Science and Technology of Polymers
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Lecture - 24
Liquid Crystalline Polymers

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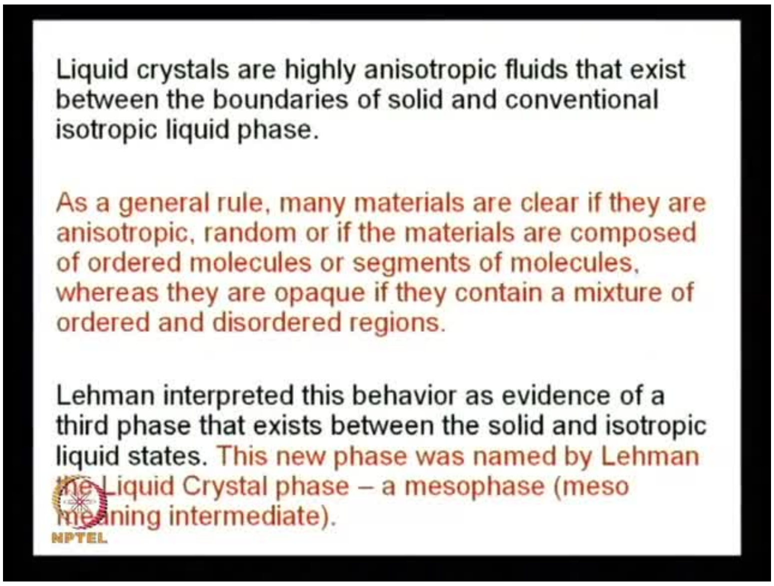

Liquid crystals are highly anisotropic fluids that exist between the boundaries of solid and conventional isotropic liquid phase.

As a general rule, many materials are clear if they are anisotropic, random or if the materials are composed of ordered molecules or segments of molecules, whereas they are opaque if they contain a mixture of ordered and disordered regions.

Lehman interpreted this behavior as evidence of a third phase that exists between the solid and isotropic liquid states. This new phase was named by Lehman the Liquid Crystal phase – a mesophase (meso meaning intermediate).

Today, we are going to discuss liquid crystalline polymers. You know polymers are semi crystalline in nature in solid state, but it is a surprise thing to you things to you that how this liquid crystalline polymer exists. You know liquids are anisotropic isotropic in nature and crystalline solids are anisotropic in nature. When you talk about liquid crystalline polymer, we have to consider anisotropic behaviour of this material in liquid state. Actually tells about some intermediate phase the boundary between liquid and solid phases, that is called liquid crystalline phase. Sometimes, it is termed as mesosphere and you can have this concept of liquid crystalline from the molecular order.

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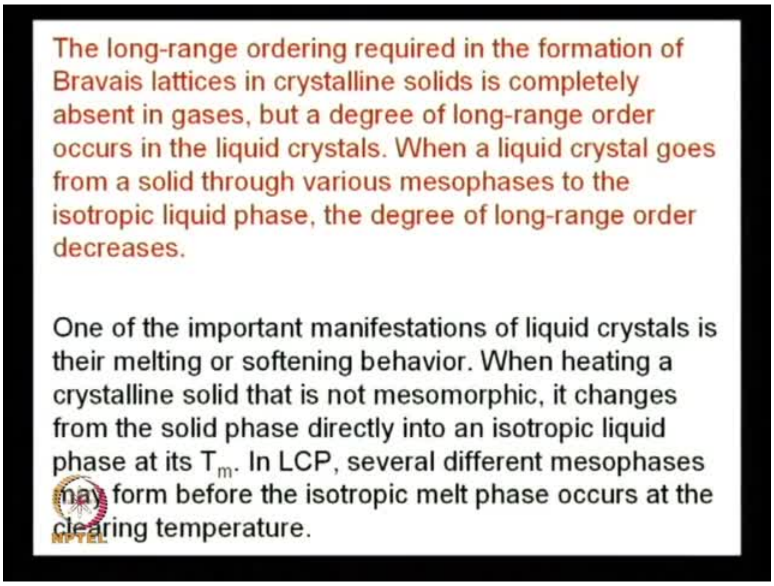

The long-range ordering required in the formation of Bravais lattices in crystalline solids is completely absent in gases, but a degree of long-range order occurs in the liquid crystals. When a liquid crystal goes from a solid through various mesophases to the isotropic liquid phase, the degree of long-range order decreases.

One of the important manifestations of liquid crystals is their melting or softening behavior. When heating a crystalline solid that is not mesomorphic, it changes from the solid phase directly into an isotropic liquid phase at its T_m. In LCP, several different mesophases may form before the isotropic melt phase occurs at the clearing temperature.

Molecular order in, due to their positional entropy orientation, and entropy as well as conformational entropy.

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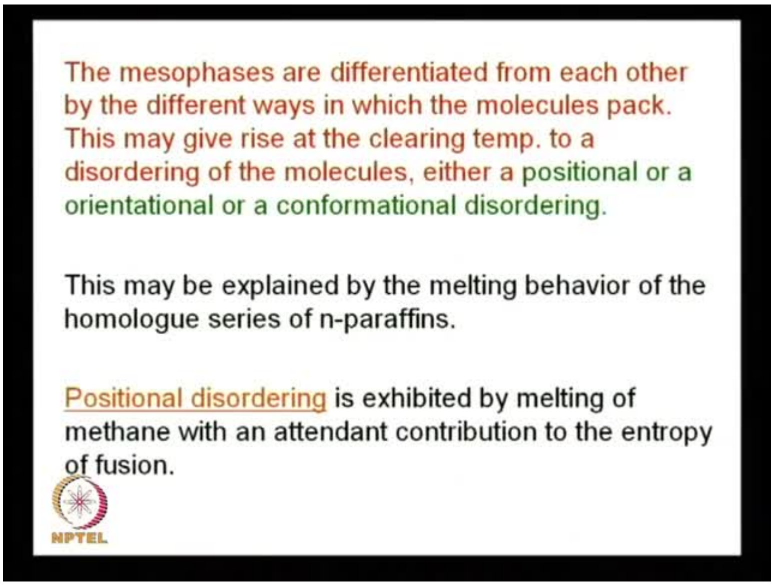

The mesophases are differentiated from each other by the different ways in which the molecules pack. This may give rise at the clearing temp. to a disordering of the molecules, either a positional or a orientational or a conformational disordering.

This may be explained by the melting behavior of the homologue series of n-paraffins.

Positional disordering is exhibited by melting of methane with an attendant contribution to the entropy of fusion.

So, you can understand well. If you take this example of methane, methane can be solidified by cooling and if you observe the melting behaviour of methane. This positional disordering of methane molecule is executed by melting of methane; with an attendant contribution to the entropy of fusion methane molecule is spiracle in shape. So, when it melts from solid phase to liquid phase.

So, only disorder you can find due to the moment of methane molecule, on methane molecule from one location to the other location. So, the disorderedness in the liquid phase arising out of this melting of methane from solid state, it occurs due to the change of change in position from one location, to the other location because the molecule is spiracle and cementrica. Then if you increase one more carbon atoms that mean if you take ethane in the homolog gas series.

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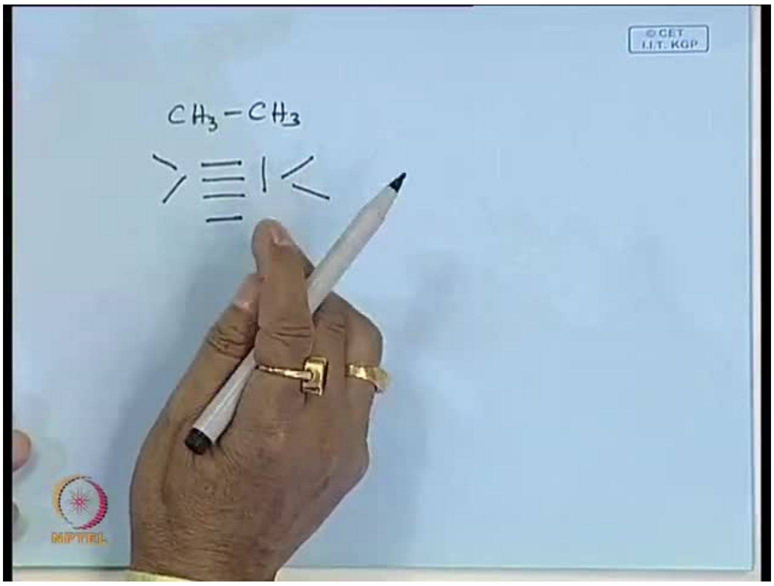

So, ethane molecule at is CH 3 CH 3 it looks like a rod, like this small rod or small line you can say now you can have different orientations of this molecules parallel, parallel sometimes perpendicular, sometimes angular, in different angles you can say. So, along with these positional that mean this molecule can moves from this place to another place, as well as it can orient itself either parallel to the original position or perpendicular to the original position or it can form certain angles to the original positions. So, we can have large number of orientations of this molecule, when we consider this orientation disordering of this ethane molecule.

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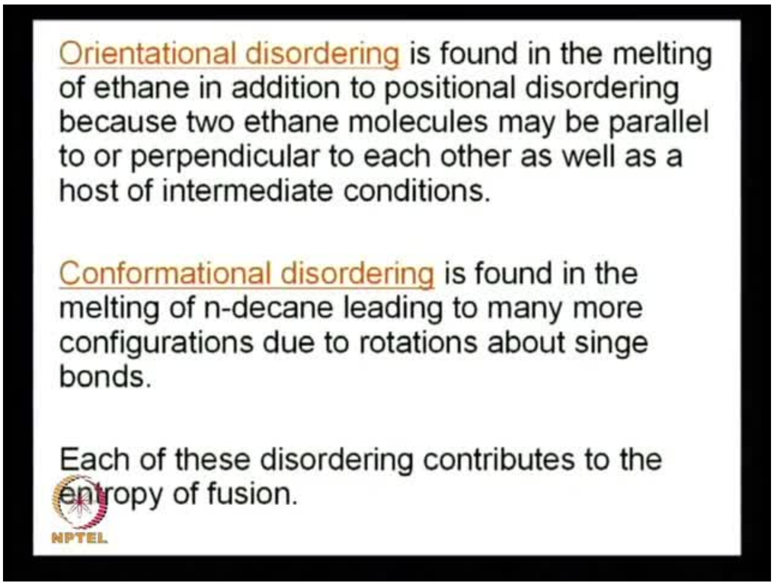

Orientational disordering is found in the melting of ethane in addition to positional disordering because two ethane molecules may be parallel to or perpendicular to each other as well as a host of intermediate conditions.

Conformational disordering is found in the melting of n-decane leading to many more configurations due to rotations about singe bonds.

Each of these disordering contributes to the entropy of fusion.

Then further increasing the number of carbon from ethane, to propane, to butane, to pentane, to hexane, to heptanes.

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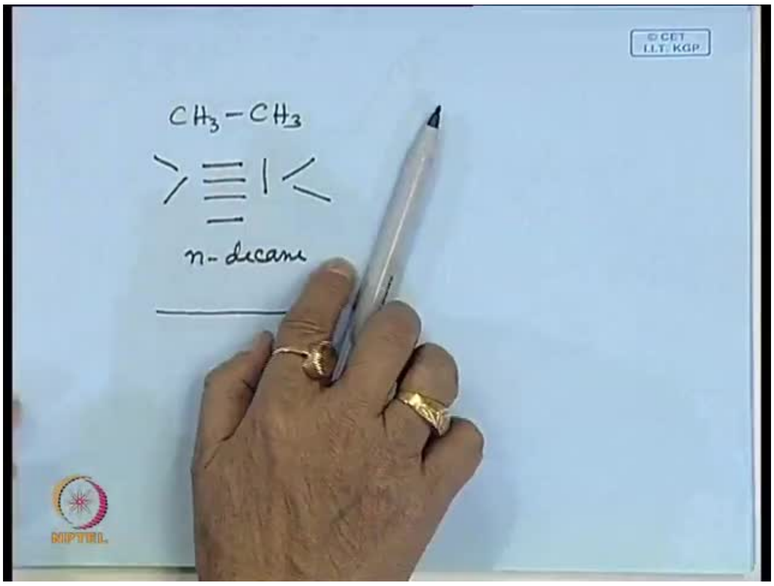

Like here one example is given. Normal decants containing ten carbon atoms that means the molecule size is bigger. Now, here in case of ethane you see this two methyl groups can rotate along carbon, carbon bonds that is possible this rotation of this carbon, carbon bonds it is possible, you can have infinite number of orientations infinite number of disorders stages steps or stages you can say, so that is more pronounced in normal deans.

So, it is found in this melting of an decants leading to many more configurations due to rotations about single bonds. So, methane gives only positional disordering, ethane give positional disordering as well as orietational disordering and normal decant or beyond methane you can get positional disordering, orietational disordering as well as conformational disordering. So, when a solid is melted that means it processed from solid phase to liquid phase, there is disorder in the molecular arrangements occurs, that means in the solid phase it may remain in ordered alignment conditions, alignment stages. It is melted it becomes disordered that means it becomes amorphous.

So, this stage of liquid crystallinity that means in the liquid phase the molecule is supposed to be such type of some ordered configurations, all right? Now, if you recall the molecules of ethylene, polyethylene polyethylene due to high compactness. It is crystallized polymer not perfectly 100 percent crystallized polymer, but it is a semi crystallized polymer crystalline may vary from 30 percent to 60, 70 percent like that and sometimes 100 percent crystallized structures can be crystallites can be isolated. Crystals can be isolated or can be prepaid polyethylene; otherwise many such polymers are semi crystalline in nature.

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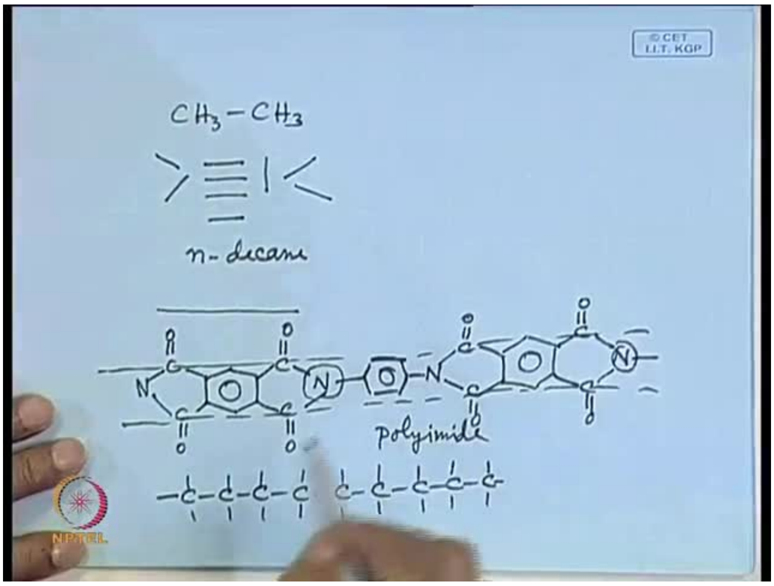

In nature when we pass from poly ethylene to other polymers like polyamides. Yesterday, I was telling you polyimide say made from phenylene dynamite. So, on we can go on increasing both sides the length of this molecule. This is amides linkage, this is amides linkage, this is amides linkage, this is ring this is a benzene ring, here will see there is a double side polymer containing ring such configurations. This is a rigid type of molecule as compared to say simple carbon structured polymers say polyethylene. Now, melting of this type of molecule, if you compare the melting behaviour of this type of polyethylene molecule, with that of polyamide molecule, you will find that it remain or prefer to remain like a rod like shapes.

So, by virtue of its molecular structure by virtue of its double strength structures, it looks like a ladder you see these are the steps of ladder, ladder like structures it forms rod shape structures. So, molecules having such types of structures preface to remain in ordered condition, even in liquid phase, I mean liquid phase, I mean in molten state, or in solution you can put this polymer in a solvent you can get a solution in that solution it can remain in a rod shaped configurations or ordered configuration or in melting condition, also it can maintain its rod shaped configuration. So, we can say such type of situations we can say there is a liquid crystalline behaviour, liquid crystalline structure of the polymer.

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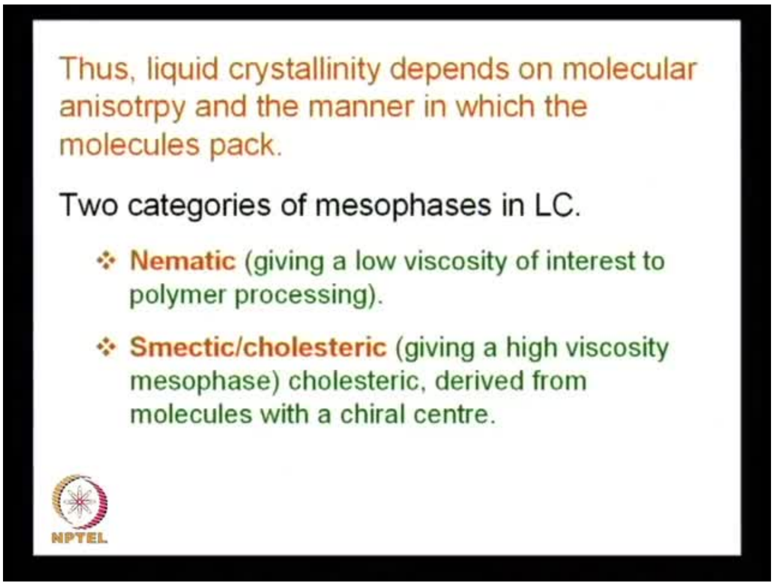

Thus, liquid crystallinity depends on molecular anisotrpy and the manner in which the molecules pack.

Two categories of mesophases in LC.

- **Nematic** (giving a low viscosity of interest to polymer processing).
- **Smectic/cholesteric** (giving a high viscosity mesophase) cholesteric, derived from molecules with a chiral centre.

We will see the models of this liquid crystalline polymer you understand how molecular composites can be prepaid from liquid crystalline polymers. How very strong fibres can be prepaid from liquid crystalline polymers, thus liquid crystalline depends on molecular anisotropy and the manner in which the molecules pack. So, it talks about this molecular anisotropic and by virtue of this configuration, it can remain, it can come closer or you can pack with molecules surrounding this molecules in this lots of configuration.

By virtue of such configuration we can get two categories of such mesophases structures in liquid crystalline materials. In the liquid phase one is Nematic and the other is Smectic or cholesteric. Nemetic actually characteristic of or gives a material of low viscosity or work viscosity, which is of interest in polymer processing whereas, Smectic shows high viscosity either in solution or in melt condition. So, two major categories of liquid crystalline polymers are Nemetic phases or Smectic or cholesteric phases or cholesteric phases, Nemetic LC or Smectic LC or cholesteric LC liquid crystalline polymers. Now, here this is what polymer processing is meant that, whenever we prepare some polymer we can get either in the form of solid or liquid or in solution, right?

If you get in the form of solid or it may be in the form of powder. So, after isolation of the polymer in the popular form we have to purify after purification get the pure polymeric material. So, in order to make a product out of that polymeric powder material, what we have to do? We have to either melt or we have to dissolve the solvent in order to process. So, that we can fabricate a finished product say fibre or film or moulded item. Whatever it may be we it leads to passed through some processing steps for that there we have to decrease the viscosity of the polymer by dissolving in the suitable solvents by melting through heat treatment, all right? That is for processing if the viscosity of the melt in the solution is very high then it incurs huge consumption of energy that will add to the cost of the product.

So, it is necessary that if the viscosities of the product polymer solution or polymer melt is low enough. So, that some product can be fabricated out of that polymer through some sceneries the cost of the final product will be less that is necessary, but in all cases it is not possible sometimes even if it is expensive you have to pass through some machineries even if it is high viscosity we have to process it to fabricate the final product.

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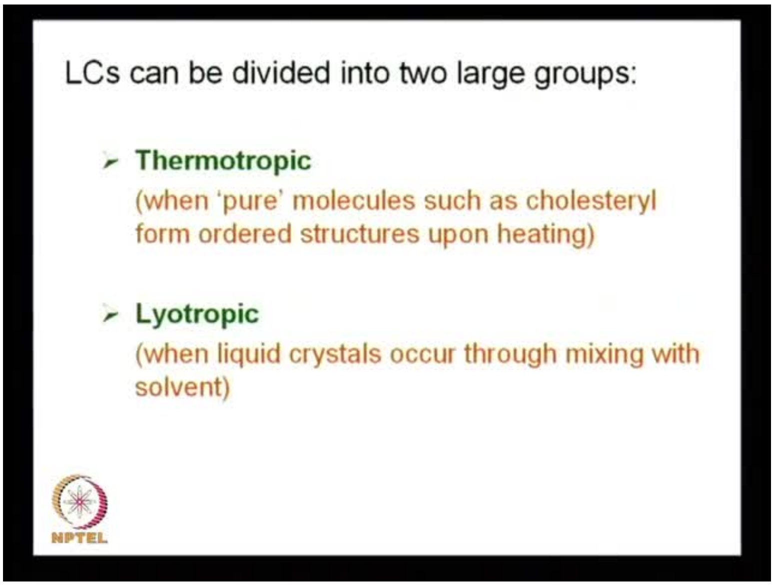

LCs can be divided into two large groups:

- **Thermotropic**
  (when 'pure' molecules such as cholesteryl form ordered structures upon heating)
- **Lyotropic**
  (when liquid crystals occur through mixing with solvent)

These liquid crystalline polymers can be divided into further, divided into two large groups. Thermotropic liquid crystalline polymers and Lyotropic liquid crystalline polymers, when Thermotropic means this is this is related to melt stage melt face. When liquid crystalline polymers or close liquid crystalline in melt condition we call it as Thermotropic liquid crystalline polymers that may be Nemetic or Smectic or cholesteric again.

On the contrary if the polymer shows liquid crystalline behaviour in solution phase we call it Lyotropic liquid crystalline polymer. So, what we have learned? We have learned categories of classification of this liquid crystalline polymer. Nemetic low viscosity, Smectic high viscosity or cholesteric high viscosity or Thermotropic or Lyotropic if it is liquid crystalline in melt condition it is Thermotropic if it shows liquid crystalline in solution it is called Lyotropic.

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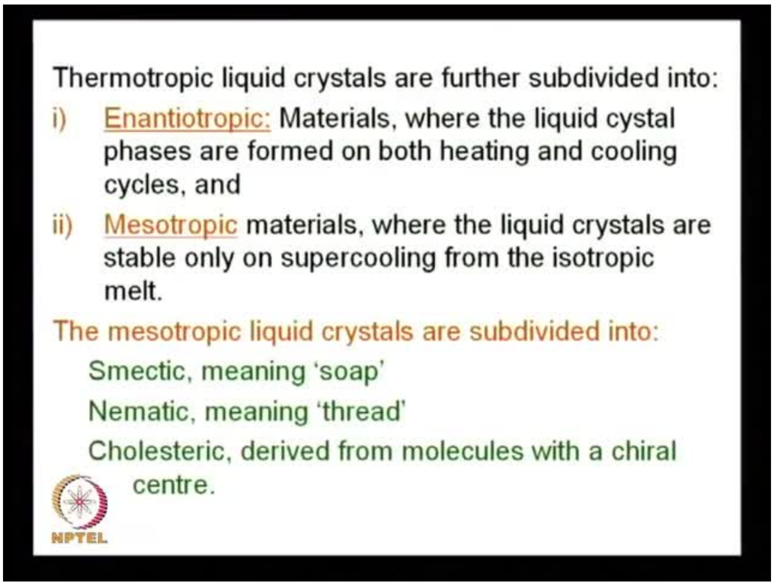

Thermotropic liquid crystals are further subdivided into:

i) Enantiotropic: Materials, where the liquid cystal phases are formed on both heating and cooling cycles, and

ii) Mesotropic materials, where the liquid crystals are stable only on supercooling from the isotropic melt.

The mesotropic liquid crystals are subdivided into:

Smectic, meaning 'soap'

Nematic, meaning 'thread'

Cholesteric, derived from molecules with a chiral centre.

Thermotropic liquid crystalline are further subdivided into Enantiotropic, which are material where the liquid crystal phases are formed on both heating and cooling cycles heating and cooling heating and cooling repeated heating and cooling, we can get this liquid crystalline behaviour. Mesotropic materials where the liquid crystals are stable only on super cooling from the isotropic melt the polymer melt may be anisotropic, but due to super cooling from some molecular order that is called Mesotropic.

Mesotropic liquid crystalline materials are further sub divided into.

Smectic, meaning soap.

Nematic, meaning thread.

Cholesteric derived from molecules with a chiral centre, it is as a chiral centre asymmetric centre.

These are affiliated necessary only to develop some concept on liquid crystalline behaviour of this polymeric material.

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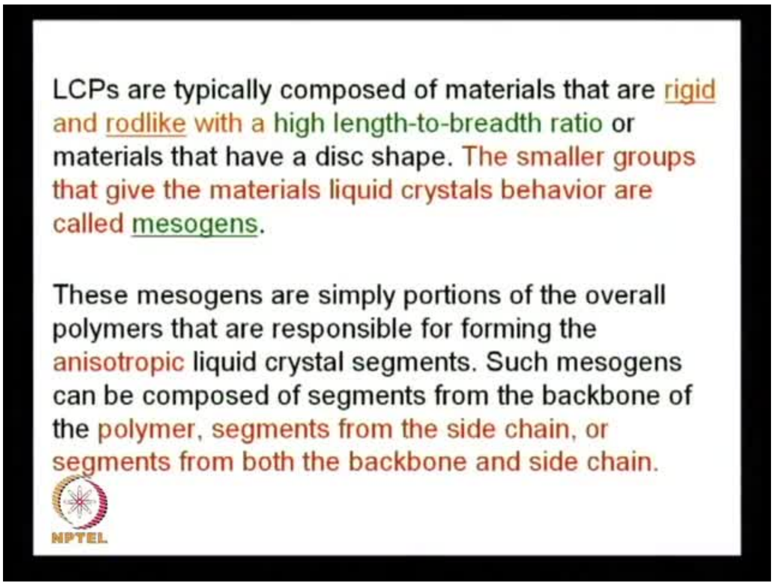

LCPs are typically composed of materials that are rigid and rodlike with a high length-to-breadth ratio or materials that have a disc shape. The smaller groups that give the materials liquid crystals behavior are called mesogens.

These mesogens are simply portions of the overall polymers that are responsible for forming the anisotropic liquid crystal segments. Such mesogens can be composed of segments from the backbone of the polymer, segments from the side chain, or segments from both the backbone and side chain.

This liquid crystalline polymer are typically composed of materials that are rigid and rod like. As I mention it is a rigid and rod like, it maintains the rigidity or rod shape configuration even in the liquid phase, either in solution or in melt with a high length to breadth ratio means high aspect ratio you can say. Say suppose this molecule you consider one second this molecule have the length of this molecule, which is related to end to end distance means distance between the two ends of this polymer molecule on isolated polymer molecule.

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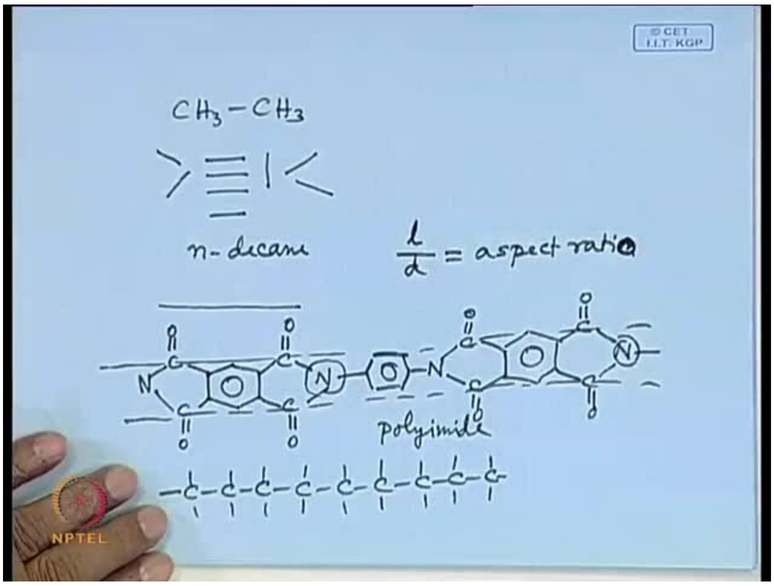

That is called l and the diameter that means if you calculate the diameter considering the bond angles and the bond distance you can get some diameters that is l by d that is aspect ratio higher aspect ratio better will be the polymer for making molecular level components. You know in fibre composites we can get very strong and durable composites provided, if we have long fibres with small diameters.

So, that we can get high interface area smaller diameters means the thinner is the fibre, thinner is the fibre means higher is the surface area, which can provide more interface area for contact between the fibre and the matrix ,which is necessary for compositions contact not only contact, this is not only physically contact, sometimes it may be physic chemical contact, there may be some chemical physical anchorage as well as chemical primary bond formation is there that will be really very strong high performance composite.

So, keeping that aspect in mind if you can design a suitable polymer molecule, which shows rigid rod like behaviour in liquid phase say in solutions or in melt that will be very ideal liquid crystalline polymers and provided again, if you can provide low viscosity so that it helps in processing the product processing and fabrication of the product. So, these are ideal situations it should be low viscous it should be as crystalline as possible lay less (( )) out process possible as well as low less viscous as possible. The smaller groups that give the materials liquid crystals behaviour are called mesogens. Now, the things are coming gradually one by one.

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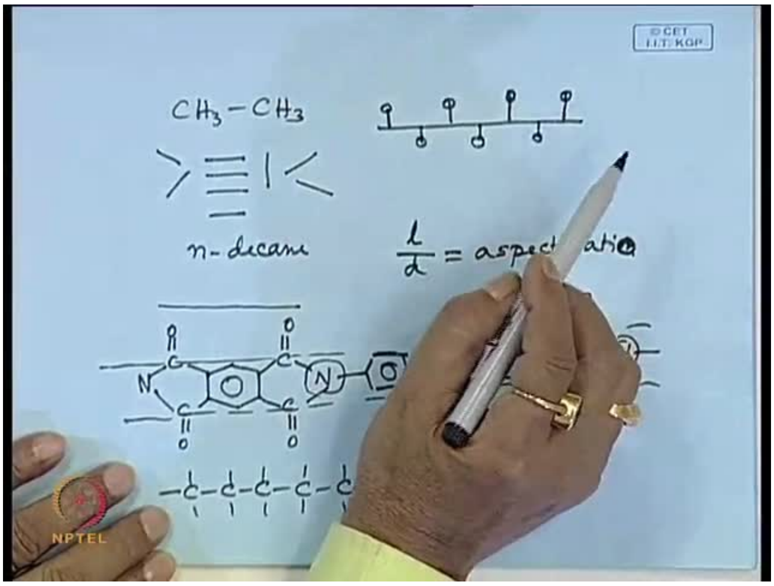

Mesogens, mesogens the themes of mesogens will be clear you see suppose this is a backbone chain to each substituent’s are there like this, like this sometimes what happens these substituent’s are pendent groups helps in molecular ordering. Say you think of linear polypropylene polymer where methyl group can make its configuration as isotactic or cinder tactic or atactic, atactic is the random configuration which is amorphous in nature soft weak polymer, where isotactic and cindertactic having regular symmetric or regularity in the molecular configuration that means substituent’s pendent group or methyl group that leads to isotacticity or cyndertacticity actually the sense is like that.

Now, these groups or pendent groups substituent’s are known as mesogens or the groups in the backbone chain like this say rings say imides’ rings or benzene rings this can also be called as mesogens or mesogens units. Which helps in getting this mesosphere means liquid crystalline phase. So, the units in a polymer backbone or polymer structure which helps to get molecular order to get mesospheric system are known as mesogens so here you can consider these as mesogens, there you can consider these as mesogens. You understand? Is that clear?

These mesogens are simply the portions of the overall polymers that are responsible for forming the anisotropic liquid crystal segments such mesogens can be composed of segments from the backbones of the polymer as I told in this case, segments forms the side chain as I told you in this case, all right? Segments from both the backbones and side chain that means you can have a polymer, where mesogens can be placed along the backbone chain you can have the liquid crystalline polymers, where mesogens are placed as pendent groups you can have polymers where both these backbone mesogens as well as pendent mesogens can contribute to this mesophases structure configuration liquid crystalline behaviour.

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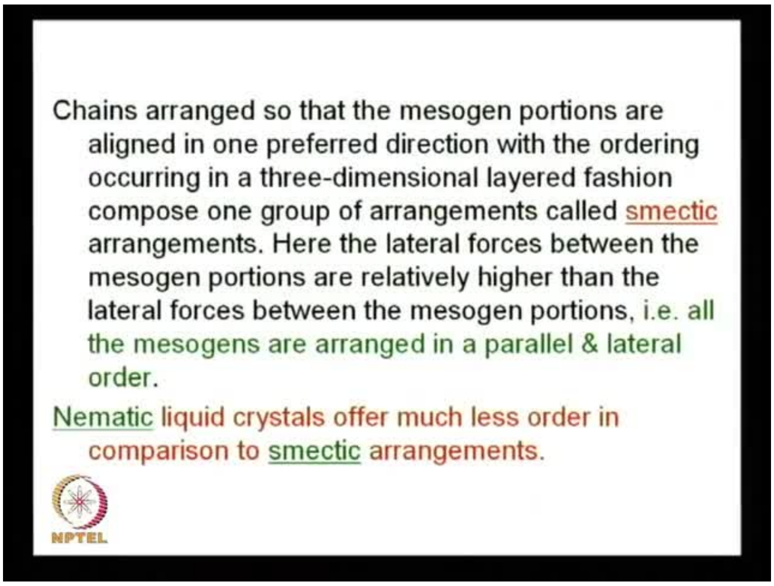

Chains arranged so that the mesogen portions are aligned in one preferred direction with the ordering occurring in a three-dimensional layered fashion compose one group of arrangements called smectic arrangements. Here the lateral forces between the mesogen portions are relatively higher than the lateral forces between the mesogen portions, i.e. all the mesogens are arranged in a parallel & lateral order.

Nematic liquid crystals offer much less order in comparison to smectic arrangements.

Chains arranged, chains are arranged so that the mesogens portions are aligned in one preferred directions with the ordering occurring in a three dimensional layered fashion composed of one group of arrangements called smectic arrangements. Say suppose you can have a layer that means in one layer you can have polymer molecules on ply say think of laminates or composite, how the laminates are made we take more than one ply’s and we assemble the ply’s like this say striking of playing cards particularly one over the other one top of the other.

So, this way we can get layers of such flies now if molecules present in each layer if we consider their order in individual layers then that can alter the liquid crystalline behaviour. Once again I repeat say suppose you have a layer of polymer molecules imaginary layer of polymer molecules in which you can have molecular alignments along with this direction in one layer you can have another layer of polymers, where molecular alignment may remains like this just perpendicular, perpendicular directions in another layer you can have molecular alignments with some angular directions neither 90 degree not parallel say 30 degree or 45 degree like this.

So, this way you can have several layers. Where each layer have different orientation of the polymer molecules in one layer it is fixed, but such orientations different from one layer to the other layer. So, that will give you some arrangements that is known as smectic arrangements you will see when I will show you some structural models later it is coming later arrangements called smectic arrangements. Here the lateral force between the mesogens portions are relatively higher than the lateral force between the mesogens portions mesogens portions that means all the mesogens are arranged in parallel and lateral order I mean I mean if you think of think of this configuration, where mesogens are placed like this you can have another molecule by this side, where you can have you can have arrangements like this these are mesogens the small spare are mesogens identical arrangement.

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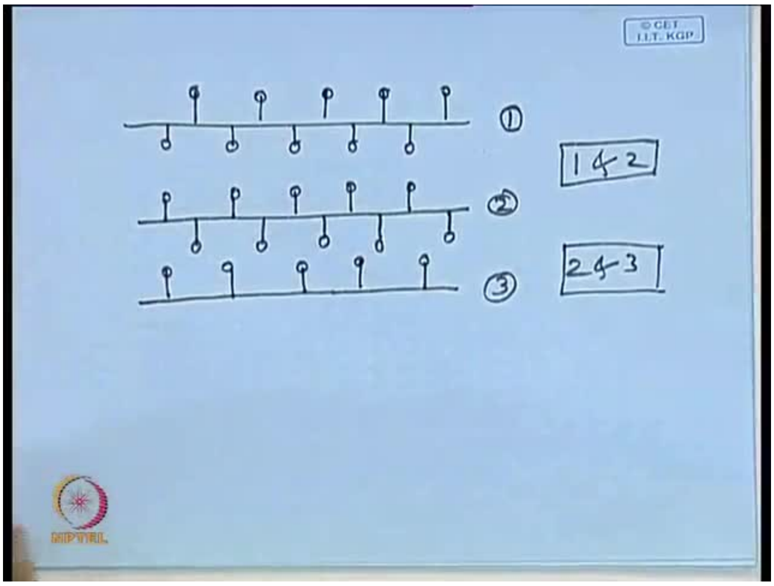

Now, this mesogens can interact with this mesogens, this mesogens can interact with this mesogens, this mesogens can interact with this mesogens. That means there will be intermolecular interactions through this small monogenic group. Now you can have arrangements also like this.

Now you will compare the interaction between 1 and 2 and interaction between 2 and 3, it can so happen that in this case interaction may be higher than this provided they are opposite nature. If these mesogens are opposite nature than say positive, negative, positive, negative type of thing by virtue of their polarity opposite polarity their interaction say suppose hydrogen bonds in these case 1 and 2 in these case one, and two interaction will be stronger considering the same sense interaction will be less between 2 and 3 because there is a distance between the mesogen group.

So, this inter molecular interactions through such monogenic group contribute to the liquid crystalline order in liquid phase crystalline ordering liquid phase. Nemetic liquid crystals offer much less order in comparison to smectic arrangements that is why Nematic LCP are of lower viscosity than smectic LCP very simple, very simple concept since intermolecular forces of interactions between through this small mesogens are less in case of Nematic so Nematic LCP exhibits lower viscosity than that of smectic LCP, clear? Now you understand why this Nematic having characteristics of lower viscosity than that of smectic one.

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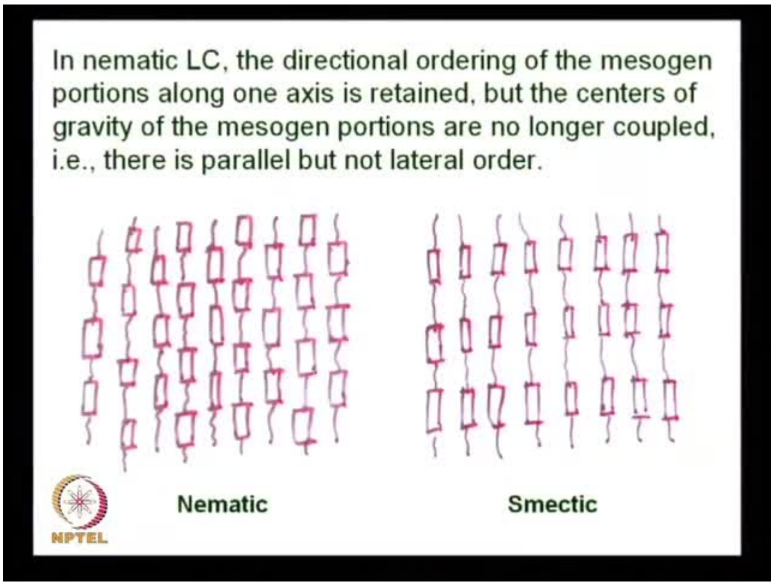

In nematic LC, the directional ordering of the mesogen portions along one axis is retained, but the centers of gravity of the mesogen portions are no longer coupled, i.e., there is parallel but not lateral order.

In nematic LC, the directional ordering of the mesogen portions along one axis is retained, but the centres of gravity of the mesogen portions are no longer coupled there is parallel, but not lateral order. Considered this one this is nematic this is smectic look at these two models nematic model and smectic model where you see these are mesogens. Which brings molecular order leading to liquid crystalline behaviour in this molecule mesogens are placed like this, in this molecule mesogens are placed like this?

So, now the distance between this mesogens and this mesogens is quite bigger than this one. So, this mesogen is close to non mesogenic portion, that is why the interactions the interactive force, which contributes to the viscosity in the liquid phase here it suppose to be less. In fact it is the case the reality you find the nematic material nematic LCP or low viscosity you compare this one, where these molecules are aligned parallel here also molecules aligned parallel, but not the mesogens are aligned parallel, here you see all the mesogens are in one line almost. So, they can have interactions between the mesogens and that can provide more or closure packing, closure interaction stronger will be the material either in fibre or in film form or in moulded form.

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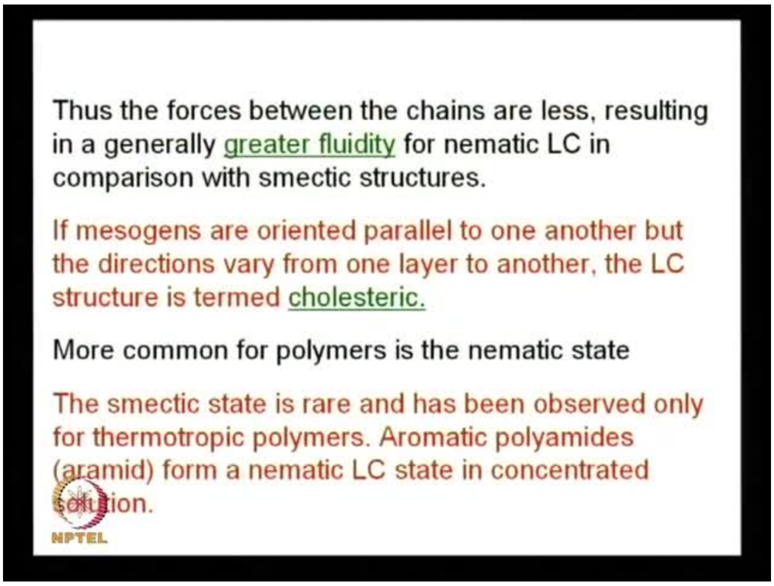

Thus the forces between the chains are less, resulting in a generally greater fluidity for nematic LC in comparison with smectic structures.

If mesogens are oriented parallel to one another but the directions vary from one layer to another, the LC structure is termed cholesteric.

More common for polymers is the nematic state

The smectic state is rare and has been observed only for thermotropic polymers. Aromatic polyamides (aramid) form a nematic LC state in concentrated solution.

Thus the forces between the chains are less in case of nematic resulting in a general greater fluidity, but nematic LC in comparison with smectic structures in comparison with smectic structures. If the mesogens are oriented parallel to one another, but the directions vary from one layer to another then the liquid crystalline is termed as cholesteric as I was telling.

Suppose, this is a plane of polymer molecules where polymer molecules are aligned in this way mesogens are also aligned in this way. Now, a plane bend it this plane contains again this polymer where the mesogens, if they are not aligned in the same directions we will get different liquid crystalline beavers. So, mesogens are oriented parallel to one another, but the directions vary from one layer to another the LC structure is termed as cholesteric that means for multi layered configurations we can get the smectic structures more common for polymers is the nematic one.

This smectic state is rare and has been observed only for Thermotropic polymers by melting only aromide polyamides as I show aromatic polyamides are amides say cable of fibre. Which is used for making for bullet proof jackets bullet proof jackets that means it has capability of absorbing huge impact without failure, that property comes from there molecular arrangements, from where it comes?

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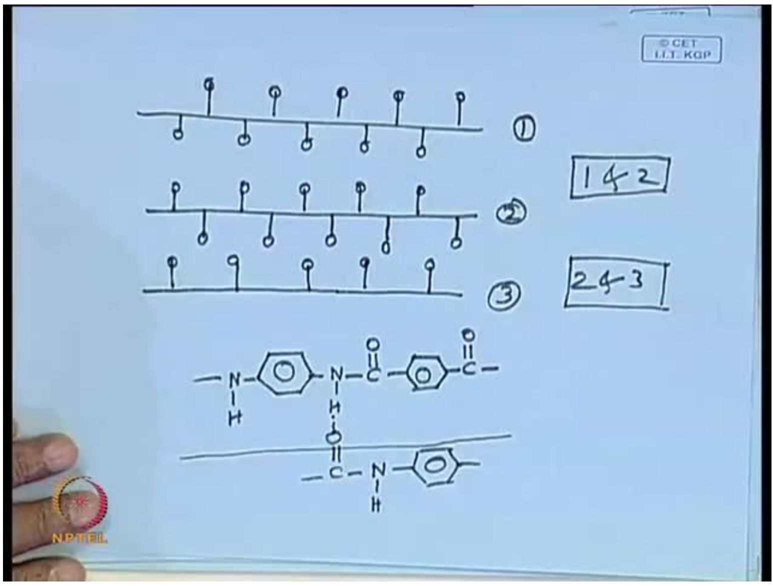

Now, this cabular fibre you see, I think you remember formula of this cabular fibre aromatic polyamide NHCO. So, it is made from (( )) and penitence, am I right? Now, here you see now this nitrogen is hydrogen is connected to nitrogen now, this hydrogen can enter into hydrogen bounding with on oxygen of a neighbouring molecule. That, means if the molecules are placed in such a way thus that one oxygen comes just below this hydrogen of another molecule.

So, it can set hydrogen bonds and the distance is maintained. So, next to this thing it will have say nitrogen over here so this way it can set the intermolecular hydrogen bonds so this way it shows liquid crystalline characteristics. So, this Aromatic polyamides or aromide form a nematic LC state in concentrated solution, considered a solution in paracrystal or metacrystal or concentrated sulphuric acid or in dymethyl acitamite or in dymethyle thermometry or just the solvents for this aromatic aramid fibre cabular.

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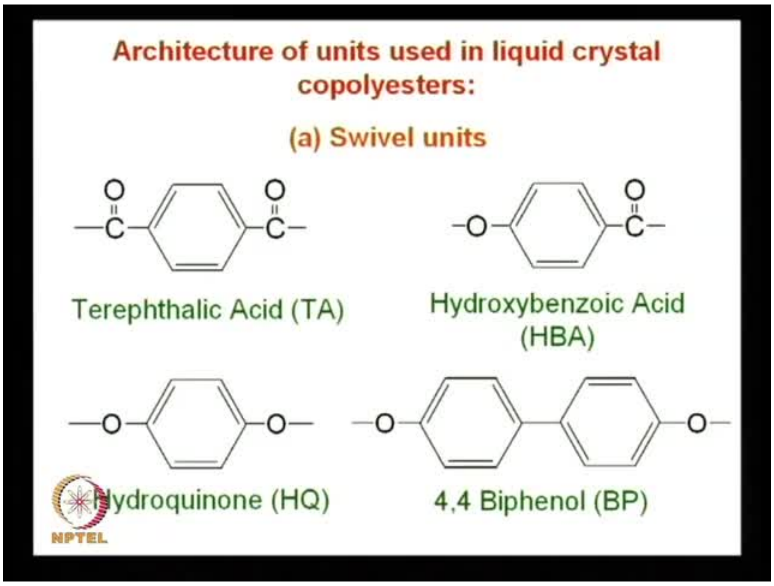
Architecture of units used in liquid crystal copolyesters:

(a) Swivel units

Now let us see the Architecture of units that means this estrogenic unit used in founding used in developing or designing this liquid crystal polyester.

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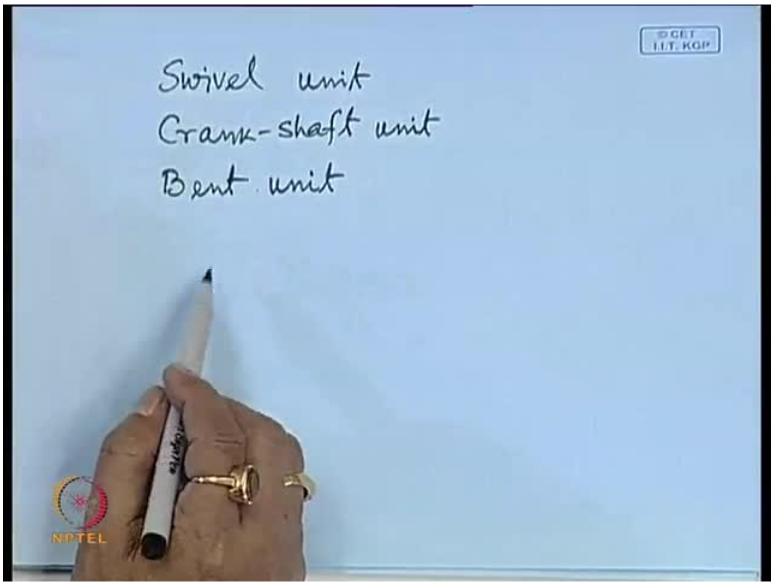
Swivel unit
Crank-shaft unit
Bent unit

So, there are swivel units crank shaft units Bent units these all are mechanical models, Swivel, crank shaft, bent these are all mechanical models. Do you have any idea of crank shaft? Have you seen any crank shaft? Circular motion transform circular motion to linear motion that is done by the crank shaft or the vice versa. Crank shaft now, you see how it looks crank swivel units you see this Terephthalic acid you know this

Terephthalic OH, OH is there, this residue from Terephthalic, this from Hydroxybenzoic acid, this side group oh group h Hydroxybenzoic Hydroquinone, Hydroquinone O, O and 4,4 Biphenol 4, 4 Biphenol. Now, if this units are present in the polymer then they can get the liquid crystalline behaviour why you see this is actually at one port linkage Para, Para linkage so this can provide more molecular symmetry as you have seen in case of this cabular here you see Para parallel linkage, but you can have linkage like this.

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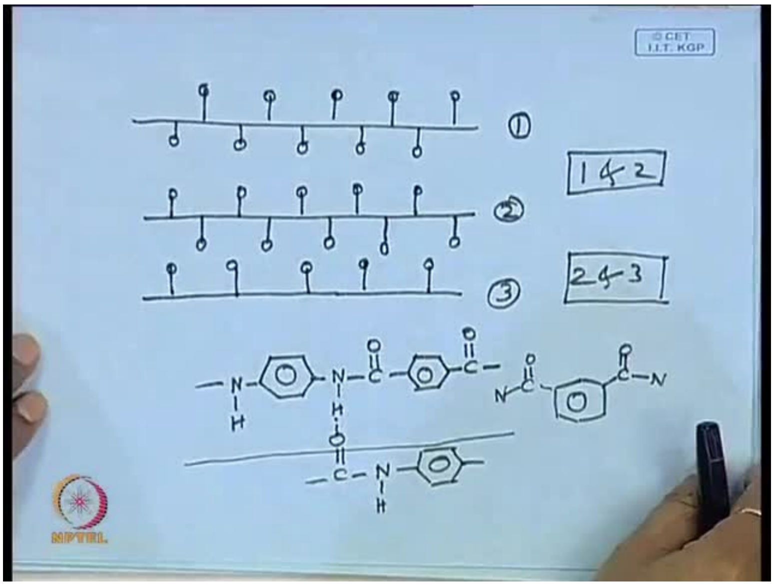

This is less symmetric than this one because this is two five linkage, two five linkage whereas, this is one four linkage. So, one four linkage in benzene can provide maximum molecule symmetry linear molecular configuration available from one four linkage. So, in both this cases we find in all these cases we find one ford linkage so linear molecular structures can be available from this kinds of units these are known as swivel units. So, if this architectural units are incorporated in polymer backbone chain structures we can get very good crystalline behaviour in melt or in solution.

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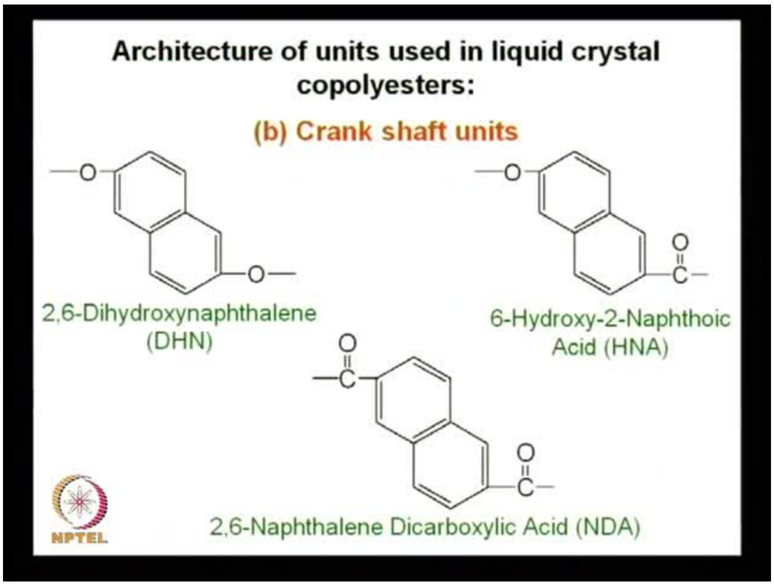

Architecture of units used in liquid crystal copolyesters:

(b) Crank shaft units

2,6-Dihydroxynaphthalene (DHN)

6-Hydroxy-2-Naphthoic Acid (HNA)

2,6-Naphthalene Dicarboxylic Acid (NDA)

Look at crank shaft unit you see here is the linkage site and another linkage site is here so two phenol linkers are fused over here say xynaphthalene so here it is 2, 6 Dihydroxynaphthalene 6 hydroxyl 2 Naphthoic acid. So, here you see Dihydroxy hydroxyl acid in previous case it is you saw dicarbonicoxide acid hydroxyl acid or Biphenol or hydroquinone, same thing you see melting point here the solubility all the properties will be radically changed if you from one architecture to architecture. In the previous case you see these are the architecture, but the groups are same carboxyl group Hydroxybenzoic acid hydroquinone or Biphenol.

Having the same groups, but with other designs it gives you the crank shaft units it actually disturbs molecular symmetry affects molecular symmetry. So, if you have molecules continuing that one four linkage Para parallel linkage there you will have maximum symmetry, higher temperature, higher viscosity, higher melting temperature causing certain problems in processing then you can incorporate in few places such units shows melting points will be decreased you will see later.

Yes please.

(( ))

What is the problem?

(( ))

Cabular is a crystalline polymer it forms the symmetric structure. Why? If you critically examine critically just try to practice on your notebook write the formula of this tabular polymer, then you have to another polymer try to get this oxygen atoms closed to the hydrogen in.

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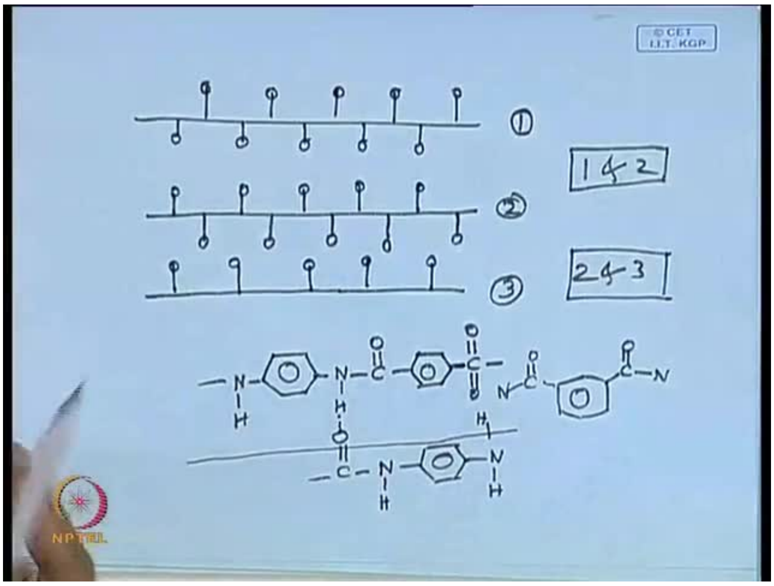

The next unit you will have hydrogen this side or this side so this is aligned this way that is also possible, then you can get more of liquid crystalline behaviour that to Nematic one, because it is not always possible that you will get the orientation of the oxygen or it will remain same this side or hydrogen will remain this side you understand?

So, it will affect alignment of the mesogens, alignments of the mesogens parallel to each other alignment of the mesogens parallel to each other, if such alignment is available then you can get melting structure it is not available you will get Nematic structure you understand because of that reason, there is some rotational flexibility is available. Here we do not know what configuration rotation it will provide in that temperatures that will dictate to the extent of Nematic phase you understand.

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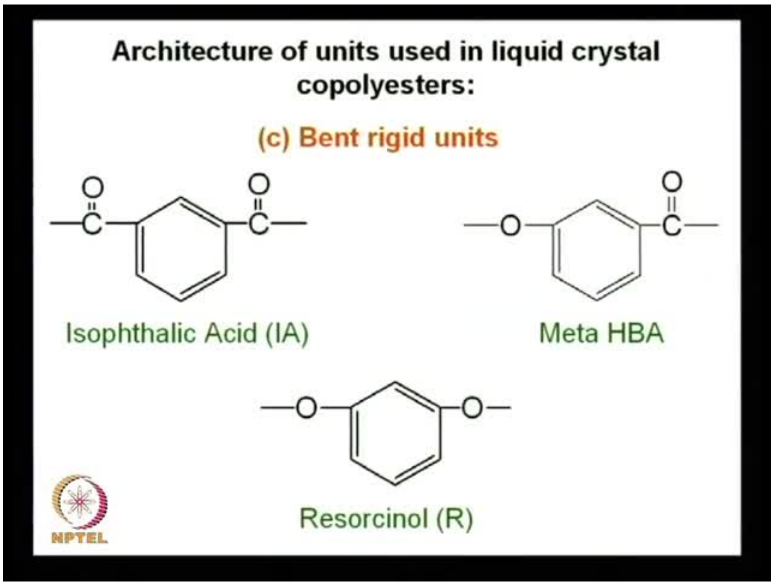

Architecture of units used in liquid crystal copolyesters:

(c) Bent rigid units

Isophthalic Acid (IA)

Meta HBA

Resorcinol (R)

So, this is crank shaft unit, then bent rigid units here you see two five positions again same group units that is resorcinol OH,OH same group, but where they are linked to the benzene link that dictates, where it will give you high melting properties or low melting properties. So, in order to get a liquid crystalline polymer you have to take the design first make a molecular design. Then you find out the reactants with such designs, then you mix this those reactants then carry out the polymerization you will get the polymers as for as you desired.

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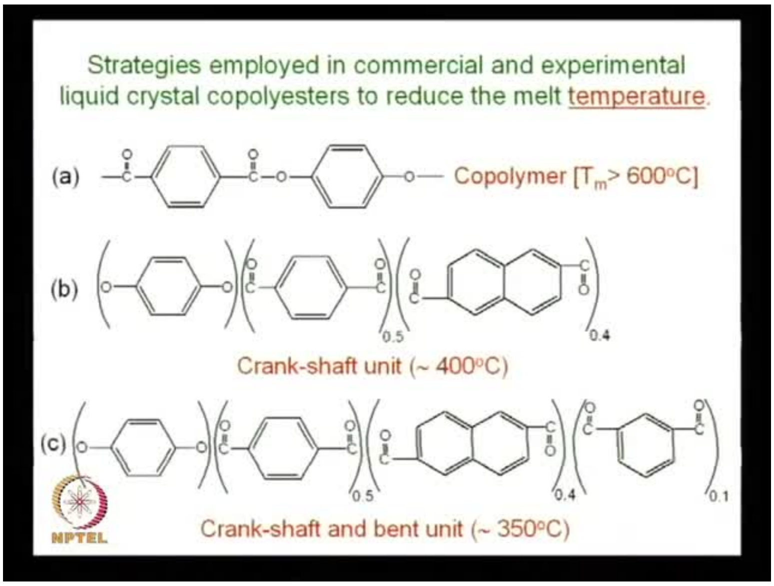

Strategies employed in commercial and experimental liquid crystal copolyesters to reduce the melt temperature.

(a) Copolymer [T_m> 600°C]

(b) Crank-shaft unit (~ 400°C)

(c) Crank-shaft and bent unit (~ 350°C)

Now, same concept will be clarified if you look into the slide strategies employed in commercial and experimental liquid crystal copolymers reduce the melt temperature. Now, you see here this is a polyester made from Terephthalic acid and say one four. It forms a polyester because of this molecular symmetry one four link age melting point is higher than 600 degree Celsius. And that too you have to it will heat this polymer in inner atmosphere either in nitrogen helium or organ.

Otherwise, if you try to melt this polymer exposed to air it will degrade compose prior to melting, that means you cannot visualized its melting phenomena in order to get this visualization melting phenomena you have to heat this polymer under inner atmosphere and that is again higher than 600 degree Celsius. So, you see why here you can get again this correlation between molecular structures with its properties, its melting point is a property how the melting point is related to its structure you can understand this again related to molecular order, that means it will give you more packing as well as the backbone chains contains rigid phenol ring.

You have seen in case of polystyrene that rigid phenol ring remains as a pendent group, where this phenyl group is present along the backbone chain shows polystyrene melts 120, 130 degree Celsius temperature. Whereas, this polymer higher than 600 degree Celsius temperature and the reason you understand, clear? Then look at this polymer now here now here these two units are kept over here in order to decrease the melting temperature of this polymer certain percentage of this unit this is a, what is this unit? This is a crank shaft unit this one. Some, crank shaft unit is placed over here, this is 0.5, this is 0.4, this is 0.1. Anyway this ratio is dictated that means you have to select this monomers select this compounds with suitable proportions.

So that quantities will dictate regulate the melting temperature because this two will provide molecular symmetry that is that will take this molecule towards structures. Whereas, this will disturb this crystalline because of this linkage, crank shaft linkage, why due to the inclusion of this 0.4 percent only say its melting temperature decreases from 600 to 400 degrees, so that is at your hand, so you can here lies the tailor ability of such polymers.

You can tailor, tailor the melting temperature of such polymers by introducing small quantity of this monomer or this reactant further you see the temperature can reduce from decrease from 400 to 350. If you incorporate these, units are kept this is also kept and again little bit of this soluble unit little bit of swivel units sorry bent units this bent unit is actually further reduce this temperature to 350 degrees.

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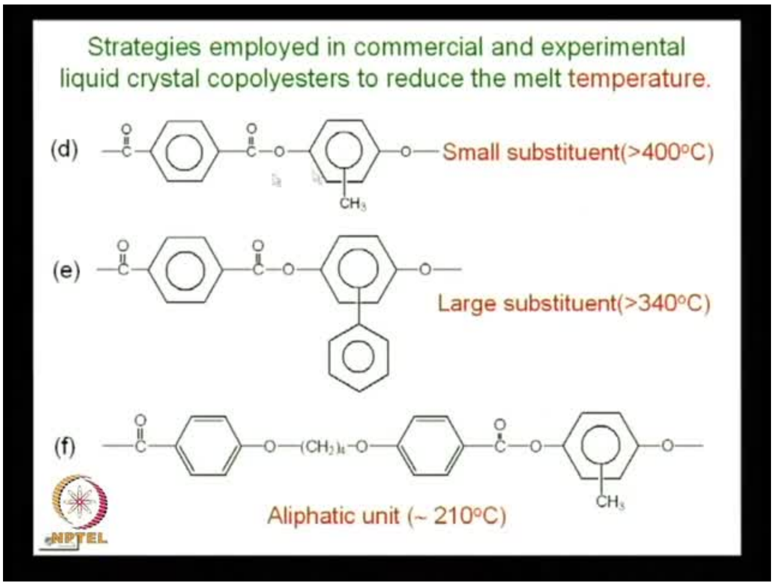

Strategies employed in commercial and experimental liquid crystal copolyesters to reduce the melt temperature.

(d) Small substituent(>400°C)

(e) Large substituent(>340°C)

(f) Aliphatic unit (~ 210°C)

Again substitutions this methyl, substitutions that can be anywhere here, here, here, here that substitutions further same the first structure this one, when any of these two rings are substitutory having ethyle substitutions. Then the temperature has come down from 600 to 400 degrees. so this is again another strategy either introducing other architecture units or you put a substitution include a substitution that is further decreased the temperature melting temperature, when the volume of the substituent is melt bigger from methyl to phenol it is come down from 400 to 340 degrees.

Then flexible units here you incorporate flexible units say four methylene unit's temperature is come down from 600 to 210. So, this show you can tailor this molecular structure tailor the properties of polymer molecular by molecular design you have the flexibility of polymer synthesis due to the presence of this functional group, this functional group will react, but the unit two is this function groups they are not reacting, but they are adjusting or controlling or regulating their melting temperature or the solubility also.

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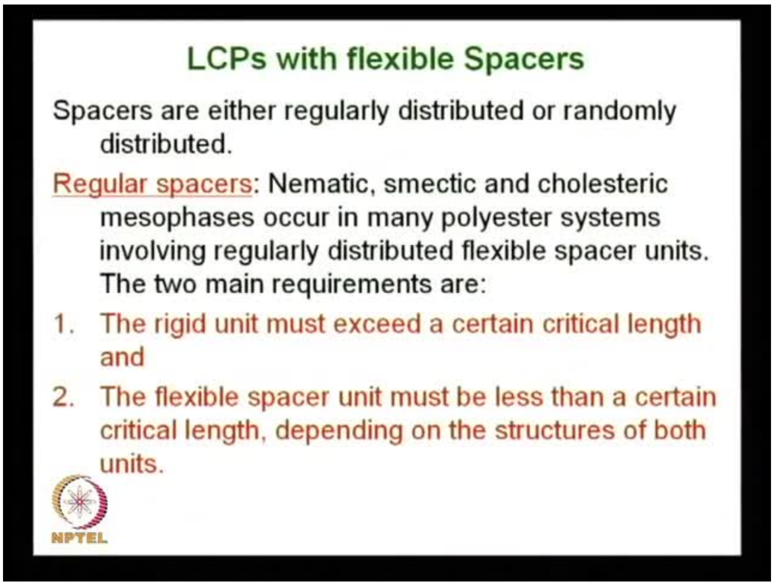

LCPs with flexible Spacers

Spacers are either regularly distributed or randomly distributed.

Regular spacers: Nematic, smectic and cholesteric mesophases occur in many polyester systems involving regularly distributed flexible spacer units. The two main requirements are:

1. The rigid unit must exceed a certain critical length and
2. The flexible spacer unit must be less than a certain critical length, depending on the structures of both units.

LCPs with flexible Spacers as I showed spacers are either regularly distributed or randomly distributed spacers means some unit place between, these two rigid units that is called spacers if that is flexible. So, that will decrease the melting temperature say compare poly butylenes teetered with polyethylene (( )) in place of ethylene you have aided buntline, which means in place of two carbons two ethylene units you have placed four methelene units melting temperature comes down flexibility increases same concept was here. You put your time devote your time I think the concept will be clear.

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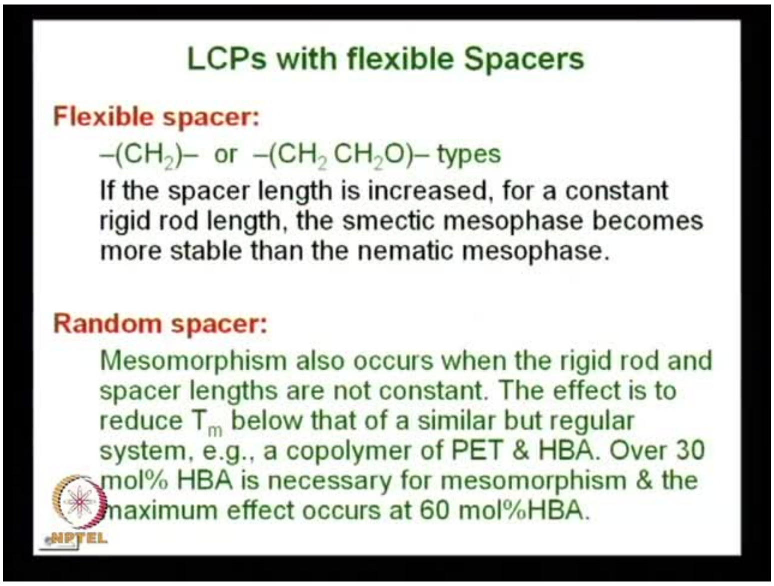

LCPs with flexible Spacers

Flexible spacer:

$-(CH_2)-$ or $-(CH_2CH_2O)-$ types

If the spacer length is increased, for a constant rigid rod length, the smectic mesophase becomes more stable than the nematic mesophase.

Random spacer:

Mesomorphism also occurs when the rigid rod and spacer lengths are not constant. The effect is to reduce T_m below that of a similar but regular system, e.g., a copolymer of PET & HBA. Over 30 mol% HBA is necessary for mesomorphism & the maximum effect occurs at 60 mol%HBA.

These are the flexible spacer units CH 2, CH 2 CH 2 O polyethylene glycol like that, or other units PEY and HBA. Hydroxide benzoic acid like that etcetera this way you can change, what I want to show you actually.

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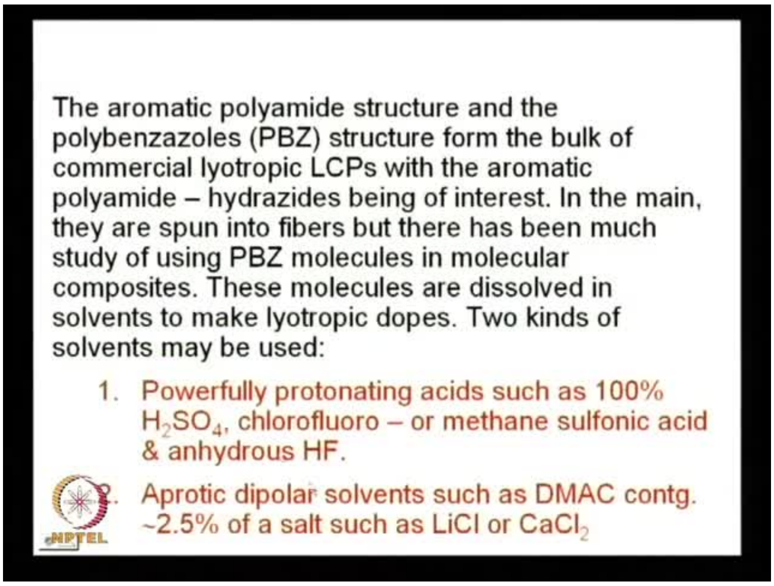

The aromatic polyamide structure and the polybenzazoles (PBZ) structure form the bulk of commercial lyotropic LCPs with the aromatic polyamide – hydrazides being of interest. In the main, they are spun into fibers but there has been much study of using PBZ molecules in molecular composites. These molecules are dissolved in solvents to make lyotropic dopes. Two kinds of solvents may be used:

1. Powerfully protonating acids such as 100% H_2SO_4, chlorofluoro – or methane sulfonic acid & anhydrous HF.
2. Aprotic dipolar solvents such as DMAC contg. ~2.5% of a salt such as LiCl or $CaCl_2$

The aromatic polyamide structure and the polybenzazoles structures form the bulk of commercial Lyotropic LCPs. Solution phases the liquid crystalline polymers, with the aromatic polyamide hydrazides being of interest. In the main they are span into fibres, but there has been much study of using polybenzazoles in molecules' in molecular composites molecular composites, these molecules are dissolved in solvents to make Lyotropic dopes. Dopes means solution is called as dopes if you put something high viscous system is called as dopes, two kinds of solvents may be used look at the solvent concentrated hydrochloric acid or chlorofluoro or methane sulpfonic acid or unhydraze hydrogen fluorides see very critical solvents very strong harsh solvents.

Aprotic dipolar solvents such as dymethaleacitemite containing 2.5 percent of salt to increase the polarity actually these materials fluoride or calcium fluoride, they increase the polarity of the solvents sometimes. When a solvent is unable to dissolve the solute, then you add certain electrolytes there it will increase the polarity of the solvents that will easily dissolve the solvents. What I want to show look at here.

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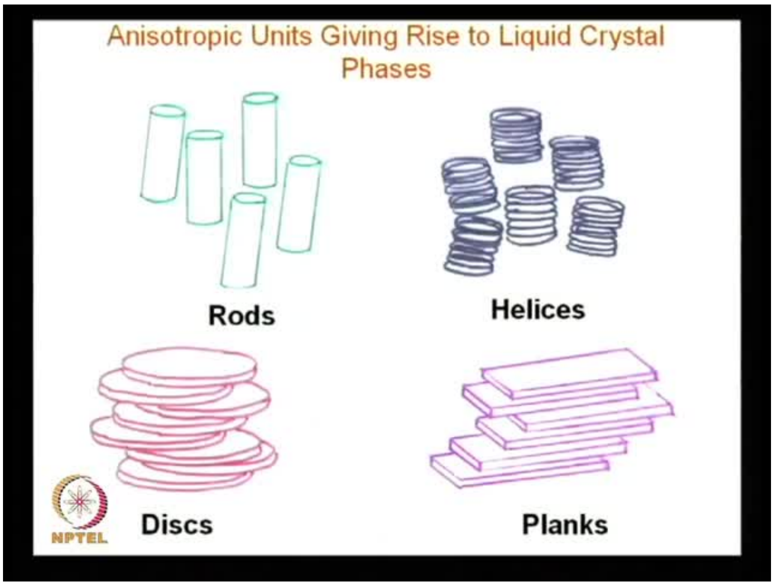

Anisotropic Units Giving Rise to Liquid Crystal Phases

Anisotropic units giving rise to liquid crystalline phases, anisotropic units which may be rod like shape, helical shape, plank type shape molecular assembly like this, which will present in polymer backbone may be rod like shapes helices, helical shapes or disc shapes or plank type shapes molecular assembly, will be like this in helical rod like disc or planks. So, that gives you the liquid crystalline behaviour.

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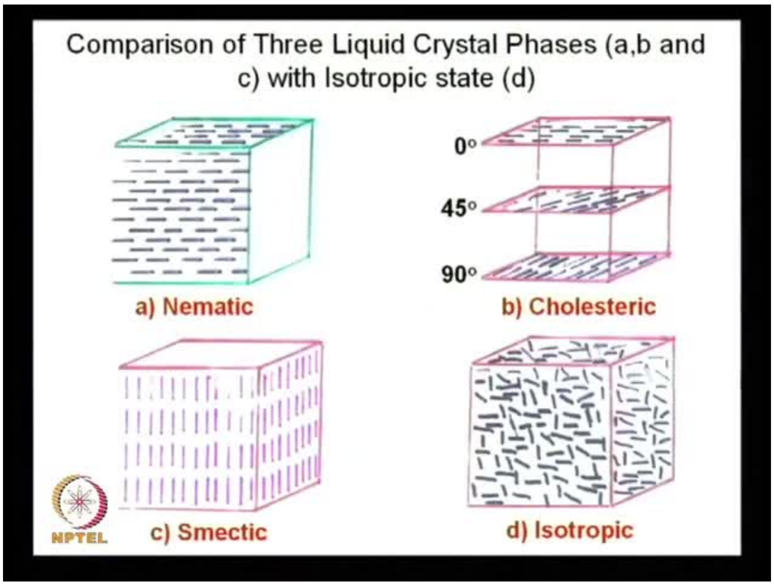

Comparison of Three Liquid Crystal Phases (a,b and c) with Isotropic state (d)

Now, you see comparison of three liquid crystalline phases Nematic, Smectic, Cholesteric and isotropic. Isotropic means these are the units they are oriented in random directions there is no fixed directions, that is why this is isotropic, but when these are arranged like this ha they are parallel, but the mesogens are not closed to each other in the parallel lines parallel molecules they are called Nematic. The interactions between these mesogen units are less, but when they are arranged parallel mesogens are arranged parallel looks like this smectic.

Now, as I told that if you have layer like structures like this one layer alignment is in this directions another alignment is in this direction, another alignment is in this direction, so this is called cholesteric. And you can consider this kind of cholesteric, and you consider this type of as molecular composites. Molecular composites you understand molecular composites, where there will be some in a dispersive medium which is continue sly metric alright. So, you can consider this as molecular laminates, so if we can develop some sophisticated of polymer synthesis, we can synthesise molecular laminates with cholesteric liquid crystalline phase structures configurations and those can provide the high performance properties.

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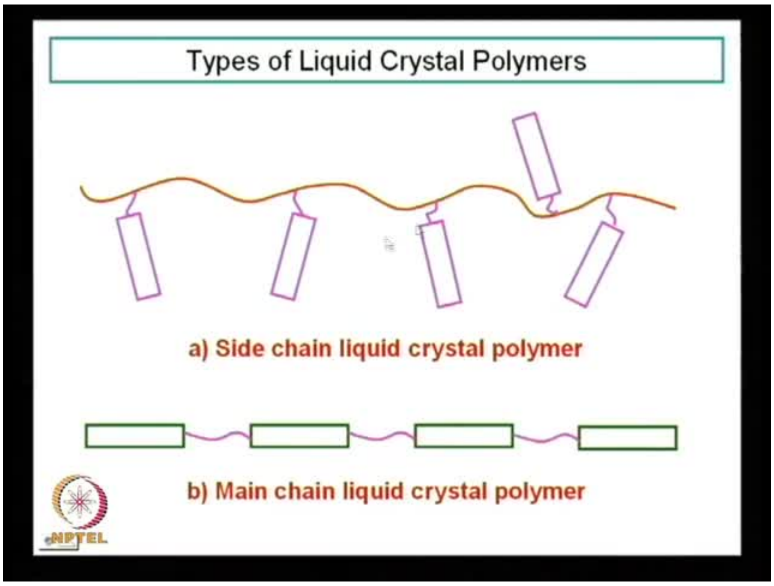

Types of Liquid Crystal Polymers

a) Side chain liquid crystal polymer

b) Main chain liquid crystal polymer

Types of liquid crystalline polymers again, they are mesogens as I show you the side chain liquid crystal polymers, that means liquid crystalline is contributed by the this mesogens at us to side chains by side chains whereas, there is no contribution from main backbone chain. Main chain liquid crystal polymers here crystalline are in main chain commercially available thermotropic liquid crystalline polymers vectra copolysters, xyder terpolymers look at these things structures.

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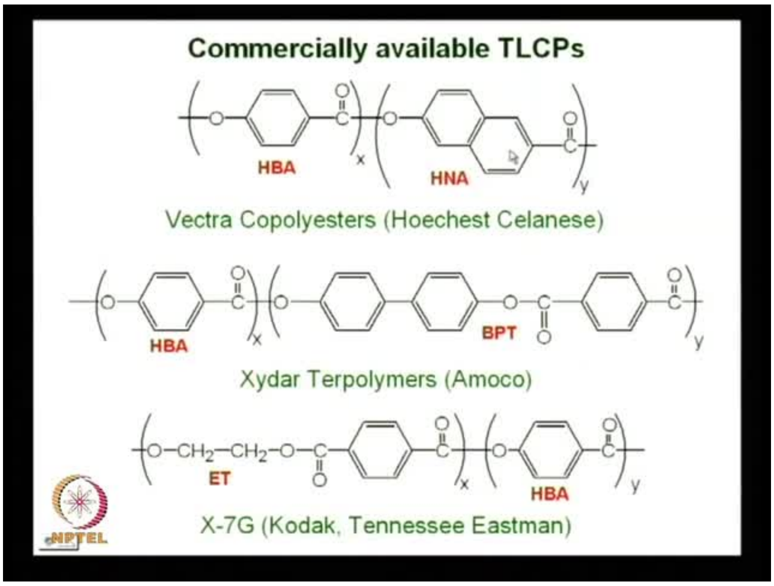

Commercially available TLCPs

Vectra Copolyesters (Hoechest Celanese)

Xydar Terpolymers (Amoco)

X-7G (Kodak, Tennessee Eastman)

Commercially available liquid crystalline polymers people are using developing this newer. And newer polymer blends using small percentage of such commercial LCPs with polyethylene high density polyethylene or polyesters or even polycarbonates, they are taking this 5 to 10 percent of this LCPs thermotropic liquid crystalline polymers commercially available liquid crystalline polymers with polyethylene polycarbonate or polyamides etcetera and they are getting much higher level of properties for high performance applications.

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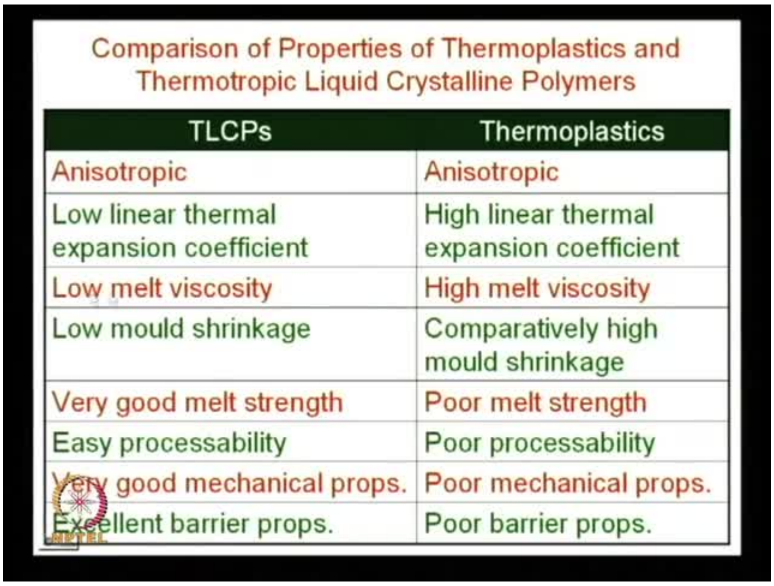

Comparison of Properties of Thermoplastics and Thermotropic Liquid Crystalline Polymers

TLCPs	Thermoplastics
Anisotropic	Anisotropic
Low linear thermal expansion coefficient	High linear thermal expansion coefficient
Low melt viscosity	High melt viscosity
Low mould shrinkage	Comparatively high mould shrinkage
Very good melt strength	Poor melt strength
Easy processability	Poor processability
Very good mechanical props.	Poor mechanical props.
Excellent barrier props.	Poor barrier props.

These are the comparison of properties please read I have already discussed these properties not difficult to understand these are the properties in tabular form.

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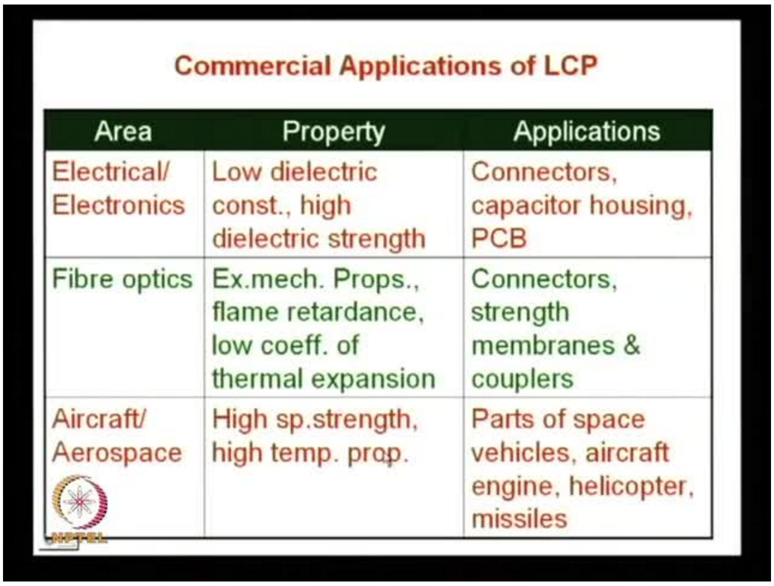

Commercial Applications of LCP

Area	Property	Applications
Electrical/ Electronics	Low dielectric const., high dielectric strength	Connectors, capacitor housing, PCB
Fibre optics	Ex.mech. Props., flame retardance, low coeff. of thermal expansion	Connectors, strength membranes & couplers
Aircraft/ Aerospace	High sp.strength, high temp. prop.	Parts of space vehicles, aircraft engine, helicopter, missiles

And look at the applications electrical or electric applications or fibre optic applications aircraft applications, aerospace applications as well as.

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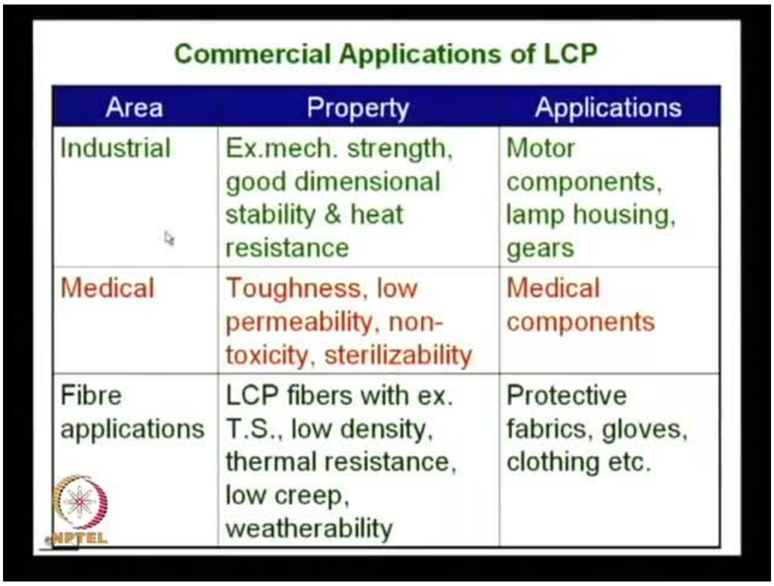

Commercial Applications of LCP

Area	Property	Applications
Industrial	Ex.mech. strength, good dimensional stability & heat resistance	Motor components, lamp housing, gears
Medical	Toughness, low permeability, non-toxicity, sterilizability	Medical components
Fibre applications	LCP fibers with ex. T.S., low density, thermal resistance, low creep, weatherability	Protective fabrics, gloves, clothing etc.

Industrial applications, medical applications, fibre applications excreta and again, this other way applications are soon over here. So, even for biometrical applications these liquid crystalline polymers today find major contributions there. And motor components lamp housing, missal activators also artificial missal activators, they are made from this liquid crystalline polymers. Electrical applications connector’s capacitors housing pump circuit board connector’s strength membranes and couplers and aircrafts parts of space vehicles aircraft engine helicopter missiles so and so.

Thank you, very much.