# Fundamentals and Applications of Supramolecular Chemistry

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**Lecture 49**

W10L49_Liquid Crystals-Types, Structure and Phase transitions in Liquid Crystals

So, hello everybody, today we are going to discuss an interesting class of systems which we refer to as liquid crystals. So, in the previous lectures, we have looked at the order that prevails in the liquid state, and for example, we have different kinds of structures that are present in solution.

For example, micelles, reverse micelles, lamellar phases, bilayers, vesicles, and inverse vesicles are all part of the interesting array of species that exist in the solution. And we have also looked at the solid state, which is the crystalline state.

Now, in between the solid state and the liquid state exists a liquid crystal-like state, which is neither completely like liquid, where the orientation of the molecules is quite random, nor that of a solid, where it is completely frozen. So, crystals are characterized by long-range orientational order, as well as long-range translational periodicity.

So, isotropic liquids have short-range ordering; there are some interactions between the molecules that actually keep them in an ordered state, but by and large, the thermal energy fluctuations are also present, allowing the molecules to rotate and translate in the liquid state.

And in between these highly disordered and ordered states exists a state where you do not have the long-range translational periodicity, like that of crystals, but you also do not have a complete lack of order.

So, there is order, there is orientational order to a certain extent, and that is where this state is referred to as a mesogenic state or also referred to as a liquid crystalline state. So, today we are going to talk about the properties of this particular state of matter, which we call liquid crystals, from a covalent as well as a non-covalent perspective.

So, if you look at this particular diagram, it essentially discusses the existence of different liquid crystalline states or phases as a function of temperature. Here, you can see the different phases that are formed as a function of temperature.

The liquid crystals, to start with, can be broadly classified as thermotropic crystals, and under the thermotropic crystals, we have the calamitic and discotic crystals. When we now go further, the calamitic crystals exist in the nematic phase, smectic phase, and cholesteric phase, and when you further increase the temperature, they eventually convert into a liquid melt, which has a more isotropic nature. That means it exists as an isotropic solution, and there is a certain temperature called the clearing point at which the liquid crystalline phase has completely converted into the isotropic liquid-like state.

And, in between this initial configuration, which is the frozen configuration, the solid, and the final clearing point, there exists a state, which is the anisotropic liquid state, where you have some degree of orientational order that we can refer to as the liquid crystalline state.

Now, we will look at some interesting examples of these kinds of liquid crystals. First, we will talk about the liquid crystals, which represent an intermediate state between solids and liquids. It has been observed that generally the molecules that form liquid crystals, with molecular shape being a very important factor. These kinds of molecules that exhibit liquid crystal-like behavior are referred to as mesogens or mesogenic substances.

So, to start with, the molecular shape is a very important factor, and they can either exist as long cylindrical shapes, that is, rod-like, or they can exist in flat, circular disk-shaped molecules as well. For example, let us look at a couple of examples.

So, if you look at compounds 1 and 2, you can see that they tend to form long cylindrical-like structures. So, these have a long cylindrical-like geometry, and in this case, you can see this is a phenyl, this is a biphenyl, there is a cyano electron-withdrawing group, and there is an electron-donating hydrophobic chain. Here, in this case of 2, we have the cholesterol moiety, the ester, and the long hydrophobic chain C8H17.

So, these refer to the long cylindrical rod-like molecules. Similarly, we can have flat disc-like molecules. For example, we can look at this hexahost where every hydrogen is replaced with the corresponding ethynyl, phenyl, and C8H17 moieties.

So, this forms a circular, flat disk-like molecule, and this is a pure organic compound. In the case of example 4, we can see that it is a copper-coordinated complex, coordinated with 4 oxygen atoms, which again forms a tightly packed geometry where you can see the planarity that exists here, and then this tends to form rod-like molecules.

So, these are different examples of cylindrical and dish-shaped molecules. Now, what are the properties of these molecules? As you can see, when the liquid crystals are formed, there tend to be intermolecular interactions between the molecules.

So, you can have these rod-like molecules, and these rod-like molecules or the cylindrical entities can now arrange in different ways. So, we can have these cylindrical entities that actually stick to each other sideways, or they can stick to each other with some lateral displacement, and they tend to form very different kinds of arrangements.

And the nature of interactions that hold these cylindrical-like entities is very, very weak interactions; mostly, these are hydrophobic interactions, and these cylindrical-like entities can actually glide or slide over each other easily with a little bit of energy.

So, that is what gives the liquid crystal its liquid-like behavior, and another competing factor is the thermal energy of the system, which is the temperature of the system. If the temperature of the system is very high, then we know that these molecules can actually disengage from the other molecules because the non-covalent interactions are very weak.

They can break these non-covalent interactions and then start swimming around in the bulk because that is the tendency of these liquid-like molecules to actually undergo dynamic disorder-like motion in the liquid state. So, temperature is very important. If you increase the temperature of the system, then these intermolecular interactions slowly break and weaken the system.

It first transitions more into the liquid state and forms an anisotropic liquid state. And finally, when the thermal energy of the system is high, the intermolecular interactions between the molecules practically do not exist, and the molecules are free to move around in the bulk medium. They form an isotropic liquid melt. So, it is important to keep in mind the nature of these liquid crystals. So, the first thing we talked about is the anisotropic shape of these mesogens.

The second thing to keep in mind is that dust particles and surface homogeneities can affect the orientation of these molecules. They are actually visualized using a polarizing microscope; when you pass plane-polarized light through the liquid crystal specimen, the arrangement of the liquid crystals in different orientations allows you to see suitably bright and dark regions with appropriate extinctions, depending on the light that reaches the analyzer.

So, we can analyze these liquid crystal-like states using a polarizing microscope. The fourth thing, as I told you, is that the domains get deformed very easily, and hence the formation of liquid crystals is sensitive to temperature. Fifth, the formation of these liquid crystals normally occurs above the melting point of the substance, but the temperature should still be low enough that the molecular motion is fairly restricted and the energies of the intermolecular interactions are strong compared to the thermal energies.

So, the liquid crystal formation is characterized by reduced molecular motion, so that there exists an overall long-range orientational order within the molecules. They exist in orientational order, with long-range interactions between the molecules, and the intermolecular interactions are greater than the thermal energies; this is important.

So, when you increase the temperature, it leads to more rapid motion of one molecule with respect to its neighbors and eventually leads to the formation of the isotropic liquid. We also now see that the different phases that exist are as follows. So, to start with, let us take this rod-like molecule.

So, this state we can see is the solid state, this is the liquid state, and this is the liquid crystal state. So, in the case of solids, as I told you, these have both long-range orientational ordering. and translational order.

In the liquid state, there is no order, whereas in the liquid crystal state, you will see that there is a change in the orientation of the molecules; they have adopted slightly distorted or disordered orientations, but overall, if you look along a particular direction, there exists long-range orientational order, although the long-range translational order is missing.

And it is with respect to this particular direction that we call the direction along which the molecules (mesogens) are ordered, along the same direction, and is a direction along which the slippage of molecules can take place along the rod-like axis.

This is what gives the nematic phase its high degree of fluidity. So, the high degree of fluidity exists in the nematic phase, and this is also the least ordered of all calamitic phases and is the last to occur before isotropic melting. Then, compared to the smectic phases, these represent a high degree of order.

So, here you can see that these were the nematic phases, where you can see the cylindrical-like arrangement of the molecules along a particular direction. But in the case of smectic, you will see that they first form these tubes along one direction, and then they stack along another direction.

So, this gives rise to a 2D structure in the case of the smectic phases. There is a high degree of order in the case of smectic phases, and these are 2D layer arrangements. Again, the interactions exist between the layers, and the molecules can easily slip past each other. So, this is what is interesting: slippage exists between the molecules.

Now, overall, what has been observed is that these smectic phases are actually obtained by slight changes in the orientation of the molecules, which impact the liquid crystal state.

And it has been observed that 12 different phases exist. Just like in solids, we have different phases; in the liquid crystal state, we can also have different liquid crystalline phases, which have been observed and are labeled as SA to SL, A, B, C, D, E, F, G, H, I, J, K, L, and the most ordered state has the highest viscosity for the most ordered structure.

So, for example, let us take this particular compound that undergoes three phase transitions; you can see that as the length increases, it tends to develop some curvature. So, we start say from A, it melts at 24 degrees centigrade, with an enthalpy change of 25.5 kJ/mole, to give rise to the smectic A phase, and then at 39 degrees centigrade, it converts to the nematic phase.

The enthalpy change is extremely small, 0.13 kJ/mol, and then finally, it converts to the liquid state by decomposition. So, it decomposes to an isotropic melt at 42.6 degrees Celsius.

The enthalpy change is 0.976 kJ/mol. So, these are very sensitive, subtle phase transitions, which take place when one phase converts into the other, and the energy change associated with this process is also small.

Overall, the temperature range over which these phases exist is also very narrow. Then we can now see. The next classification, which is referred to as the cholesteric kind of crystals, shows a cylindrical rod-shaped molecule, and the next molecule is below this, but in a slightly tilted orientation.

Then the next one is in a slightly tilted orientation, and the next one is also in a slightly tilted orientation. In this way, the consecutive molecules, which are stacked along a particular direction, have a slightly tilted orientation, and you can see that eventually, when you get to this last molecule here, you can only see the top face of the molecule.

It has a perpendicular orientation compared to the first molecule from which the stacking started. Thus, this arrangement is referred to as a cholesteric arrangement, forming the liquid crystal state. It is essentially characterized as follows: The cholesteric state is a helical pneumatic phase with a helical pitch, and the pitch is 200 to 2000 nanometers in length.

So, we see that they change the orientation with respect to one another, and they essentially form a chiral arrangement. These are chiral/optically active arrangements. This arrangement leads to the optically active state, and why this cholesteric state is very interesting is that the phenomenon of liquid crystals was first observed in 1888 by Friedrich Reinitzer, who was actually a botanist, in acetate and benzoate derivatives of cholesterol, and so these were named cholesterol phases.

Another very interesting property of this chiral phase is that when you increase the concentration, they tend to assemble further with themselves and form interesting phases which we refer to as the blue phase before they convert into the isotropic melt. So, for example, let us take cholesterol nonanoate.

In this case, we have the solid at the melting point of 78.6 degrees; it converts into a cholesteric phase; at 91 degrees centigrade, it forms this blue phase 1. It is in equilibrium; the enthalpy changes by 0.07 kJ/mole, then it goes to 91.3, a very slight change, to the blue phase 2, and finally at 91.45 degrees centigrade it converts into the isotropic melt.

So, these are the cholesteric-like phases, and here the enthalpy changes: 0.53 kilojoules per mole, whereas here it is 0.017 kilojoules per mole for the blue phase 1 and blue phase 2. Then we can go to the discotic phases, and in the case of the discotic phases, what we have is a disc-like molecule, which can actually stack, and the next stacking can also happen in this way.

So, this is the discotic columnar arrangement, and I showed you an example. So, these molecules are circular shaped or flat disc-like molecule, and therefore, they can stack along one direction, primarily held by van der Waals interactions, pi...pi stacking interactions between the functional groups which are responsible for this stacking.

And when you have the stacking along a particular direction, these eventually are very interesting because they can lead to charge transfer. So, you can transfer electrons, when you apply a potential from one direction and you have a stack, you can have now the electronic conduction, the electrons can flow along this particular path, because you have given it the necessary direction. And therefore charge transfer can take place, and this is of relevance in OLEDs, molecular switches and wires.

So, it essentially consists of this periodic arrangement, of these stacks, one on top of each other, and then these stacks can further translate, to form this kind of 2D layer like structures, which correspond to the discotic phase. So, we have looked at the discotic phase, and now coming to the lyotropic phase, in the case of lyotropic liquid crystal phase, these are made up of amphiphiles plus solvent.

The solvent can be water, or then this can be some organic solvent, and therefore we know that in order to form this kind of lyotropic phases. For example, here you can see this is a lyotropic arrangement, this resembles something called a micelle, and therefore there is a certain CMC, which we called a critical micellar concentration, to form this lyotropic phases.

And as you increase the temperature, they eventually melt to give you the isotropic solution. So, the lyotropic phase are characterized by this formation of micelles, about which we have explored, and this also is a case of a liquid crystal state. So, with this background in mind, we can now go and look at some interesting examples of supramolecular liquid crystals, which are actually held by non-covalent interactions.

And again here, there are some prerequisites which are of interest to design this kind of liquid crystalline materials. As I told you, this must be thin, or flat like molecules, and length must be at least 13 angstrom, and to have that, it will be nice if you can have alkyl chains which are present, branching must not take place, branching is not allowed and what you need is anisotropic polarization.

So, that along one particular direction in which you have the formation of these stacking of these molecules, the formation of the hydrogen bonded chains forming this supramolecular liquid like crystal molecules, you will have more polarization in one direction compared to the other directions.

So, we can take examples of these. For example, we can have R, Rx is equal to Cn, Rx is equal to n, then we can have the hydrogen bonded, this is the hydrogen bonded dimer, so we can have these kinds of molecules.

So, first of all we can have this highly anisotropic rigid shape, ok, which can give rise to the formation of LCM's, which we call as the liquid crystal materials and we can also now have these kinds of hydrogen bonded dimers, which can form this long chains. Then we can also modify further.

We can have polar groups to enhance the non-covalent interactions. For example, we can have the bis methoxy substituent. So, we have this oxy azoxybenzene and instead of methoxy we can also have cyano, acid and ester moieties as well.

And we can also have other cases, where we can have further extensive hydrogen bonding. So, we have the carboxylic side, and now we have the nitrogen side, and we can have this hydrogen bond, which forms a mesogen, this is a mesogen and a strong hydrogen bonding which forms a stable rigid arrangement, and it leads to the formation of nematic phases, the melting point is 214 degree centigrade.

So, we have a representation of a supramolecular liquid crystal system, and we can also have other examples as well, where we can have cases where we can actually put side chains, that will lower the melting point of these systems.

So, overall, we have seen that there are many interesting examples and we can also for example, in the end consider halogen bonded system. For example, we can consider pentafluoroiodo compound, this forms a strong halogen bond with this compound.

So, neither of the starting materials A or B are mesogens, but the combination, that is a halogen bonded adduct, gives the smectic A phase, which is formed on cooling the melt, at 84 degree centigrade. So, overall, I hope I have been able to convince you that liquid crystal entities are very interesting.

We have both covalent as well as non-covalent entities which can form liquid crystals and exhibit liquid crystalline state. So, that brings us to a closure of the discussion on liquid crystals. We will now look at another fascinating class of system which are called supramolecular gels in the next lecture.

Thank you.