic category. Generally organic polymers are flexible, have a low density, and are stable over a wide pH range.

Most of the synthetic polymers are classified based on their mechanism of formation. Some of them are chain polymers, and others are condensation polymers. One of the simplest but highly utilized synthetic chain polymers is polyethylene (PE). This is formed by the repetition of ethylene units. However, two important varieties of PE are LDPE and HDPE which found very good industrial applications. HDPE

is more rigid than LDPE due to higher crystallinity (Felgel-Farnholz et al. 2023). A linear polyethylene is a HDPE, whereas a branched polyethylene is a LDPE.

A series of other polymers like PVC, polypropylene (PP), polystyrene (PS), PTFE or Teflon, polyvinyl alcohol (PVA), polyvinyl acetate (PVAc), polymethyl acrylate (PMA), polymethyl methacrylate (PMMA), and PAN can be also formed in a similar fashion. A vinyl group  $\text{CH}_2=\text{CH}-$  undergoes substitution with several atoms/groups like  $-\text{chloro}$ , phenyl, cyano, and alcohol to yield these polymers (Flory 1953). For example, the polymer PVC was formed by the repetition of vinyl chloride monomers. “PVC” is a strong plastic that can be made softer and more flexible by adding plasticizers.



Nevertheless, the polymer Teflon is widely used because of its non-reactive and hydrophobic nature. It does not interact with water as well as water-containing materials, so it is used mostly in cookware like non-stick pans. Non-reactivity arises from the strength of the carbon-fluorine bond (Hanford and Joyce 1946).

On the other hand, a range of synthetic polymers fall under the condensation polymer category. For example, polyester or PET, a synthetic fiber, is a condensation polymer of ethylene glycol (alcohol) and terephthalic acid. These polymers found application based upon their broad classification as thermosets, thermoplastics, elastomers, and synthetic fibers. Thermosets are mostly used in adhesives as they don't undergo structural change after getting set. An elastomer being a flexible polymer found several suitable applications. Apart from polyester, a few other important synthetic condensation polymers include nylon, Bakelite, melamine, polyurethanes, polycarbonates, and epoxies (Carothers 1929).

Most of the synthesized organic polymers have carbon backbone in their structure. The insertion of the heterochain (e.g., oxygen, sulfur) in the polymeric structure can change the polymeric properties for achieving required applications. Some examples of heterochain polymers are polyamides, polyesters, polyurethanes, polysulfides, and polycarbonates that have other elements in their chain (Flory 1953).

A few common applications of some synthetic polymers are presented in the following table.

Polymers	Applications
1. Polyethylene (PE)	Used in plastic bags, plastic films, containers, bottles, food packaging, flexible pipes, toys, housewares, etc.
2. LDPE	Used in manufacturing various containers, dispensing bottles, wash bottles, tubing, plastic parts of computer components, molded laboratory equipment. Also used in packaging like foils, trays, plastic bags, etc.
3. HDPE	Used in manufacturing toys, chemical containers, shampoo bottles, pipe systems, milk jugs, recycling bins, grocery bags, cereal box liners, flower pots, etc.

(Continued)



	<b>Polymers</b>	<b>Applications</b>
4.	Polypropylene (PP)	Used in appliances such as refrigerators, radios, and TVs. Also used in package films, pipes, storage tanks, set covers, dishwasher-safe plates, trays, cups, and many toys.
5.	Polyvinyl chloride (PVC)	Manufacturing of adhesives, coatings, and fibers. Raw material in automotive under body coating.
6.	Polystyrene (PS)	Used in protective packaging, containers, lids, bottles, trays, tumblers, disposable cutlery, making of models, toys, etc.
7.	Polytetrafluoroethylene (PTFE) or Teflon	Used in coating frying pans, baking sheets, other cooking utensils, automotive parts like gears, slide plates, seal gaskets, plain bearings, medical devices, and insulation.
8.	Polyvinyl alcohol (PVA)	Used in paper making, textile warp sizing, as a thickener, as emulsion stabilizer, and in biomedical devices such as in the manufacturing of contact lenses, artificial heart surgery, drug-delivery systems, wound dressings, etc.
9.	Polyacrylonitrile (PAN)	Used for making textile fibers, military aircraft, tennis rackets, tents, high-tech bicycle, pressure vessels, fishing rods, carpets, etc. It is also used as electrolyte separators in batteries.
10.	Polyvinyl acetate (PVA)	Emulsified polyvinyl acetate used as water-based adhesives including pastes and glues, bookbinding, lamination of metal foils. Non-emulsified polyvinyl acetate is used as a thermosetting adhesive. Used as a raw material for the manufacture of other polymers.
11.	Polymethyl acrylate (PMA)	Used in acrylics and in sheets for laminated safety glass as a spinning solvent, designing of LED bulbs.
12.	Polymethyl methacrylate (PMMA)	Used in making basins, bathroom fixtures, sink. In medicine, used in contact lenses, bone cements, and membrane dialysis. PMMA is also used to make attractive signboards and durable lenses for automobile lighting in buildings for decorative purposes.
13.	Nylon	Used for making textiles like sarees, shirts, neckties, socks, curtains, sleeping bags, rain coats, swim wear, cycle wear, etc. It is also used in making ropes, car seat belts, fishing nets, tire cords, strings for sports rackets and musical instruments, paint brushes, etc.
14.	Polyester	Used in textiles such as clothing, upholstery, curtains, blended with other fibers such as cotton and wool. Also used in automotive components like bumpers, door panels, dashboards, as substituent for metal. Used as insulating material in buildings, vehicles, electrical equipment.
15.	Polyurethanes	Used as coatings, films, foams, adhesives, sealants, elastomers, foundation garments, and swim suits. They are also used as a leather substitute such as cushion materials, carpet underlays, furniture, and packaging. Protector for laptops, outer cases of mobile electronic devices, sporting goods, medical devices, etc.

*(Continued)*

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<b>Polymers</b>	<b>Applications</b>
16. Polycarbonates	Used to make a variety of lenses, such as those for automobile headlights, safety glass lenses, SCUBA masks, and sunglasses or eyeglasses. Windscreens of small motorized vehicles such as motor cycles, helicopters, small airplanes are made up of polycarbonates. The light-weight polycarbonates used as displays include some LCD screens, mobile screens, plasma screens by replacing glass. Aliphatic polycarbonates are used to create nanomedicine materials with increased biocompatibility and degradability.
17. Polyamides	Synthetic polyamides are commonly used in textiles, automotive industry, carpets, kitchen utensils, sportswear, etc. In industry, it is used to synthesize different kinds of substances such as tents, fishing nets, ropes, and tennis rackets. For example, nylon-6,6 is used for making swimwear, hoses, machine parts due to its waterproof properties and nylon-6 is widely used in gears, fitting, and bearings in automotive industry. Kevlar, another synthetic polyamide, is widely used in the manufacturing of motorcycle helmets, brakes, clutch lining, etc.
18. Polyimides	Used in aerospace, flexible printed circuits, automotive, heaters, bar code labels, pressure-sensitive tape, electrical insulation, safety, loudspeaker components, high-density electronic interconnects, high-temperature mechanical seals, photovoltaic modules, etc. They are used as surface coating in supersonic aircraft.
19. Bakelite	Bakelite is used in industrial electrical applications such as electronics, power generation, and aerospace industries as well as for wire insulation and other automobile components like brake pads. Bakelite also finds its use as non-conducting components of phones, radios, and other electrical equipment, including insulators, bases, and sockets for light bulbs and electron tubes.
20. Epoxy resins	Epoxy resins are extensively used because of their excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties, and good electrical insulating properties. Epoxy adhesives are used in the construction of aircraft, automobiles, bicycles, boats, golf clubs, snowboards, etc. It is used in the electronic industry for printed wire boards, insulators, switchgear, motors, generators, and transformers. Nevertheless, for embedding electron microscopes, water-soluble epoxides, named “durcupan,” are frequently utilized.
21. Silicones	Used in surface coatings, manufacture of laminates, as foaming agents in airplanes and missiles, as elastomers, and as a filler to reinforce silicone rubbers. Used in many products such as electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants and cooking utensils), textiles and papers (e.g., coating), automobile (e.g., gaskets), and office machines (e.g., keyboard pads).

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Polyurethane, which is a thermoplastic, is also considered as one of the most applicable polymers due to some of its inherent properties like elasticity, transparency, and resistance to oil, grease, and abrasion. It is a hydrophilic polymer that can react with water. This thermoplastic elastomer consists of urethane groups ( $-\text{NH}-\text{CO}-\text{O}-$ ) in the main polymer chain (Akindoyo et al. 2016). However incorporation of some other groups like ester, ether, amide, and urea produces some copolymers with suitable industrial applications.

Due in large part to their excellent tensile strength, synthetic co-polymers have found a wide range of uses. Because two or more distinct monomers are combined, co-polymers are able to withstand pressure. The atoms of different monomers can form strong bond between them because of electronegativity differences. They are generally categorized into linear, alternate, block, and graft co-polymers depending upon the arrangement of chains (Saldívar-Guerra and Vivaldo-Lima 2013). Several types of acrylic, vinyl acetate, and styrene-based co-polymers have found extensive applications in industries.

### 1.3.16 Recent Advances in Organic Polymers

In the modern era, with the advancement of technology, polymeric materials have potential countless applications. These include applications in electronics (Shaw and Seidler 2001), water treatment (Donga et al. 2019), hydrogen storage (Kato and Nishide 2018), drug-delivery systems (Liechty et al. 2010), solar cells (Brabec et al. 2003), sequestration of carbon dioxide (Wang et al. 2017), and energy storage capacitors (Feng et al. 2022). Due to their diverse applications, many efforts have been made recently in the design and study of novel polymeric materials. The classification of polymers falls under various categories because of their structures, broad applications, and varying properties. Thus instead of classifying them under one category they are classified as synthetic, semi-synthetic, or natural; organic and inorganic; linear, branched, and cross-linked polymers; homomer and co-polymers; addition and condensation polymers; and elastomers, fibers, thermosetting, and thermoplastics. This section gives a brief account of the recent developments in the field of polymer science particularly organic polymers.

Clean energy has become a necessity of modern society, and organic polymers may play a pivotal role in the design of novel materials to harvest clean energy. The major challenge in the sustainable development of society is the increasing population which invariably puts pressure on natural resources. The ever-increasing population results in an increase in the consumption of fossil fuels and hence increases air pollution and global warming. There has been an exhaustive effort to pave the way toward clean energy either by using solar cells or designing novel photocatalysts for water splitting (Takanabe 2017).

Although photolysis of water is considered to be the holy grail approach for hydrogen production toward sustainable energy, there was very limited success in the field until the employment of graphitic carbon nitride polymers ( $\text{g-C}_3\text{N}_4$ ) (Wang et al. 2021). Conjugated organic polymers due to their tunable properties have attracted much attention in the pursuit of sustainable hydrogen production from

water as compared to their inorganic counterparts. One such organic polymer is graphitic carbon nitride, a layered conjugated organic polymer, which has become the center of attraction since the last decade due to its various unique properties such as ease of synthesis, being metal-free, and having an environmentally benign nature, and a band gap of 2.7 eV. These properties make the polymer the most suitable candidate for hydrogen production. Despite the abovementioned properties, the pristine g-C<sub>3</sub>N<sub>4</sub> has some bottlenecks such as limited active sites, high charge carrier recombination, and low specific surface areas which have to be overcome before it is used as catalyst in full scale for water splitting. Engineering the g-C<sub>3</sub>N<sub>4</sub> is one of the many possibilities to make the material more efficient for water splitting. Elemental doping is one of the engineering techniques where a heteroatom is incorporated in g-C<sub>3</sub>N<sub>4</sub>. In one such study, the bulk g-C<sub>3</sub>N<sub>4</sub> was doped with elemental cobalt and it was observed that the incorporation of Co not only results in the narrowing of the band gap but also increases the specific surface areas, thereby making the separation of photoinduced carriers more efficient (Chen et al. 2017). In another attempt g-C<sub>3</sub>N<sub>4</sub> was doped with elemental iron and it was observed that the Fe-doped g-C<sub>3</sub>N<sub>4</sub> nanosheets have a broader absorption spectrum than the bulk g-C<sub>3</sub>N<sub>4</sub>. Moreover, the prepared material is more efficient than the bulk g-C<sub>3</sub>N<sub>4</sub> in case of hydrogen-evolving reaction (Gao et al. 2017). Non-metal-doped g-C<sub>3</sub>N<sub>4</sub> has also been observed to be more efficient than the pristine g-C<sub>3</sub>N<sub>4</sub>. In one such study, Jiang et al. (2019) observed that the photocatalytic performance was significantly increased after it was doped with oxygen. Apart from g-C<sub>3</sub>N<sub>4</sub> there are porous organic polymers that can be a platform to carry out photocatalytic water splitting. Porous organic polymers are generally defined as a group of covalently connected polymer materials with high porosity and specific surface area. They are made of different light elements (carbon, boron, hydrogen, oxygen, and nitrogen) and strong covalent bonds. Porous organic polymers gained popularity due to their versatile properties such as being tunable, i.e., their geometry and dimensions can be controlled during the synthesis process. Since porous organic polymers are connected through strong covalent bonds they have high chemical and thermal stability. There have been continuous efforts to prepare porous organic polymers to carry out the hydrogen and oxygen evolution reactions (Xu et al. 2018). Porous organic polymers can be grouped into three classes: conjugated microporous polymers (Jiang et al. 2008), covalent triazine frameworks (Jiang et al. 2018) and covalent organic frameworks (Cote 2005). The application of porous organic polymers for water splitting is still in the infancy period, and the material has to compete with the state-of-art materials such as metal oxides and graphitic carbon nitrides. There is no doubt that the addition of porous organic polymers into the family of photocatalysts will give us more options to explore the myriad landscape of photocatalysts and help the scientific community to design environmentally benign novel photocatalysts.

Hydrogen storage is another area where the organic polymer has tremendous potential. Hydrogen (H<sub>2</sub>) due to its properties such as energy density and clean combustion, an abundance in the form of water is going to become the major energy source and will replace the non-renewable petroleum energy resources.

The major bottlenecks in using  $H_2$  as energy source are its storage and production (Cousins and Zhang 2019). Hydrogen can be stored using highly porous organic polymers through adsorption. These approaches have various advantages such as low cost, easy to scale up, metal-free, and environmentally friendly. In this case four groups of highly porous polymers have been extensively used for hydrogen storage: (i) hyper cross-linked polymers (HCPs) (Wood et al. 2007), (ii) Polymers of Intrinsic Microporosity (PIMs), (iii) Conjugated Microporous Polymers (CMPs), and (iv) Porous Aromatic Frameworks (PAFs) (Germain et al. 2009).

Ease of functionalizing pore environments, large accessible surface areas, and high porosities make solid-state porous materials promising materials for hydrogen (Chen et al. 2022). Similarly amorphous POPs, because of their ease of processibility and good mechanical stability, make them viable candidates for hydrogen storage. The processing cost is relatively low and free of heavy metal making the materials and processes friendly to the environment.

Conducting polymers have been extensively investigated as a potential hydrogen storage due to the low cost, ease of synthesis, and processibility to achieve the desired morphological and microstructural architecture, ease of doping and composite formation, chemical stability, and functional properties.

Organic polymers are being extensively used for targeted drug-delivery systems and controlled drug-delivery systems (Mahato et al. 2020). Drug delivery refers to a combination of methods, technologies, formulations, or processes used to deliver the therapeutic agent into the body to achieve the desired therapeutic effect (Aimetti et al. 2009). When a drug is administered to the body because of various factors only a small amount reaches the sites of action. The various factors include metabolism of the therapeutic agent or the drug while en route to the site, reaching wrong sites (tissues or organs), or quick removal of the drug from the site. This affects the efficiency of any drug greatly. The above shortcomings can be overcome if targeted drug-delivery approaches or smart drug-delivery approaches or controlled drug-delivery approaches are applied. In this method, to minimize the side effects and to attain the maximum efficacy of the drugs, the drugs are administered at an appropriate time, dosage, and location (Zishan et al. 2017). Recently, in medicine organic polymers have become an inseparable and indispensable part as drug-delivery systems. The objective of a sustainable drug-delivery system is to control drug release, reduce drug frequency, thereby increasing the efficiency and decreasing the side effects of the drug (Allen and Cullis 2004). Considering the efficiency of the targeted drug-delivery system over the conventional systems many studies were done on carriers of the drug. The vesicular carrier systems, microparticulate systems, monoclonal antibodies and fragments, and polymeric carriers are the most commonly used carriers for targeted drug delivery. The advancement in polymeric science helped scientists and pharmacologists to design new drug carriers, thereby making polymers an inseparable part of drug-delivery systems. The development of novel drug-delivery systems or controlled drug-delivery systems depends on the carriers that are used to deliver the drugs to the specific site. It is observed that polymer-based drug nanocarriers can increase the solubility of hydrophobic drugs, decrease their cytotoxicity toward

normal tissue, prolong drug availability, favorably alter biodistribution, improve utilization efficiency (Mahajan et al. 2007) and thereby may show promising pharmacokinetics both at the cellular and whole body levels, e.g., polymeric nanocarrier poly(D,L-lactide-co-glycolide). Various organic polymers utilized in drug delivery are poly(D,L-lactide-co-glycolide), polyglycolic acid, poly-L-glutamic acid, polylactic acid, poly(*N*-isopropylacrylamide), dextran, dendrimers, chitosan, and so on (Mathiowitz et al. 1997). Amphiphilic polymers such as micelles, dendrimers, and nanomicelles, containing both hydrophilic and hydrophobic parts, have been extensively studied as they are thought to be good candidates as polymeric carriers in drug delivery (Srivastava et al. 2016). Smart polymers are another class that changes their properties according to the environment such as pH. In summary, it can be concluded that the future of drug delivery is very bright, and the inclusion of technologies in treating diseases will become more and more efficient.

In general, when the term good conductors comes to our mind, we generally picture metals, salt solutions, and fused salts and usually treat organic solids and liquids as good insulators. However, this notion is changing since the discovery of conjugated organic polymers capable of conducting electricity. In 2000 Heeger, MacDiarmid, and Shirakawa were awarded the Nobel Prize in Chemistry for their work on the discovery and development of conductive polymers (Yang and Pierstorff 2012). The two branches of materials science which have witnessed exponential growth in the twentieth century and almost touched all aspects of modern life are semiconductors and polymers. The history of conjugated polymers dates back to polypyrrole and PANI. Synthetic metals are defined as organic polymers which possess both the properties of metals (such as electronic, electric, magnetic, and optical) and those of polymers (such as mechanical properties and processibility). Moreover, with the discovery that the conductivity of conjugated organic polymers can be easily tuned or controlled, there has been exponential growth in the application of conjugated organic polymers in organic photovoltaic devices, light-emitting diodes, sensors, and field effect transistors (MacDiarmid 2001). The most commonly studied conjugated organic polymers are polyacetylene, polythiophene, polyphenylene-vinylene, polypyrrole, polyfuran, polyphenylene, and PANI. It is observed that synthetic metals exhibit high electrical conductivity in their oxidized and reduced states. Porous organic polymers have a very large surface area and as a result, make them an ideal candidate for gas trapping and hence can be used as chemical sensors for heavy metals, explosives, biological molecules, sensors for volatile organic compounds and solvents, and sensors for anions (Bao and Lovinger 1999). Engineering polymers represent another class of organic polymers that can withstand high temperatures and have high physical and mechanical properties which make them good candidates for their use in aerospace electronics and robotic systems (Mittal 2011). Stretchable electronics are another area where organic polymers have potential applications. Stretchable polymers, because of their unique physicochemical properties, are envisioned as the future of electronic devices. Stretchable electronics consist of electronic materials integrated with an elastomer or stretchable material. Stretchable polymers have the potential to be applied in

biomedical engineering, healthcare, and human-machine interface (Lim et al. 2015).

Thus it is seen that in the near future polymers will become the epicenter of research and development. Moreover, it is believed that organic polymers will play an important part in deciphering the solutions to the problems that arise after the indiscriminate use of resources.

## 1.4 Conclusion and Future Scope

It is well known that nature from the beginning selected biopolymers for survival and growth. Likewise, humans also started their journey from Stone Age and passed through several stages to reach the present age where polymer material is always one of the best choices of interest. Polymer technology is a branch of science where extensive research is going on for the introduction of novel material which can meet our daily requirements in a sustainable fashion. Presently, researchers are looking for intelligent polymers which are specially designed materials having multidimensional applications that can extend the scope of polymer science. In this chapter, a thorough development in the field of polymer science has been nicely described in a concise manner. Starting from the origin of polymers, their history and discovery, types and mode of classification, the recent advancements in polymer sciences, and their important practical applications have been properly incorporated with suitable examples. This book also explains about the scope and limitations of various techniques used in the synthesis and study of properties of various types of organic polymers. In addition, important applications of polymers in material science such as in OLEDs, semiconductors, superconductors, and PMCs have been presented. The modification of polymers and the research involved for the same will definitely help mankind in future.

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