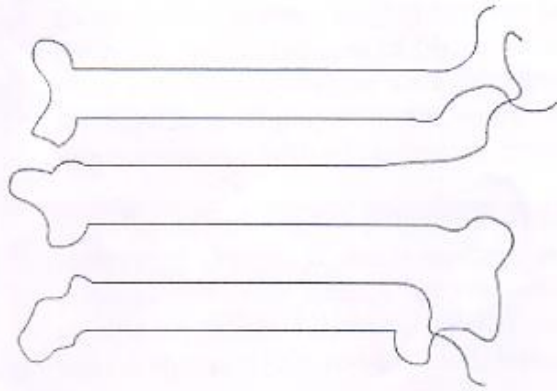
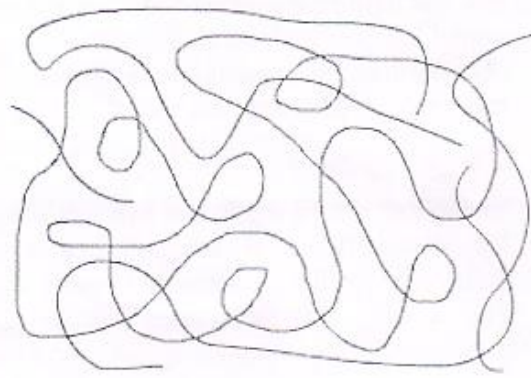


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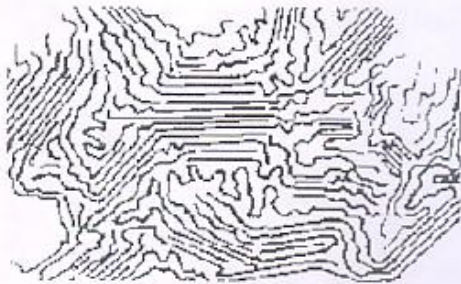


Crystalline



Amorphous

There are some polymers that are completely amorphous, but most are a combination with the tangled and disordered regions surrounding the crystalline areas. Such a combination is shown in the following diagram.



The crystalline areas formed by folding and stacking of polymer chains  
Fringe-micelle model =

An amorphous solid is formed when the chains have little orientation throughout the bulk polymer. The glass transition temperature is the point at which the polymer hardens into an amorphous solid. This term is used because the amorphous solid has properties similar to glass.

In the crystallization process, it has been observed that relatively short chains organize themselves into crystalline structures more readily than longer molecules. Therefore, the degree of polymerization (DP) is an important factor in determining the crystallinity of a polymer. Polymers with a high DP have difficulty organizing into layers because they tend to become tangled. The cooling rate also influences the amount of crystallinity. Slow cooling provides time for greater amounts of crystallization to occur. Fast rates, on the other hand, such as rapid quenches, yield highly amorphous materials. For a more complete discussion. Subsequent annealing (heating and holding at an appropriate temperature below the crystalline melting point, followed by slow cooling) will produce a significant increase in crystallinity in most polymers, as well as relieving stresses.

Low molecular weight polymers (short chains) are generally weaker in strength. Although they are crystalline, only weak Van der Waals forces hold the lattice together. This allows the crystalline layers to slip past one another causing a break in the material. High DP (amorphous) polymers, however, have greater strength because

the molecules become tangled between layers. For uses and examples of high and low DP polymers. In the case of fibers, stretching to 3 or more times their original length when in a semi-crystalline state produces increased chain alignment, crystallinity and strength. In most polymers, the combination of crystalline and amorphous structures forms a material with advantageous properties of strength and stiffness.

Also influencing the polymer morphology is the size and shape of the monomers' substituent groups. If the monomers are large and irregular, it is difficult for the polymer chains to arrange themselves in an ordered manner, resulting in a more amorphous solid. Likewise, smaller monomers, and monomers that have a very regular structure (e.g. rod-like) will form more crystalline polymers.

- The Factors affecting on the degree of Crystallinity or Crystallization.

- ① The particular type of polymerising process.
- ② The rate of cooling following polymerisation or processing
- ③ The type of molecular chain arrangement.
- ④ (regular chain arrangement along the polymer chain giving the structure a high degree of symmetry).
- ④ Degree of polymerisation. تعداد یونٹوں کی تعداد اور وزن کے تناسب سے
- ⑤ orientation in processing of films and fibers.
- ⑤ The shape and size of the monomers substituent groups.

## Orientation and Crystallinity

The physical properties of a polymer of a given chemical composition are dependent on two distinct aspects of the arrangement of the molecular chains in space:

1. The arrangement of a single chain without regard to its neighbour: rotational isomerism.
2. The arrangement of chains with respect to each other: orientation and crystallinity.

In semicrystalline polymers the distinction between orientation and crystallinity may at times be an artificial one. Many polymers when cooled from the melt form a disordered structure called the amorphous state. Some of these materials, such as polymethyl methacrylate, polystyrene and rapidly cooled (melt-quenched) polyethylene terephthalate (PET), have a comparatively high modulus at room temperature, but others, such as natural rubber and atactic polypropylene, have a low modulus. These two types of polymer are often termed glassy and rubber-like, respectively, and we shall see that the form of behaviour exhibited depends on the temperature relative to a glass-rubber transition temperature ( $T_g$ ) that is dependent on the material and the test method employed.

Although an amorphous polymer may be considered as a random tangle of molecules (Figure 1.9(a)), it is apparent that completely random packing cannot occur. There is no distinct structure as, for example, revealed by X-ray diffraction techniques.

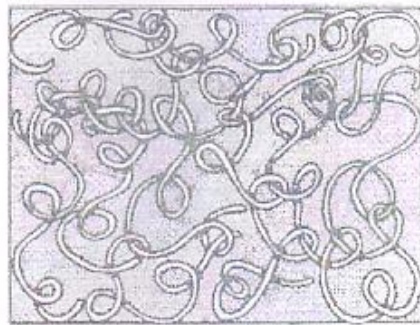
When an amorphous polymer is stretched the molecules may be preferentially aligned along the stretch direction. In polymethyl methacrylate and polystyrene such molecular orientation may be detected by optical methods, which measure the small difference between the refractive

index in the stretch direction and that in the perpendicular direction. X-ray diffraction methods still reveal no evidence of three-dimensional order, so the structure may be regarded as a somewhat oriented tangled skein (Fig. 1.9(b)) that is oriented amorphous but not crystalline.

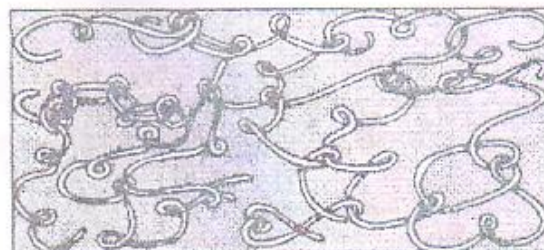
In polyethylene terephthalate, however, stretching produces both molecular orientation and small regions of three-dimensional order, termed crystallites, because the orientation processes have brought the molecules into adequate juxtaposition for regions of three-dimensional order to form.

Many polymers, including polyethylene terephthalate, also crystallize if they are cooled slowly from the melt. In this case we may say that they are crystalline but unoriented. Although such specimens are unoriented in the macroscopic sense, they possess isotropic bulk mechanical properties, they are not homogeneous in the microscopic sense and often show a spherulitic structure under a polarizing microscope.

PET  
 1. غير متبلور  
 2. Amorphous and oriented  
 3. Crystalline and semi-crystalline  
 ← Stretching



(a)



(b)

Figure 1.9 Schematic diagrams of (a) unoriented amorphous polymer and (b) oriented amorphous polymer