Instability and Patterning of Thin Polymer Films

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Lecture No. #08

Meso Scale Fabrication Approaches

Hi, hope you have enjoying the course so much. If you remember so far, we have in the previous couple of classes, we talked about the generic nature of instability, we talked about some of the effects of surface tension, we talked about how surface tension exists across a curved surface. And then eventually, we showed how the radius of curvatures of a curved surface sort of lead to instability depending on the scenario. Now, at this point we sort of change gears a little bit, and eventually shift to more on patterning, which I can promise is going to be slightly more simpler as compared to what we have talked today. And next few lectures may be five or six, we will focus more on patterning related issues, and we get started with one of the most important surface patterning techniques, which we have already mentioned in our introduction class is that is photolithography.

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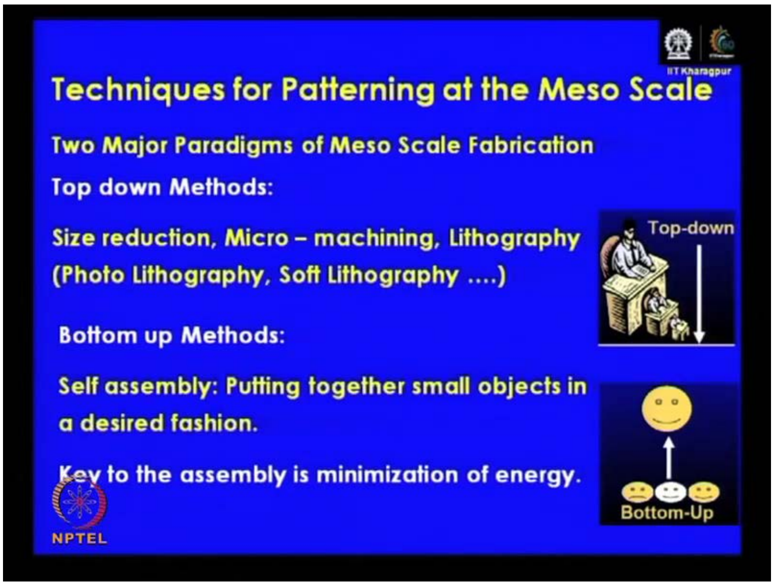

Techniques for Patterning at the Meso Scale

Two Major Paradigms of Meso Scale Fabrication

Top down Methods:

Size reduction, Micro – machining, Lithography (Photo Lithography, Soft Lithography ….)

Bottom up Methods:

Self assembly: Putting together small objects in a desired fashion.

Key to the assembly is minimization of energy.

So essentially, if you are talking about so, pattering you can say we we have talked in the introduction about what patterns are. You sort of have seen these are also some sort of structures which you eventually create on the surface. But when we talk about so called submicron or meso scale, what happens is the patterning technique or the fabrication techniques change. There are whole lot of research, and development that goes on in the area of microelectronic, microfabrication which which has lot of issues, because of several facts that your sample size or the substrate size is different. So, your cutting tool or size of the tools that you need to fabricate them becomes different, your holders become different, many cases manually you cannot do the things you need robot arms and things like that. But apart from that, if you compare microscale, meso scale or nanoscale structure as compared to a bulk; you are essentially talking roughly at a length scale, which is somewhat at the interface of the molecular level things and the macroscopic things.

If you regard that molecule the size of an inorganic molecule is roughly an angstrom; then if you are trying to make something which has width or size of, let us says 10 nanometre. You are essentially talking of hundreds of molecules; may be at best thousands of molecules. As compared to anything, which is macroscopic, which is large which is few centimetre or few metres in size, which essentially talks of billions of molecules. So in principle, it might be possible to sort of built your meso scale structure block by block. And here blocks are essentially the molecules, the basic architectural material for a, for basic building block of any material.

So, what is the classical difference or the standard, I mean the essential difference in the approach. You can, I mean if you are talk in terms of shaping something. What you do? You start off with a job blank, and then you cut it, turn it, use a lathe machine, whatever you want to do to get the desired shape. So, you start off with something, if you want to say make a cylinder of steel or iron or whatever, you will start off with a job blank and then you will sort of do the turning operation; and eventually you will lead to something cylindrical. So, you start off with something which is bigger, and then you hammer it down or size it down your desired shape.

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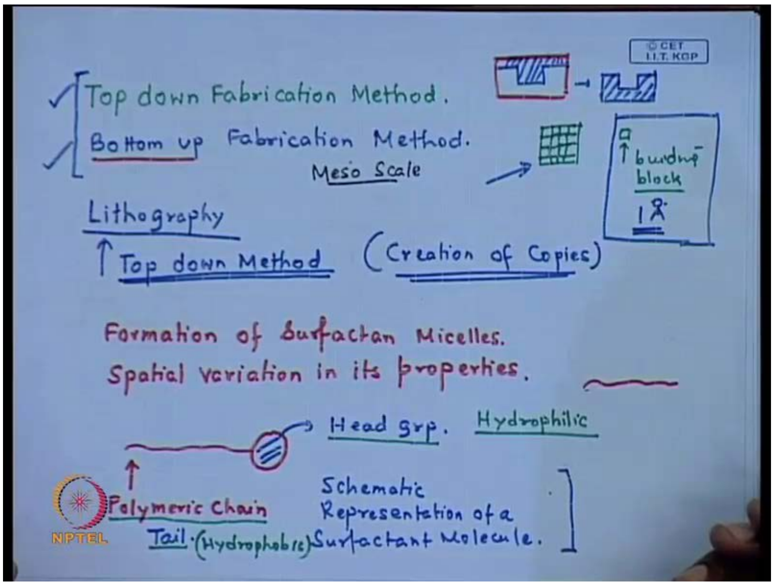

Top down Fabrication Method.

Bottom up Fabrication Method.

Meso Scale

building block

1Å

Lithography

Top down Method (Creation of Copies)

Formation of Surfactan Micelles.

Spatial variation in its properties.

Head grp. Hydrophilic

Polymeric Chain

Tail (Hydrophobic)

Schematic Representation of a Surfactant Molecule.

So, this type of an approach is essentially what is known as the top down fabrication methods. In contrast, if you decide that I want to create something like this. And well, I know that ultimately the constituents of this particular block is molecules, let us say this is one molecules. So, let me do something that I bring in, let us say desired number of 16 molecules or something to make it. So, what you are doing here? Instead of starting off from something which is bigger, which is larger than the you are essentially building block by block. So, this is one essentially building block. And you are fabricating structure, essentially by bringing in different number of molecules, very loosely speaking this is I mean, this is an idea you will sort of immediately understand. So, this type of an approach, you can immediately see is conceptually completely different from the top down fabrication method. And these are what are known as the bottom up fabrication technique or method.

Now, two things you need to understand at this point of time; when you are talking of macroscopic objects, simply because of the size, you just cannot afford to sort of built an entity block by block. Though, human life probably starts building at that way from one zygote cell eventually turns out into an whole human embryo. But if we talk about the inorganic world or the nonliving world, essentially it is very difficult to sort of build something which is very very large by sort of picking up molecules individually. The second issue is that as I told, typically molecule is of the size of an angstrom.

So, your conventional techniques of bringing in something and sort of gathering them together to build something larger, how are you going to bring one molecule? If I want say you make a box of let us say packing box of cardboard to the shape of a rectangular parallelepiped. You bring in a huge cardboard with your hand, you cut it with scissors, you arrange them in perfect order, stitch the edges and you make the box. But then if I tell you that you bring in sixteen molecules and make one face of a nano parallelepiped; the question to ask is how are you going to hold your molecules? In the lab, many of you see that we hold use a small item called a tweezer to hold things and samples; so that they do not get spoiled to your finger prints. But even that is the tip is about a few hundred microns, which is roughly 10 to the power 6 orders, 10 to the power 4 to 5 orders higher than the size of one single molecule. So, well conceptual this is very, very elegant, but there are real issues of how to handle it or how to address it.

They are all fortunately some settings where the molecules themselves sort of arrange into some sort of an order. So, this we people are trying to sort of exploit them as a viable fabrication technique or patterning technique. Now, one of the classicist example of this type of a molecular self assembly or this method is somewhat you know often referred to as the method of self assembly. So, essentially the molecules assemble together to form a desired structure. There lot of research that is going on these issues and eventually, we will see that subsequent part of the course when we talk about instability and associated pattern formation. We will also be eventually talking of something which is not exactly self assembly, but it is very similar the thermodynamically as well as the motive force, its energy minimisation criteria; these things are pretty similar which we will term eventually as self organisation.

Now, the question to ask at this point is what exactly can be self assembled. Though, photolithography is not a self assembly technique or it is not a bottom up fabrication method. Or most of the patterning techniques that are used either in the microelectronic industry or in other segments, with particularly let us say with polymeric materials or other soft materials. Which fall into that category of lithography, I am coming to the origin of this word, what really lithography means. Lithography is definitely a is regarded as top down method, but we will see that whether we can really regard it as top down method or we can sort of classify it into something slightly different as some sort of a creation of copies.

So, a sort of a very simple way to put it would be whether you sort of want to have a distinction between printing out something and Xeroxing something, something like that. So, we will come to that, but before that though I am not going to take up bottom up fabrication in greater detail today. One of the simplest example of bottom up fabrication is the formation of surfactant micelles. We all know that we use soaps and detergents to clean our things, hands, clothes, etcetera etcetera. But and we also many of us probably know that soaps and detergents the basic building block is the surfactant molecules. But I will just take a minute to sort of given you a brief idea, what a surfactant molecule looks like. And then you have already discussed some ideas regarding hydrophobicity and hydrophilicity; so, you will immediately understand what happens.

Well, as compared to other molecules which are sort at the molecular level uniform, chemically uniform I would say; a surfactant molecule is a special class of molecule which has a special variation in its properties. Now this is, please remember that I am giving you an extremely simple view of the, of a surfactant molecule; I am not touching up on the chemistry anybody, who is more interested can look into it. Typically, this is the structure of a surfactant molecule. We know that polymer molecules sometimes have long chains; so, this is a essentially polymeric chain which often is regarded as the tail of the surfactant molecule. And this is in most cases, inorganic head group. Now, based on it, this is the schematic representation I would say of a surfactant molecule, nothing more than that. If you are really interested to find out what surfactant molecules are, I mean please refer to any standard any textbook on related topic. The key thing to understand or which you should understand at this point of time that this head group and this tail group have different wettability or they exhibit different levels of hydrophobicity and hydrophilicity. This head group is traditionally hydrophilic; in contrast the tail is hydrophobic.

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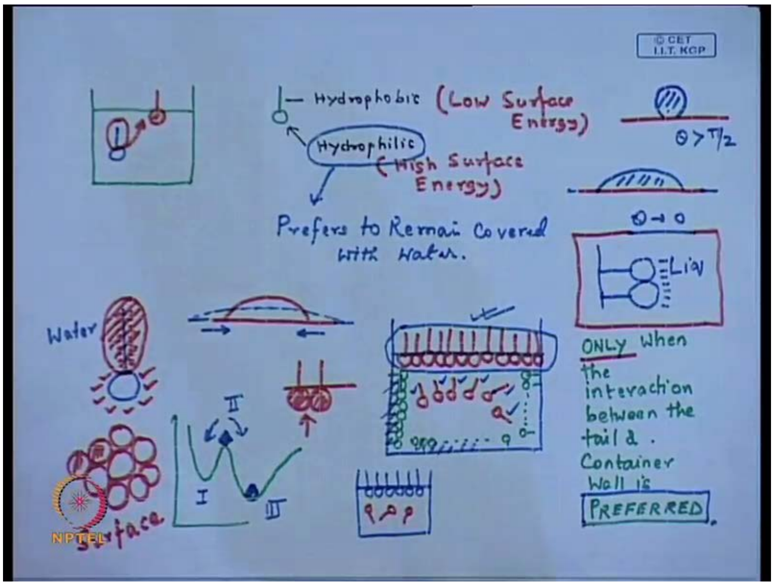

So, what happens is; now, suppose you have a container of water; and you decided decide to add a surfactant molecule to this water. Now, what we know that we just discussed that this part is hydrophilic, and this part is hydrophobic. So, from the discussion we have had so far, you probably know that this part has high surface energy; this part has low surface energy. If you try to remember the configurations we had, corresponding configurations we when we considered the young's equation, this will exhibit a droplet morphology like this, this corresponds to a droplet morphology like this, this corresponds to a droplet morphology like this. Or in other words, if you now consider a surface made up of this material this so called hydrophobic material; a water droplet will try to shrink and theta will be probably higher than pi by 2.

In contrast, a surface made of this material on that water will either preferentially spread. Even if there is a finite theta that will definitely be closed to zero and definitely less than pi by two or may be theta can tend to zero. What does it mean? This means that this surface prefers to remain covered with water. In contrast, this surface does not, it sort of prefers to expose to air remain expose to air rather than getting covered with water. So now, if you force a surfactant molecule lets draw an exaggerated view, let us say this surrounded by water. So, what happens is, these parts of the molecule are not liking the environment they are subjected to. In contrast, this part of the molecule that head group is preferring.

So, this results to something which is known as the hydrophobic repulsion, which we have sort of covered, but we will again cover in greater detail. And this unfavoured situation, thermodynamically unfavoured situation of that tail group sort of allows the molecule or eventually results, in the migration of the molecule to the surface and eventually, it takes a configuration like this. What it means? That your head group sort of remains inside water, where it is thermodynamically favoured; the tail group sort of angles out of the water, it is no longer covered with what water its exposed to air which again is thermodynamically favour . So, now if you see that this motion of the molecule from here, let us say the point at which you injected it right up to the surface of the water is not due to any hydrodynamic flow or any pressure you have applied, but this is again a type of a flow which is triggered by surface tension effects.

Exactly similar to the example we considered that you take a drop on a surface and then you spread it and you see a retraction of the contact light. So, it is the surface energy penalty of the tail part of the of a surfactant molecule in contact with water that sort of results in this particular motion. So, here you see that though this is a very simple example, it happens all the time, you can sort of try to correlate it with lots of things. You see that wherever you add water becomes detergent, if you add some detergent to air water, so it sort of you put it on your hands its sort of slips. So, what happens is, on your hand, you when you put your hands in a bucket containing a detergent solution or water to which detergent has been added, the water that sort of covers your hand. So, there is a thin layer of water that forms the moment you dip it, that water layer actually has this hydrophobic tails face to air. So, when you rub your hands now like this, surface of the hands are not coming in contact, but what is coming in contact are two two thin liquid layers; both of which are covered or decorated with a layer of surfactant molecules.

Now, this surfactant molecules sort of have very low surface tensions low friction properties and sort of slip. It is a very simple back of the envelope type of an example, but we will take up some of these issues in greater detail. Now, so this is perfectly fine though this is a thought experiment, but this is reality this indeed happens, so not a problem. Now think of a situation that you go on adding more and more surfactant molecules. What will happen? What will happen is this; so first there are few surfactant molecules, so they migrate to the surface randomly here and there.

More and more surfactant molecules, eventually the surface gets completely filled up with this molecules. So, surface is fully covered, there are if you think in terms of adsorption isotherms like a Langmuir isotherm or Langmuir, if you talk of an instrument called the Langmuir-Blodgett trough, one can nicely generate the surface pressure as a function of the ordering at surface, may be at a subsequent lecture we will take it up. But at the point at this moment let us try to understand, how one of the most fundamental or easiest bottom of fabrication technique of formation of a surfactant micelle occurs. Now, if you add more molecules what is going to happen? There is a possibility. So, what is the motive force? The motive force is since the liquid is water and the tail group does not like it. So, essentially it, the tail will try to stay away from the water; so now, the question comes whether the wall of this container, the tail prefer to stick to the wall.

If say, you have a material to which the hydrophobic tail of this molecules sort of is preferentially adhered again there are lots of complex issues, but finally, whether it will attach or not depends on issues related to surface and interfacial tension which we did talk in one of our previous classes. So, there might be possibility that the molecules prefer to get oriented like this. In a scenarios, all the surfaces gets covered, but this will occur. Let me clearly state you, only when the interaction between the tail part and the container wall is preferred. Preferred here means from the standpoint of thermodynamics, energy is minimized that is the key driving force. If you remember, already we have talked while explaining metastable state or unstable equilibrium. We have talked that a system over here will depending on a little bit of perturbation will migrate either to this steady state or this steady state. So, all you have to doing is to give a little bit of perturbation and then the transition of the system from here to here is sort of you can say automatic, you do not have to bring the system over here.

What is the driving force here? the driving force here either at state one or state three as compared to state two is minimization of energy. So, when I say that something is preferred, in nature only one thing is preferred that way, all natural processes tend towards minimization of energy. So if the, I repeat, if the container of the wall sort of has a preferential interaction with the tail group, then the molecules will go here decorate the surface of the container. But irrespective of what material you are using for your container, this dynamics will indeed occur, because this is a entirely dominated by the interaction of the molecules with respect to the liquid here, which is water.

Now when, so in other words, if you have a beaker material which does not have a preferential affinity towards which the, to which the tail groups does not have a preferential affinity then this will not result. So, this is rather case specific, this is independent, this is going to happen anyway. So, anyway either of the two, whether it is preferential, if it is preferred the interaction is preferential, then the surfactant molecules go here. If it is not, then they refuse to go here. Suppose, even this wall gets fully covered with molecules; so, what is the idea? If the tail molecules can sort of attached to the wall, the liquid or the water which is on this side does not see the tail molecules. Or there is no direct interaction between the tail molecules, molecules of the surfactant tail with the liquid. So, this sort of energy penalty is reduced; so, this is sort of a favoured configuration. Same is here and the surface, water molecule interacts only with the head molecules or the head group molecules which are hydrophilic the interaction is preferred. So, other question to ask is, up to what level the free surface, the liquid air free surface will be packed with surfactant molecules.

Well, that is going to be dominated eventually by the static repulsion. That is there will be compact I mean when the, if you see from the top, when the head group molecules sort of touch each other. They cannot interpenetrate, because of the hard sphere thing etcetera etcetera. We have already talked issues like that. So, this is the sort of the morphology or the packing order you are going to achieve at the surface. So, this is at surface. These are the head group molecules and compared to these molecules. So, the tail sort of dangles outwards like this, if you really consider in sort of 3 D picture. So, after even this has been achieved, what happens? If you at more molecules. So now, another molecule that comes in has no place to go, because the liquid air interface is packed.

Many cases, either the wall is also packed, liquid wall interface is also packed or the molecule does not prefer to go to the wall. So, for the molecule depending on the interaction of the tail, the wall and the liquid are equally unfavoured. So, if you have many such molecules floating freely, each one of them is sort of having an unfavoured interaction between its tail and the surrounding liquid. So, what can be a possible solution for sort of getting over for overcoming this type of an unfavoured interaction? Which unfavoured here means that this is resulting in lot of energy penalty; so, there is a lot of interfacial energy that is associated.

So eventually, the system is a high energy system. So, it tries to attain a stabler configuration by minimization of some part of its energy. So, what can be a likely solution if you think for a minute? I will repeat the question. So, here you have a beaker of water let us say, where the surface is completely decorated or completely full with the surfactant molecules already. In case, the beaker surface or the container surface and the tail groups have a preferred interaction; let us also say that whatever molecules had to go onto the wall. They are also sort of complete the tail the wall is also filled up; there is no place at the wall. And then you add even more number of molecules which are now they do not have a place to go. So, they can neither migrate to the wall nor they can migrate to the surface. And there are many such molecules, each one of them has a unfavoured interaction between the tails and the surrounding water. So, what can be a solution?

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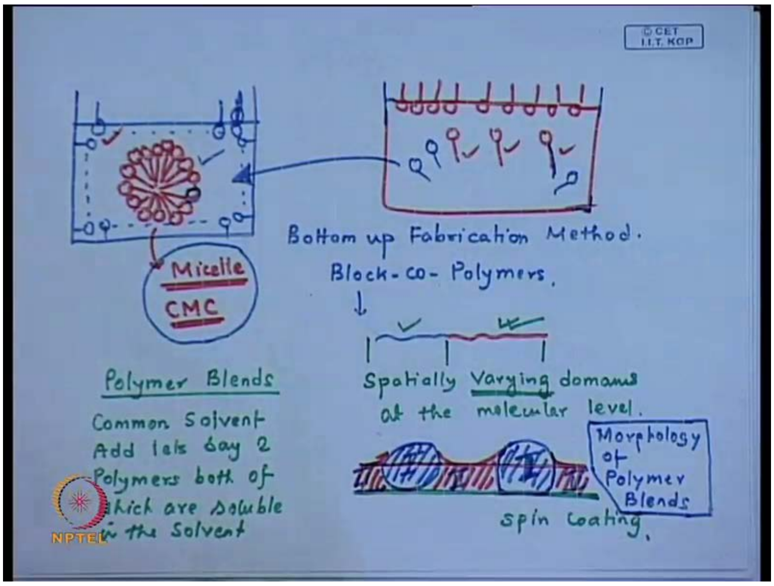

Bottom up Fabrication Method.

Block-co- Polymers.

Spatially Varying domains at the molecular level.

Polymer Blends

Common Solvent
Add lets say 2 Polymers both of which are soluble in the Solvent

Morphology of Polymer Blends

spin coating.

Well, the solution is that these molecules. So here I am not repeating it. So, this is filled up, this is filled up, this is also filled up; so, as compared to this configuration, where each molecule is sort of roaming around overing around freely, within the water, within the liquid. If you know consider an arrangement like this, what about that? For the drawing it is not that good and this is a sort of 3 D arrangement sort of a spherical sort of an arrangement of these molecules. Now, if you consider this structure what happens is? Now, there is a tight packing of the head group molecules here, so they are tightly packed. Forget about the drawing, my artwork is not that good. So, the water is not coming in direct contact with the surfactant molecules any more.

So in other words, this surfactant molecules are making a virtual case, spherical case like this; where the outer surface of that case is decorated has only the hydrophilic head groups and the hydrophobic tails are sort of hidden within that case. So that way, now the thermodynamic interaction becomes favour, because the hydrophobic molecules are sort of encapsulated within or sort of or hidden and they do not come in contact with water any more.

So, if you look at the interaction from the thermodynamic standpoint, the interactions are now between water and the hydrophilic head group; which is favoured interaction exactly as what was happening at the surface. And then, this tails are sort of encapsulated inside, so it is a tail. So, the tails are either sort of the you have sort of a wide space over here or the tails are sort of entangle, if they are very long that possibility. You cannot rule out, so there can be some bit of static interaction. But even this tail interaction is much preferred, then a hydrophobic tail water interaction. So, this is what is called a micelle.

And you probably have come across a term called CMC, which is the critical micelle concentration. Or in other words, it is the, it refers to the surfactant concentration beyond which or at which the micellization process starts. So, you must understand from the if you just do the way we talk, like you take a take a beaker or a container full of water and you go on adding surfactant molecules that is eventually go on increasing the surfactant concentration. You must realize the moment you start adding surfactants, it is not going to be form micelles. Because the first few molecules will go to the liquid air surface, cover it fully, only then depending on the material this is something slightly contradicting view. So, this view shows that your CMC depends on the material of construction, but reality is that, even if you consider that the difference will not be much. So, again let us try to understand our science in a very simple fashion, let us not talk about the classical definitions.

So, depending on whether you have a favoured material at the wall, the some of the molecules might migrate to the surface; if you do not have a favoured material the molecules would not migrate. So, the molecules will sort of start dangling freely in the water. Now, in order to create this type of a structure, you need some adequate number of molecules. Even if you have, let us say my interface is fully covered and somehow you have three molecules dangling in water. So, if that be the case, unfortunately though these interactions are not favoured, these molecules will not be able to form a micelle. Because of the simple fact that the three or four or I mean, this is just an example do not be very specific about the numbers. They do not have the ability to form that encapsulation or form that spherical domain, where the hydrophobic tails can be completely hidden; this is a very simplistic view, I think you have got it. So, if there are no adequate numbers of molecules, which can sort of, form this hydrophobic domain. How many numbers of molecules are needed in order to form this? Let us not get into all those details.

This depends on very many things the diameter of the head group the size the how long you would have the size of the tail, exact interfacial energy etcetera etcetera. But that is not the intention of my talk today or the, of this class. The idea is that if you know have adequate number of such molecules, these molecules sort of reorganize. You do not have to do anything you do not so that; so, these molecules sort of reorganize to form a structure or a micelle like this.

So, you understand that there has to be a certain number of molecules present in the system, to sort of allow the formation of these micelles, this is number one. So, that concentration at which the micellization process starts is known as the critical micelle concentration, this is number one. And the other important thing is that from these molecules, why at all we started to discuss on this particular topic. So, these free molecules which you added in the liquid medium, how they form this structure? If you look into that that is something at into the bottom of fabrication technique, we talked about towards the beginning of this class. You see that these are the building blocks, so we talked that may be something you just arrange the molecules block by block, like a children play with toys like lego and something like that.

So, one question we posed to us at that point of time, that if you want to build an object block by block using molecules, how do you handle the molecules? How do you really sort of bringing the molecules together in the desired shape to fabricate the necessary object or entity. Now, this is one answer. So, based on the; so, eventually from this random structure to a transition to a rather order micelle, when you have adequate number of molecules is not a endangered by you. So, you are not triggering it or no one is triggering it. And you are not apply as I repeat this. So, in order for this reorganization to take place, they are the molecules actually move in a desired fashion within the liquid medium. And this movement is not due to any hydrodynamic movement of the liquid layer.

As an engineer you must realize, a chemical engineer you must realize that a beaker full of liquid is actually a stagnant pool of liquid, there is no flow. So, if you try to solve by navier-stokes equation for this setting, what you will get? That u, v, w, are zero. That is the flow components of bulk velocity in the three direction u, v and w; they are zero. Or even if you write it for r theta z coordination system, if you solve the equation for a stagnant liquid pool this is the simplest problem you can handle; there is no pressure gradient there is no gravity driven flow, so there is no motion. So, the motion; however, you see that you had some random molecules here and the molecules have sort of organized into a desired order like this. So, this motion is again triggered by the surface energy penalty number one. And this sort of gives a clue that from a from some random discrete molecules or the building blocks, there can be some scenario at which you can sort of get some order structures like this.

Now, so this is what is the concept of micelle formation of surfactant molecules. Probably the easiest example of bottom up fabrication method, but this is a very important example with surfactants, with a class of materials call block copolymers. Again this is something that instead of it is not a single polymer molecule, but a block copolymer molecule we will have a different polymer domains. So, let us say this is one block that is why that is the origin of the name, this is the block one and this is the block two. So, one key message that comes out that surfactant molecule or a block copolymer molecule exhibits this type of micelle formation; while your normal molecule even normal polymer long chain molecules do not exhibit this type of a behaviour. Is that micellization probably is possible or not probably it is indeed possible, in materials which have specially varying domains at the molecular level.

So in other words, this it is vary in such a way that as compared to its surrounding medium, which can be liquid, which can be the polymer matrix itself. Individual domain or individual blocks sort of exhibit different behaviour, it can be weighting can be one such behaviour there can be other types of behaviours also. For example, the entropic interactions can be different. So, even in a block copolymer system, which we probably will take up in one of the later classes, you see micelle formation. Even in polymer blends for example, its even simplest system. So, block copolymer you have to synthesize the molecules in a very critical fashion, synthesis of block copolymer is a nontrivial issue; there is lot of research that goes on, but polymer blends are rather easy. So, you take a common solvent, even in a undergraduate chemistry, organic chemistry lab, you can make it take a common solvent, add let us say two polymers, both of which are soluble. In the solvent, if you now cast it on a flat surface by a method called spin coating something we will cover later probably in this class. You will not get a uniform film like this, you would not get it you will get different domains. So, this domain segregation let us say this is molecule one and this is two. So, lot of research again goes on the morphology of polymer blends. But if you try to realize it from the standpoint of our discussion; there are interactions.

So, interactions between the two polymer groups, so, the two polymers present, as well as the difference in the interaction of this two groups with the substrate that leads to this domain segregation. The critical point to ask is this domain segregation is not done by you. So, you do not really pick up a tweezer or a spoon or a or your fingers to place some amount some molecules of polymer one over here, and then sort of fill up the other part the empty or the vacant areas with the molecules of polymer two.

So, this phase segregation or whatever is occurring or happening is happening based on the thermodynamics of the system. So, the energetics of the system itself takes care of the segregation or the micelle formation or in surfactant molecule or in a in a even in a block copolymer system. So, conceptually these are some of the examples, where you can have a bottom up fabrication. Top down fabrication method we are all too familiar with you just hammer down something, chisel down something, etcetera, etcetera. But what becomes important, as you will see in the subsequent discussion that even at the microscale or the meso scale or the nanoscale; even the conventional top down methods you cannot adopt. You sort of, because of the scaling or the length scale associated with it things change.

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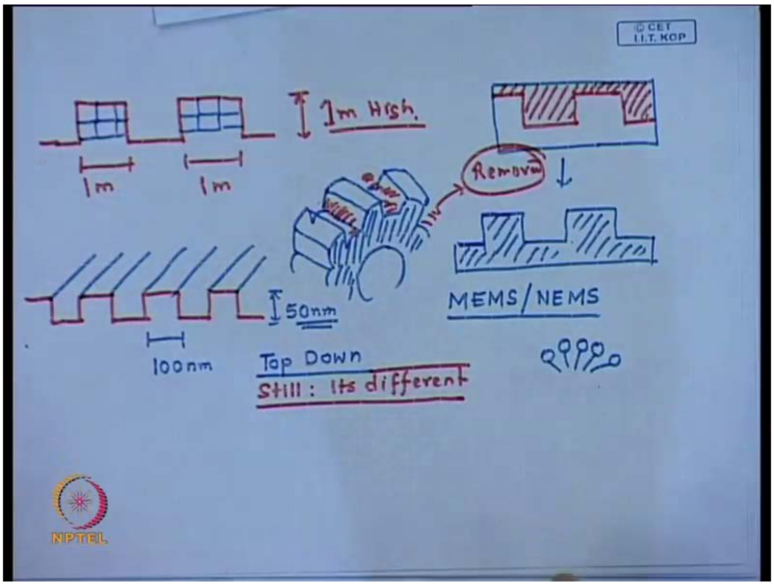

So, if you really now want to make a structure like this, let us say. If suppose, these are one meter wide and this is also let’s say one meter high, what would be the easiest way to do? Easiest way to do is sort of you can place bricks over here, but if you place bricks that probably becomes an example of bottom up approach anyway. Or you can sort of take a job blank like this and using some conventional cutting technique in your workshop, you sort of chip out this material. You throw it away, so you are left with this. Mechanical engineering, some workshop course irrespective of your engineering branch, I am sure you have done. So, there can be several techniques by which the material can be sort of taken out, standard items like gears and all these things. So, if you look at a gear it has threads like this on its surface; so something like. So, what ideally would do? You would start off with a cylindrical job blank and chip out or cut remove materials over here to make this tooth or teeth of the gear; so, this is sort of remove. So, this is top down fabrication, perfectly fine.

But then, if I tell you that well you make a make the same structure, but now this each of this protrusion is let us say 100 nanometer and its height is also 50 nanometer. Now, will your standard techniques of fabrication mechanical fabrication that you use in your workshop, will work you again in a in the area of MEMS, we talked about it in the introduction, if you remember or NEMS. You actually need to fabricate gears, but which are not of the size of a few centimetre or few meter a few centimetre, but they are of the size of a few microns.

So, essentially you need to replicate this, but at a micro level or at a submicron level. So, how do you do that? So, your fabrication technique, though this is bottom this top down, but the fraction technique has to change. So here, it remains top down, but still it is different. Bottom up, of course we have seen that you can create some desired structures. But whether you can really create something like this as sharp as this; let's say a structure like this that is dividable that is still at the research level people are working on it, because it offers lot of flexibility there are lot of things you can do. So, this is the thing I sort of up to based on the discussion up to this point, we should sort of sum it up in this way. That probably you understand by now, what exactly is top down fabrication method and what exactly is bottom up fabrication method. Well, building a step like this using bricks in a way I would regard that to be also bottom up fabrication method, but then the question is how the bricks were made probably they were made by some top down method.

So, at the meso scale, at the macroscopic scale most of the fabrication techniques we do are sort of top down. But if you look at the construction of a house, which you use a sort of individual bricks in a way you can regard that to be some sort of bottom up fabrication. So, there are examples of top down and the bottom of fabrication techniques adopted at the microscopic scale, but. So, what top down you have the conventional machining techniques or the machines like's lathes, standing instrument, boring, etcetera etcetera. For bottom up, you sort of need to fabricate whether it is actual bricks or you sort of look at children's toys like lego.

You have the individual building blocks, but the most important thing is that the building blocks, the transportation of the building blocks, handling of the building blocks can be done with your hand or with even by the some mechanical means. At the meso scale also I will put it like, this you have both these types of fabrication approaches possible, but the handling mechanism are the mortality changes for both of them. So in top down method, what happens is? You still sort relay on the same technique of starting of with something big and preferentially checking out some portion of it to get your desired structure, but your standard or conventional machines, sort of do not work anymore. So, you need to relay on some other specialized techniques.

And at this scale, at that at the meso scale, for your bottom up fabrication, your building blocks now get changed to no longer remain there; you do not have artificial building blocks like brick or something like that it is now the natural building block that is the molecule. So, then comes the question that what can trigger motion of molecules to sort of create things in a perfect order. So, based on that we had seen or we saw some examples like where a micelle can form. So, essentially this formation was triggered by an unfavourable interaction between the hydrophobic tails of surfactant molecules and water. So, it is the essentially it is the interaction of the hydrophobic tail or part of the molecule with respect to the surrounding medium; that has lead to this formation of this structure.

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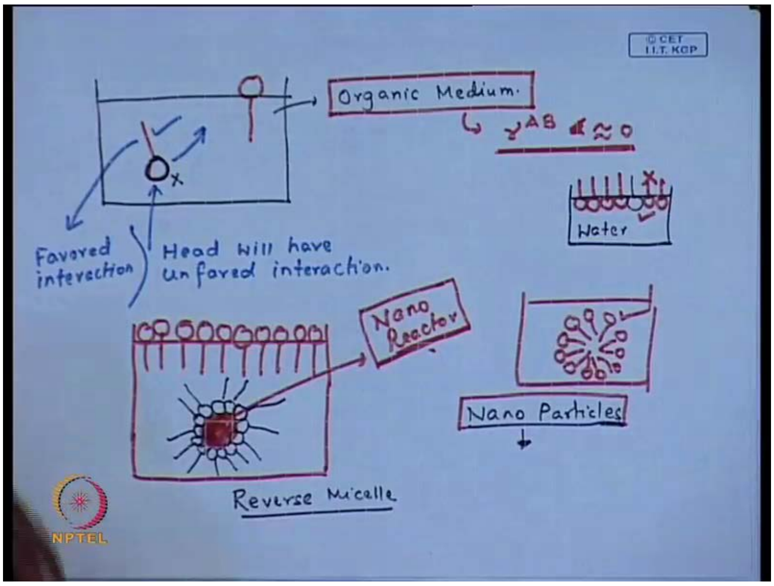

Now, let us pick up just take quick example before we wind up this particular lecture, suppose instead of water you have an organic medium; and you place your same surfactant molecule to that organic medium. Now based on the discussion, we had on surface tension, you probably would know note that this organic medium has much lower A B component of surface energy often it can tend to zero also. So, these are not polar solvents. So in other words, this type of organic liquid, when it is brought in contact with a molecule of surfactant molecule; what will happen? You believe me for the moment later you will realize it yourself; that in an organic medium, the head group unfavoured interaction. While this tail, now will have a favoured interaction.

If you compared it with what you saw in a organic medium, the scenario has just reversal now. Here, we had a favoured interaction of the head group and an unfavoured interaction of the tail group. So, that lead to migration of the surfactant molecule to the interface, which was sort of a preferred location, where the tail could sort of dangle out and the head remain in contact with its favoured thing. So based on that, based on this concept can you predict what is going to happen here, because here also, you have a part of the molecule that is not having a preferred interaction. So, if you put on your thinking cap and think what happens? Well, does the molecule stay in the medium itself or it again migrates to the surface. So, probably we will all agree that depending again on the exactly following the same logic that, if you have an unfavoured interaction there will be a motion of the molecule within the medium triggered by surface energy penalty of the surface energy penalty.

So, this molecule will also migrate towards the surface; it seems the surface is the most favoured location it is a dispute less area. But as compared to the ordering of a surfactant molecule in water which was like this, do you feel that the ordering will still remain the same? The answer is no, because now, this interaction is not favoured; however, this interaction is favoured. Here, a surfactant molecule took this confirmation or this configuration based on the fact that this interaction was favoured and this interaction was not favoured. So, following that logic, if we if I ask you to now predict what is going to be the likely morphology or likely orientation of a surfactant molecule at the interface; well, probably you have got it right it will be like this. So now, from an organic medium the head sort of prefers to remain expose to air; and the tail which has a favoured interaction with the organic medium remains happily in contact with the medium. So eventually, what will happen in this case also, that you go on adding more and more number of surfactant molecules, your interface again gets cramped up fully filled up, but it is in contrast with this configuration.

Where the tail was dangling out, here the head group sort of prefers to stay away from the liquid medium. Now, if you go on adding more number of molecules here, what we saw here, that a micelle formed. Here, if you add some number of more number of molecules what happens is, here the micelle form, because the head groups had a favoured interaction with the water. However here, the tails have a favoured interaction with the organic medium and the heads do not have.

So now, that tails sort of help forming a structure that allows hiding the head groups. So, you get a structure like this. Again a sort of a spherical 3 D structures, spherical selected structure, where in comparison to a regular micelle, where the outside surface was entirely decorated by the head group. What you see here that outside you have that tails. And the head groups are which are hydrophilicc or which are which are not having a favoured interaction with the inorganic with organic medium, you have are sort of hidden inside; so, this is what is called a reverse micelle. And many of you know that there is lot of hectic activity, hectic research activity that is going on in the field of nano particles.

And these reverse micelles, approaches based on reverse micelles or an extremely favoured root for synthesis of nano particles. Because what you can see that this area which has formed here, in a reversal micelle sort of acts as a nano reactor. So, you can have your reactance, which can react to form the particle of a desired material, but since, the structure it is already confine, these structures are rather stable in this medium. So, after synthesis the material cannot grow beyond this particular size. So automatically, the size of the particle sort of gets fixed by the size of the micelle. So, you can an engineer, I mean a scientist can eventually do lot of things one can pick up the choice of surfactant, the concentration of surfactant, the choice of medium, etcetera.

You can tailor the interaction and can create sort of differ reverse micelles of different sizes, which intern can sort of control the size of the particles you synthesize. So, in a (( )) I will stop here for this particular lecture, what we saw that we saw some very basic examples of bottom of approach in in the meso and nano scale, and classic examples are very easy examples mankind or human beings know it for a long long time, in the formation of micelles and reverse micelles of with surfactant molecules depending on what type of medium you use, whether it is an aqueous medium or an inorganic medium.