

## I. INTRODUCTION

Polymers are giant molecules or macromolecules which have been built by combining a number of mostly identical monomers or simple compounds of low molecular weight. When the participating monomers are of different kinds they are called co-polymers. Many polymers consist of long chains of molecules in which the monomers are connected together in the form of chains. These long chains sometimes are arranged parallel to each other to form single crystals. Alternatively they may be so arranged that large numbers of them are nearly parallel so as to form a quasi polycrystalline entity mostly oriented in a particular way. These types of polymers with large amount of preferred orientation are known as fibrous polymers. In fibrous polymers the forces acting between the adjacent chain molecules are relatively weak while those between the successive monomers in the chain are very strong. This results in the substances being formed of bundles of long chains. These long chains largely influence the microscopic and macroscopic properties of the polymers which obviously will tend to be highly anisotropic. Physical and chemical properties of polymers<sup>1.1-1.19</sup> in general depend upon the inter and intra-molecular organisation of atoms as well as on their mutual three dimensional arrangement in space. These properties are controlled by means of physical treatments like annealing and by chemical treatments like hydrolysis, swelling, cross-linking, and by various other means including addition of low molecular weight compounds in the main molecular chain.

Thus to understand and to modify the properties of polymers, it is necessary to obtain a systematic knowledge about the correlation between the atomic and molecular architecture of polymers and their respective physical and chemical properties. This means that arrangement and disarrangement of atoms in polymers are to be understood in great details to correlate these with their physical and chemical properties. The atomic arrangement in polymers is a multistage process in which finally the macromolecules interact to form large and complex structures including occasional irregularities in the chain structures. In the light of innumerable X-ray diffraction studies<sup>1.20-1.21</sup> of the internal structure of metals, alloys, minerals and various other substances it is quite obvious that studies in those lines will be of great significance in the elucidation of molecular order in the macromolecules of polymers including fibrous polymers.

It has been stressed above that fibrous polymers contain large molecules mostly in the form of long chains. When these long chains under suitable conditions of growth are placed side by side in a regular way and at regular intervals they form crystals. Because of factors like irregularity in the molecular chain, a wide range of variation of the molecular chain length and kinetic considerations, the formation of polymers often results in irregular coiling and folding of the chains thus resulting in an amorphous entity. However it has been shown that in most fibrous polymers, the regularity in atomic arrangements attains neither a perfection as observed in a crystal nor an

extent of imperfection as in amorphous substances. The state of atomic arrangement in such substances is intermediate between these two extreme forms. Such states have been described by several authors<sup>1.22-1.31</sup> to be "paracrystalline" which are characterised by a special type of distortion. Thus polymers can be broadly classified into three groups viz. crystalline, amorphous and paracrystalline from the standpoint of their structural regularity. These three categories of polymers are generally dealt with separately to derive their structural characteristics as well as their properties.

#### 1.1 Crystalline polymers :

Crystals of fibrous high polymers consist of bundles of fibres called fibrils arranged mostly parallel to each other. These fibrils in turn consist of long chain molecules parallelly oriented. However the stable crystalline structure depends very much on the conformation of the molecules attained on crystallization. The conformation of the chain molecules are dependent on the intramolecular hydrogen bonds, internal rotation within the molecule due to Vander Waals repulsion, geometrical shape of the chains, nature of interaction between molecular chains etc. Crystallization of a polymer is possible only when a balance between the above factors is achieved. An example is polyvinyl alcohol which does not crystallize well because of unfavourable side chain geometry despite their hydroxyl groups and hydrogen bonds which contribute strong intermolecular forces. On the other hand polyethylene with a molecular interaction energy of only 2 KCal/mole crystallizes well because of balance of other factors. Crystals

of fibrous high polymers are found to possess the following characteristics.

- (1) In the case of linear high polymers the molecules pass through many unit cells. However these molecules are linked to atoms in adjacent unit cells by chemical bonds. Thus the unit cells in the chain directions are less independent than in the lateral direction.
- (2) Well developed single crystals can not be formed unless the molecular chains themselves possess periodicity.
- (3) The crystals of synthetic high polymers are inherently highly defective because the molecules are not all of equal length.

Growth of single crystals of polymers was first announced in 1957.<sup>1.32-1.34</sup> However some of the work<sup>1.35-1.37</sup> done previously also pointed to the possibility of growth of single crystals. Single crystals of polyethylene and several other synthetic polymers are generally thin and lamellar in habit. Electron diffraction and electron microscopic studies have proved that the molecular chains are normal to the lamellae. Thus the molecular chains must be folded back and forth between the two principal faces of each lamella.<sup>1.35,1.38</sup> Single crystals of polyethylene was first grown from dilute solutions. Later it was observed that rapid growth from melt of concentrated solutions of polymers results in the formation of dendritic crystalline structure termed spherulites. It has been concluded from X-ray and optical studies that the entire structure of a given spherulite originates from a single primary nucleus and crystallization proceeds continuously

from the nucleus outward. Several other intermediate crystalline structures termed as axialites and hedrite have also been obtained from slow crystallization of concentrated solutions of polymers.<sup>1.39-1.41</sup>

Polyethelene and many other synthetic high polymers assume the folded chain structure, as described above, on crystallization. The thickness of such lamella being of the order of  $100 \text{ \AA}^{\circ}$  whereas the dimensions of the plane of the lamella are of the order of several microns. Unit cells are however much smaller than the lengths of the molecules. There are also some other types of molecular aggregates of high polymers which form crystalline phases. Collagen<sup>1.42</sup> which is a composite helical molecule possesses a long period of about  $640 \text{ \AA}^{\circ}$  along the chain direction and small equivalent period of about  $10 \sim 15 \text{ \AA}^{\circ}$  in the lateral direction. Biological membranes, pleated sheets of polypeptide chains, polyamides which are generally rich in hydrogen bonds form layered orderly arrangement of molecules.<sup>1.43</sup> A single molecule of haemoglobin in the crystalline state consists of four subunits of globular molecules consisting of tangled aperiodic polypeptide chains which come together to form crystals having a large unit cell. Thus proper understanding of the crystalline structures of these wide ranging solid high polymers constitutes an important task to elucidate the properties of those materials.

#### 1.1(A) Studies on crystalline polymers :

The analysis of the crystal structure of a molecular compound necessarily includes both the determination of the