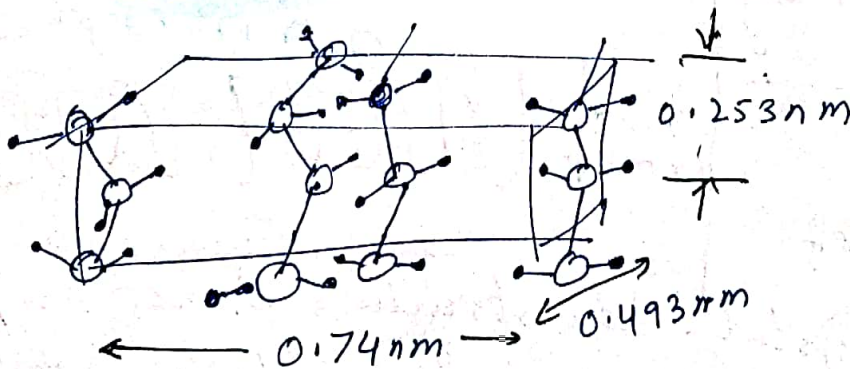


Microstructures within polymers.

Common plastics like PS & PVC are amorphous. These amorphous materials therefore lack any grains or grain boundaries. Their structural characteristics are found ~~at~~ on a scale comparable to that of molecules. This situation can be modified by a filler or stretching to align the molecules. So they don't have a conventional microstructure.

Crystallinity in polymers.

Many polymeric materials possess significant crystallinity: PE can be sufficiently crystalline. The unit cell can be defined by X-ray diffraction



- unit cell - or orthorhombic
- 90° angles.
- chains are aligned longitudinally
- Molecular crystal (PE)

Based on above fig.
Calculated density = 1.01 g/cc

fig 3.34

* Old concept

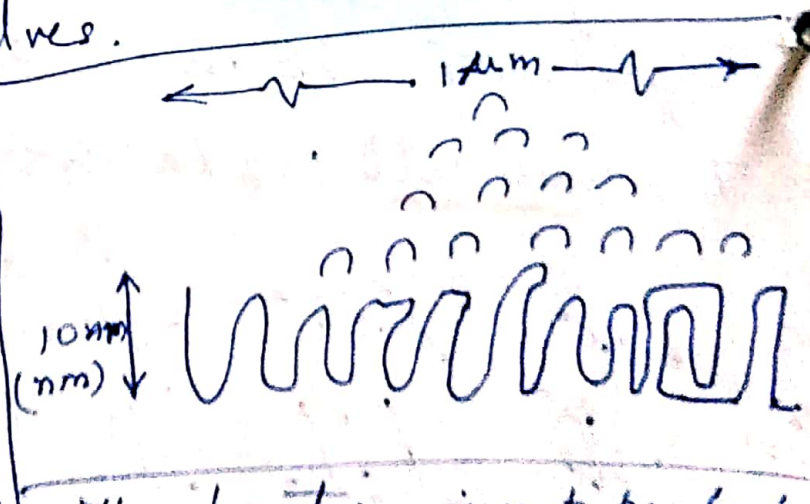
A partially crystalline polymer contains crystalline regions, separated by amorphous borders. This structure is called 'fringed micelles'. Long molecules could be part of both. These ~~were~~ found paralleling other molecules within the micelle, (just like spaghetti) ~~but~~ and extending into the adjacent unordered regions.

→ This part is still valid today:—

An individual macromolecule can reside in both crystalline & amorphous regions of a solid. ~~The~~ Much of the crystallinity arises, ~~the~~ due to the folding of molecular chains on themselves.

Crystallization by chain folding.

A linear molecule folds back onto itself



to produce a crystal. The structure is not perfect because large molecules may start to fold at separate locations and therefore may become part of two growing crystals. There is also some variation in the lengths of the U-turns.

which provides varying amounts of amorphous regions between the crystals.

Folds occur approximately every 10 nm. with 50 to 100 carbon atoms in each reversed segments of the chain. A number of molecules can join the ~~to~~ same growing crystal, so that the lateral dimension may approach 1 μm or more. Amorphous regions remain since the folding process is seldom perfect.

The consequences of partial crystallinity can be understood by the data in Table (7-5)

Characteristics of PE (at 20°C, except for thermal exposure)		
Property	LDPE	HDPE
Density g/cc (Mg/m^3)	0.92	0.96
Crystallinity %	~0	~50
Thermal expansion $^{\circ}\text{C}^{-1}$	180×10^{-6}	120×10^{-6}
Thermal conductivity (watt/m^2) ($^{\circ}\text{C}/\text{m}$)	0.34	0.52
Tensile strength, MPa	5-15	20-40
Young's modulus, MPa	100-250	400-1200
Heat resistance for continuous use, $^{\circ}\text{C}$	55-80	80-120
10 min temp. exposure, $^{\circ}\text{C}$	80-85	120-125

The catalyzed reaction that is used for making HDPE leads to the more idealized polymer chain without regularly spaced $-CH_2-$ side units. Thus, the molecules can mesh together more favourably for the long range order of a crystal. This leads to greater density and less free space in the product.

Generalizing the ability for linear polymers to crystallize

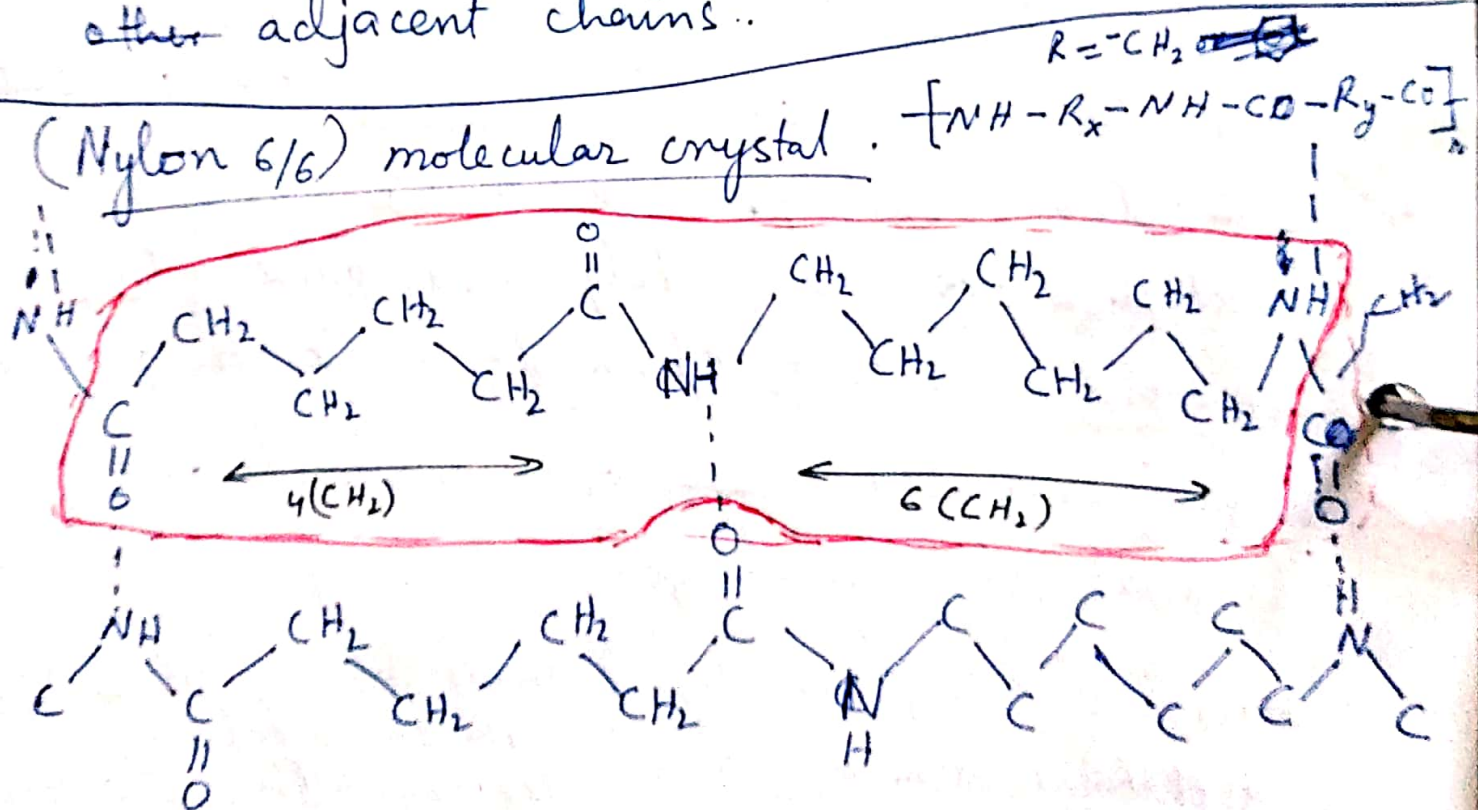
✓ A chain with spatial irregularities crystallizes ~~more~~ less readily. Thus atactic polymers crystallize less completely and possess larger amorphous contents than do isotactic polymers.

✓ Chains with large size side radicals are difficult to crystallize.

benzene ring in P.S. } these these interfere
large Cl Chlorine atom in PVC } with chain folding in
the crystallization process
thereby precluding crystallization

~~Crystallization is facilitated by the presence of polar groups. \rightarrow Crystals form more~~

Crystallization is facilitated by the presence of polar groups. Poly. crystals form more readily in nylon than in PE, even though both contain the same (CH₂) segments. However there are negligible chances of bonding between adjacent chains of PE. In fact the hydrogen atoms (exposed protons) at the ends of covalent bonds experience mutual repulsion with those of other adjacent chains.



The polar C=O groups bond to the next chain through hydrogen bridges. This bonding favours a matching of adjacent molecules and leads to more complete

crystallinity than in PE. Within crystals, the molecules are not kinked and coiled.



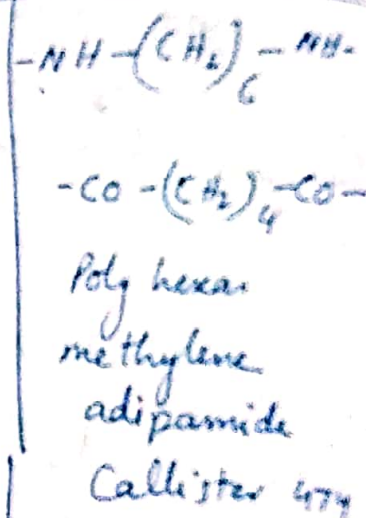
The periodic presence of this hydrogen bridge helps to align adjacent molecules into the ordered crystalline pattern.

Polyblends

Plastics with two or more phases are commonly called polyblends. They can be formed by mechanical mixing, by phase separation, or from block and graft copolymers.

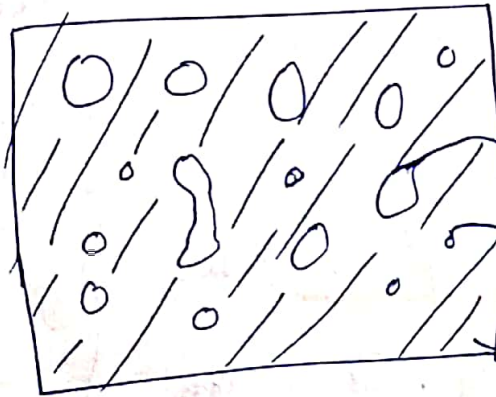
Their development has led to a number of products with enhanced properties.

Mechanical mixing is used to make ^{the} simple blends. Phase separation is used to make two phase mixtures - eg. a change in temperature, or the removal of a solvent, can introduce immiscibility. (mutual



insolubility) that physically segregates the two polymeric species from a previously single phase soln. Emulsification procedures can also be used to make such mixtures.

Microstructure in fig contains a matrix that is a random copolymer of vinylidene & vinyl chloride (PVDC & PVC). The dispersed phase is a copolymer of styrene & methyl methacrylate (PS & PMMA).



Polyblend (Plastic film for food packaging) The dispersed phase is a PS-PMMA copolymer.

The matrix is a PVDC-PVC copolymer. Both phases are amorphous and mutually insoluble (immiscible).

Both the phases are amorphous. ~~These these~~ This two-phase system has a miscibility gap. The polyblend is used in the food-packaging industry, where high transparency and low oxygen transmission is required. Both the amount and the size of the dispersed phase are important for optimum properties.

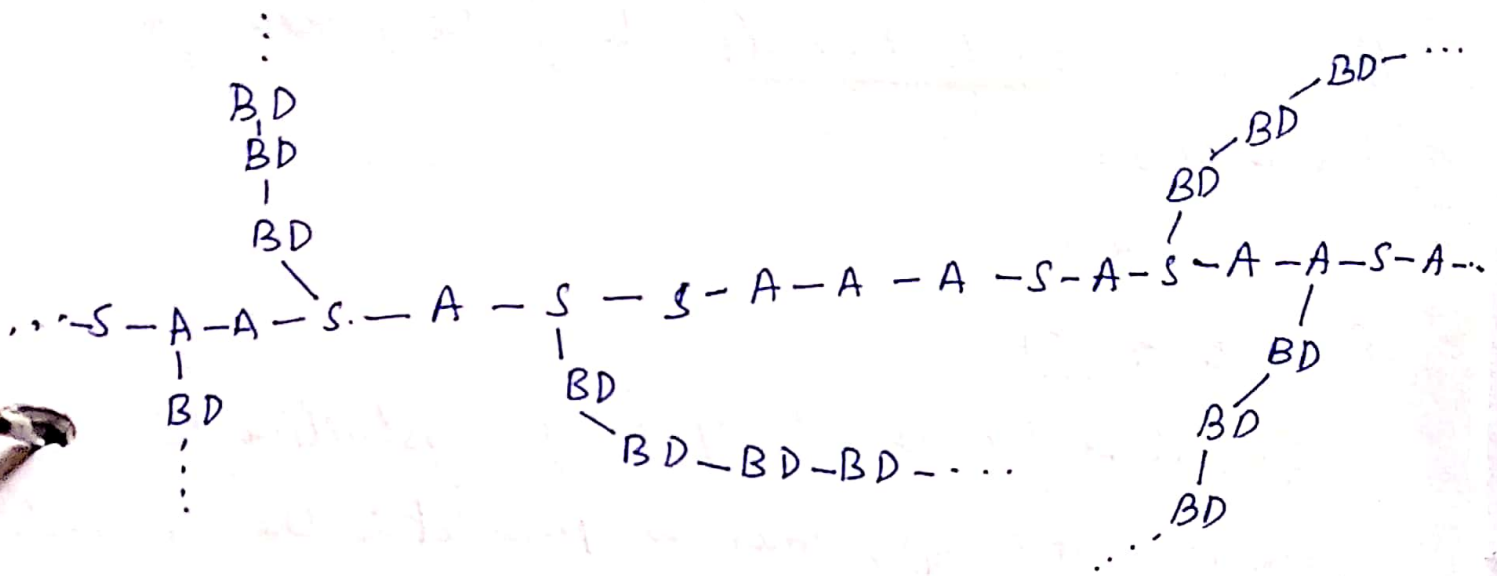
Adjacent domains are tied together by the covalent bonds within the molecular chains. Bonds between chains are weaker, secondary bonds.

Buna-S (^{an}artificial rubber) is such a copolymer. It contains blocks of styrene mers and blocks of butadiene mers.

During processing, similar blocks of each species cluster to form small domains and a two-phase mixture. These domains, which are sub-micron in size (10 to 100 nm), provide a microstructure that contains a rigid PPS and flexible PBD, a combination that leads to greatly increased toughness.

There is a significant difference between the microstructures formed by block copolymerization and those formed by mixing or phase separation. In block copolymerization the same molecular chain extends from one domain (phase) into the next. This structure gives the strong covalent connection of the intramolecular bonds between the two phases. In contrast, the molecules

at the phase interface are only weak, secondary intermolecular bonds in the normal ~~of~~ polymeric two phase mixture.



Graft copolymer (schematic of ABS polymers)

ABS = Acrylonitrile - Butadiene - Styrene

A random copolymer of styrene and acrylonitrile possesses butadiene grafts. Although attached to the main chain, the rubbery butadiene grafts can develop elastic domains as in the block copolymers. These domains provide toughness in the harder S-A plastic

Graft copolymers provide a variant for the establishment of bonds across phase boundaries. The widely used ABS plastics are an 'alloy' possessing a matrix of a copolymer of styrene and acrylonitrile onto which butadiene mers have been grafted. Elastomeric

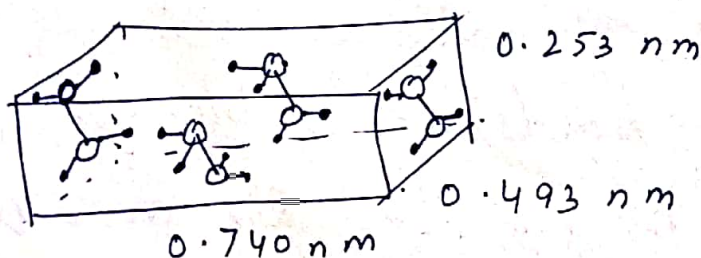
domains form in the product during processing. They are tied to the neighbouring domains of the ~~SAN~~ styrene-acrylonitrile copolymer by the strong covalent bonds along the molecular backbones.

Example 7-5.1

Calculate the density of fully crystalline PE
 Solution = A $(C_2H_4)_n$ mer is parallel to the two ends of the rectangular cell, for an equivalent of one mer per unit cell. Likewise, a mer is parallel to the two sides. Together they comprise a total of two mers per unit cell.

$$\rho = \frac{2(24 + 4 \text{ amu}) / (6.02 \times 10^{24} \text{ amu/g})}{(0.253 \times 0.74 \times 0.493) \cdot (10^{-27} \text{ m}^3)}$$

$$= 1.01 \times 10^6 \text{ g/m}^3 \text{ or } 1.01 \text{ g/cc}$$



Comments = densities normally lie in the range 0.92-0.96 (due to presence of free space) depending on the degree of crystallinity.

Example 7-5.2

- (a) Determine how much more free space exists in the LDPE ~~of~~ than there is in the HDPE.
- (b) How does the free space relate to the properties?

Procedure :- The "free space" is the volume in excess of the true volume of the crystal.

Calculation

(a) Basis :- 1g PE

$$\text{HDPE volume :- } (1\text{g}) / (0.96\text{g/cc}) = 1.042\text{ cm}^3$$

$$\text{LDPE volume :- } (1\text{g}) / (0.928\text{g/cc}) = 1.087\text{ cc}$$

$$\frac{\Delta V}{V} = \frac{(1.087 - 1.042)\text{ cm}^3}{1.042\text{ cm}^3} = 4.3\%.$$

(b) The free space decreases the levels of stress or thermal energy required for deformation. Therefore, the LDPE has the lower strength, elastic modulus and thermal resistance.

T_g is below ambient temp. \Rightarrow molecular rearrangements supplement thermal vibrations to expand the volume

of the amorphous portions of the PE; therefore

$$\alpha_{LDPE} > \alpha_{HDPE}$$

Comment :: The thermal conductivity of HDPE is greater than that of LDPE because heat is conducted through nonmetallic solids by elastic waves. These waves travel more readily in the ordered structure of crystalline materials.

(751) ^{p250} A polyethylene with no evidence of crystallinity has a density of 0.9 Mg/m^3 . Commercial grades of LDPE have 0.92 Mg/m^3 , whereas HDPE has a density of 0.96 Mg/m^3 . Estimate the volume fraction of crystallinity in each material.

Let $x = \text{vol. fraction of crystalline part}$

$$(1.01)x + 0.9(1-x) = 0.96 \text{ or } 0.92$$

$$(1.01 - 0.9)x + 0.9 = 0.96 \text{ or } 0.92$$

$$0.11x = 0.06 \text{ or } 0.02$$

$$x = \frac{0.06}{0.11} = 0.545 \text{ or } 54.5\%$$

$$x = \frac{0.02}{0.11} = 0.182 \text{ or } 18.2\%$$

fully crystalline PE = 1.01 Mg/m^3

zero " " = 0.9 Mg/m^3

$$\frac{0.92 - 0.9}{1.01 - 0.9} = \frac{0.02}{0.11} = 0.182 \text{ or } 18.2\% \text{ crystallinity}$$

$$\frac{0.96 - 0.9}{0.11} = \frac{0.06}{0.11} = 0.545 \text{ or } 54.5\% \text{ crystallinity}$$

752
P250

From the densities in problem 751, calculate the amount of free space in LDPE & in HDPE.

• 1 gm basis Volume

$$\frac{1 \text{ gm}}{0.92 \text{ g/cc}} = \text{LDPE} = 1.087 \text{ cc or } 8.7\%$$

$$\frac{1 \text{ gm}}{0.96} = \text{HDPE} = 1.042 \text{ cc or } 4.4\%$$

fully
crystalline

$$\frac{1 \text{ gm}}{1.01} = 0.99 \text{ cc}$$

Volume in excess of true volume or free space in LDPE =

$$= 1.087 - 0.99 = \frac{0.097}{0.99} \text{ or } 9.8\%$$

$$\text{in HDPE} = 1.042 - 0.99 = \frac{0.052}{0.99} = \frac{19.25}{375} = 5.25\%$$

~~0.193~~