

MATERIALS SCIENCE

POLYMERS

1) Types of Polymer

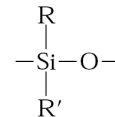
(a) Plastic

Possibly the largest number of different polymeric materials come under the plastic classification. Polyethylene, polypropylene, polyvinyl chloride, polystyrene, and the fluorocarbons, epoxies, phenolics, and polyesters may all be classified as plastics.

They have a wide variety of combinations of properties. Some plastics are very rigid and brittle; others are flexible, exhibiting both elastic and plastic deformations when stressed, and sometimes experiencing considerable deformation before fracture. Polymers falling within this classification may have any degree of crystallinity, and all molecular structures and configurations are possible. Plastic materials may be either thermoplastic or thermosetting; in fact, this is the manner in which they are usually sub-classified.

(b) Elastomers

A common type of elastomer is natural rubber. Other synthetic materials that exhibit rubber like properties also come under the heading of elastomers. Natural rubber is still utilized to a large degree because it has an outstanding combination of desirable properties. However, the most important synthetic elastomer is **Styrene Butadiene Rubber**, SBR, which is used predominantly in automobile tires, reinforced with carbon black. **Nitrile Butadiene Rubber**, NBR, which is highly resistant to degradation and swelling, is another common synthetic elastomer. For many applications (e.g., automobile tires), the mechanical properties of even vulcanized rubbers are not satisfactory in terms of tensile strength, abrasion and tear resistance, and stiffness. These characteristics may be further improved by additives such as carbon black (Section 15.2). Finally, some mention should be made of the silicone rubbers. For these materials, the backbone carbon chain is replaced by a chain that alternates silicon and oxygen atoms:



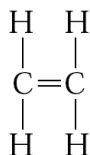
(c) Fiber

The fiber polymers are capable of being drawn into long filaments having at least a 100 : 1 length-to-diameter ratio. Most commercial fiber polymers are utilized in the textile industry, being woven or knit into cloth or fabric. To be useful as a textile material, a fiber polymer must have a host of rather restrictive physical and chemical properties. Fibers may be subjected to a variety of mechanical deformations – stretching, twisting, shearing, and abrasion. Consequently, they must have a high tensile strength and a high modulus of elasticity, as well as abrasion resistance. Convenience in washing and maintaining clothing depends primarily on its melting and glass transition temperatures. Furthermore, fiber polymers must exhibit chemical stability to a rather extensive variety of environments, including acids, bases, bleaches, dry cleaning solvents, and sunlight. In addition, they must be relatively nonflammable and amenable to drying.

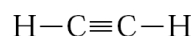
2) Hydrocarbon Molecules

Polymers are made up of polymers are organic in origin – made up of hydrocarbons. The hydrocarbons have covalent bonds between carbon and hydrogen atoms (one carbon atom to four hydrogen atom).

Single and double bonds:



Single and triple bonds:



Unsaturated bonds:

Molecules that have double and triple covalent bonds are termed unsaturated.

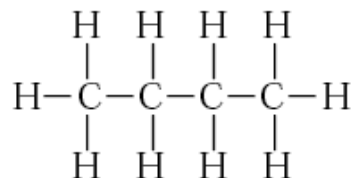
Saturated bonds:

For a saturated hydrogen bond, all bonds are single ones, and no new atoms may be joined without the removal of others that are already bonded.

Isomerism:

Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomenon termed isomerism.

normal butane has the structure



isobutane is represented as follows:

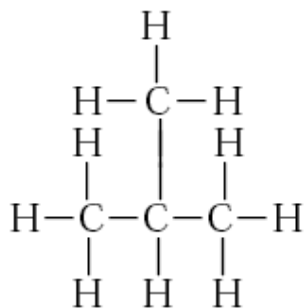
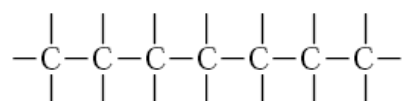


Table 4.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Name	Composition	Structure	Boiling Point ($^{\circ}C$)
Methane	CH_4	$\begin{array}{c} H \\ \\ H-C-H \\ \\ H \end{array}$	-164
Ethane	C_2H_6	$\begin{array}{c} H \quad H \\ \quad \\ H-C-C-H \\ \quad \\ H \quad H \end{array}$	-88.6
Propane	C_3H_8	$\begin{array}{c} H \quad H \quad H \\ \quad \quad \\ H-C-C-C-H \\ \quad \quad \\ H \quad H \quad H \end{array}$	-42.1
Butane	C_4H_{10}	.	-0.5
Pentane	C_5H_{12}	.	36.1
Hexane	C_6H_{14}	.	69.0

3) Polymer Molecules

Polymer molecules are large and they are called **macromolecules**. They have covalent interatomic bonds. A chain of carbon atoms forms the backbone of polymers. These long molecules are composed of structural entities called **repeat unit**.



Monomers refer to the small molecule from which a polymer is synthesized.

4) Addition Polymerization

The **addition polymerization process** is a process where monomers like ethylene is transformed into polymers like polyethylene. It is a three-step process consisting of (1) **initiation**, (2) **propagation** and (3) **termination**.

Initiation

The initiation of the polymerization process begins with a catalyst. To explain this process we will consider the formation of polyethylene initiated by hydrogen peroxide (C_2H_2).

With the application of heat, the hydrogen peroxide molecule breaks up into two free radicals. One free radical bonds with an ethylene monomer and they become a free radical called an active monomer. The double bond between the carbon atoms is now replaced with a single bond.

The second step is the propagation process where the newly-formed activated monomer breaks the double bond of another monomer molecule and forms a single bond with that activated monomer. This addition occurs again and again to make the long polymer chain.

The last step is the termination process where the earlier remaining hydrogen peroxide free radical bonds with the long chain to form a stable bond.

The Chemistry of Polymer

Consider the hydrocarbon ethylene (C_2H_4) which has molecular structure:

Homopolymer:

Homopolymers are polymers made up of a single repeating monomer such as AAAAAAAAAA.

Copolymer:

A copolymer is made up of more than one type of monomer. The four distinct types of copolymer are:

Random copolymer:

Different monomers randomly arranged with a long chain such as AABABBBBAAAAABA

Alternating copolymer:

Different monomers alternating between themselves to form a long chain such as ABABABABABABAB

Block copolymer:

One type of monomer forming long block among them before bonding with a block of different monomer such as AAAAAAABBBBBBB

Graft copolymer:

Appendages of one type of monomer are grafted to the long chain of another such as AAAAAAAAAAAAAAAAAA

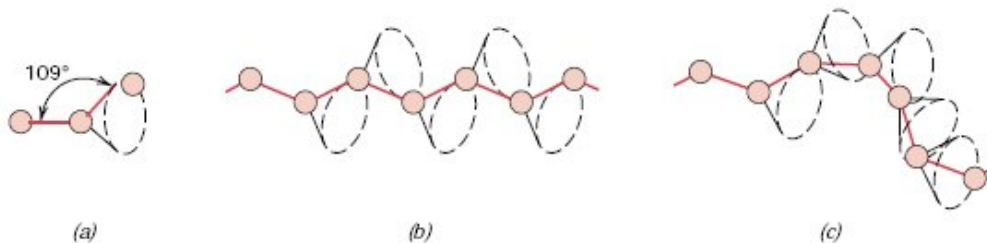


Molecular Weight

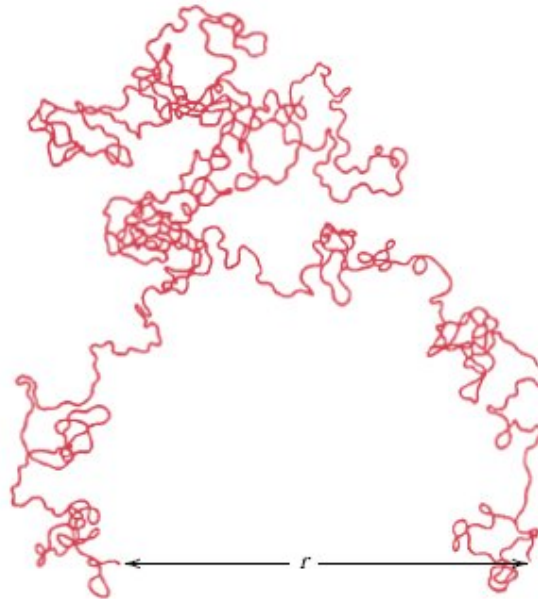
Polymers have extremely large molecular weights with very large chains. During polymerization, polymers do not grow to the same length – molecules do not have the same weight. Hence an average molecular weight is used.

Molecular Shape

A single chain bond is capable of rotating and bending in three dimensions.



Polymers consist of large number of molecular chains, each of which may bend and coil as below.

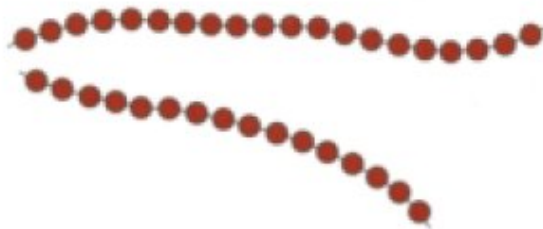


Molecular Structure

The physical characteristics of a polymer depend on not only its molecular weight and shape but its structure also.

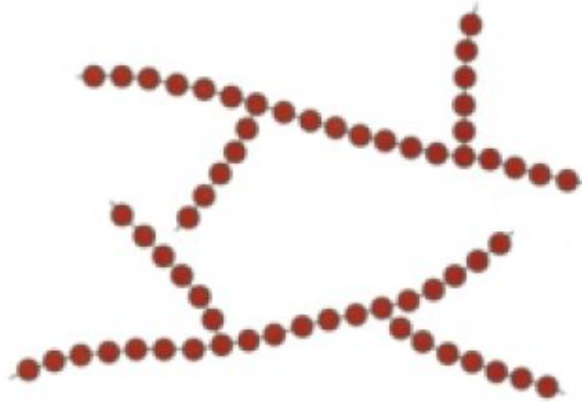
Linear polymers

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible. There may be extensive van der Waals bonding between the chains. E.g. polyethylene, poly vinyl chloride, polystyrene, and nylon.



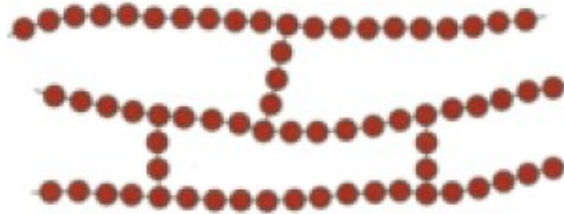
Branched polymers

Side-branch chains may bond to the main chain. The chain packing efficiency is reduced therefore lowering the polymer density. Polymers that form linear structures may also be branched. For example, high density polyethylene (HDPE) is linear, while low density polyethylene contains short chain branches



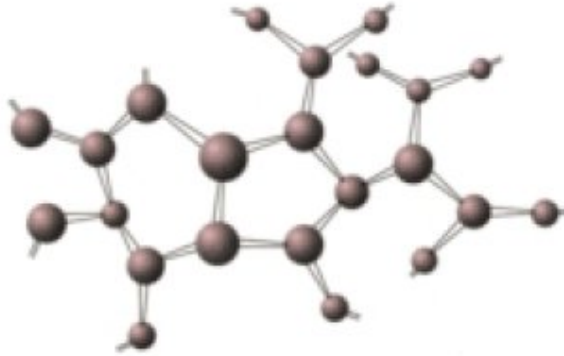
Crosslinked polymers

In crosslinked polymers, adjacent linear chains are joined one to another at various positions by covalent bonds.



Network polymers

Polymers that form three-dimensional networks and are termed network polymers. Highly crosslinked polymers maybe classified as network polymers.



Polymers usually have two or more different structures but one may be more dominant.

5) Thermoplastic and Thermosetting

Thermoplastic polymers are normally very long chains of carbon atoms covalently bonded together. Thermoplastics require heat to make them formable and after cooling they retain the shape they were formed in. These materials can be reheated and reformed into new shapes without changing their properties.

Thermosetting polymers are network polymers. They become permanently hard during their formation, and do not soften during heating. Heating to excessive temperatures will cause the crosslink bonds in the polymer to break and the material degrades. Thermosetting polymers are harder and stronger than thermoplastic polymers. They are better suited for high temperature applications.