Fundamentals and Applications of Supramolecular Chemistry
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Lecture 50

W10L50_Supramolecular Gelators

So, hello everybody. Now, today we are going to discuss a new class of materials which we refer to as gels. Now, in particular, we are going to discuss supramolecular gels. So, let us look at this process via a diagram.

So, we have the supersaturated solution, and when we cool this supersaturated solution, it will lead to processes of nucleation and growth, and the process of nucleation and growth will give rise to particles that are being created, or aggregates, and depending on how these particles further grow, it can give rise to an amorphous precipitate. If it is a very controlled and slow rate of evaporation of the solvent, it will lead to the formation of crystals.

And then, in between the amorphous phase and the crystalline state, if we are cooling, there is an intermediate state, which we refer to as the gel state, where essentially what happens is that you have these long fibrous assemblies, and these fibrous assemblies now get entangled with each other to form a 3D matrix, giving rise to the gel state.

So, the gel substance is a viscoelastic solid-like material, which is composed of an elastic cross-linked network and a solvent that is the major component. Almost 90 to 95 percent is the solvent component here, and the rest is the gelating material that has an elastic cross-linked structure.

The solvent is the major component, and when water is present, it is referred to as a hydrogel because water is the major component that fills the voids created in this fibrous network.

So, when you have these fibrillar structures, they are formed because of the process of self-assembly of the gelator molecules. Therefore, we are going to particularly focus on supramolecular gels. So, in the case of supramolecular gels, we have low molecular weight gelator substances, which we call LMWGs.

What happens with these substances is that they essentially first interact in a supramolecular fashion by forming, say, a hydrogen bond assembly, and they form a chain. So, there are strong interactions that mediate the formation of these chains, and they form these one-dimensional supramolecular assemblies.

And then these fibril-like structures can now laterally interact with the other fibrils to form the 2D network and eventually assemble into a 3D network, and during this process of cross-linking in the other two directions, they can essentially get trapped in a matrix and form this kind of fibril structure, which is now forming this matrix.

And now there is a large amount of space where the solvents can get trapped. Essentially, because the solvents are now trapped, this is due to the forces of adhesion between the solvent molecules and the low molecular weight gelators. And therefore, this kind of freezes the motion of the solvent molecules. So, now most of the solvent molecules get trapped in this three-dimensional matrix, which is created by the interlocking of these fibrillar structures, giving rise to a low molecular weight gelator substance.

And this low molecular weight gelator, once it is formed, is almost entirely solvent, and a small amount of it is the low molecular weight gelating substance. So, these low molecular weight gelators form the supramolecular association, where they form these fibrous aggregates that get entangled during the process of aggregation and form a matrix that traps the solvent via forces of adhesion between the solvent and the gelator molecule.

So, this process, if it had occurred in a very ordered fashion, such that these fibrillar assemblies would have created a supramolecular periodic 3D array, would have given rise to a crystal formation. Sometimes it is also suggested that gelation is a process of interrupted or arrested crystallization.

These long-lived supramolecular assemblies, which are formed, are stable and exist in a solution; however, they are not able to crystallize further in an ordered fashion because they tend to get trapped and locked into these highly disordered states, in which we have this fibril structure-like assembly.

So, the gel network is actually a physically entangled network structure that has disordered regions along with the crystalline cross-linkers. Therefore, it is a physical entanglement process.

So, this is also a process of interrupted or resting crystallization, which leads to the formation of these low molecular weight generators. And by and large, these fibrillar networks are formed, say, for example, by 1D arrangement, through strong hydrogen bonds or pi...pi stacking, which mediates these self-assembly processes. And then the other interactions, which happen across the strand in the other two directions, can give rise to the overall gel-like substance.

So this leads to the formation of the low molecular weight gelators. Now we would also like to see that gel formation depends on the origin, constitution, and type of

cross-linking that creates the 3D network and the medium it encompasses. For example, the naturally occurring gelators are macromolecular in nature, and they are formed by physical cross-linking.

For example, we have gelatin and starch, which are formed via strong chemical bonds. These cannot be re-dissolved, and the processes are thermally irreversible. For example, polyamide and polyethylene. Now we can look at this classification in a broader sense. So, we have the gels, we have the source, natural or synthetic medium.

One is the natural source, and the other is the medium in which we get the gels. Here we have four different classifications: organogels, hydrogels, ionogels, and aerogels. So, the organogels contain organic solvent, hydrogels contain water, the ionogels are formed from ionic liquids, and in aerogels, gas is the fluid phase.

And we can also have a constitution; that is, we can have low molecular weight gelators, we can have macromolecular gelators, and depending upon the extent of cross-linking, we can have physical cross-linking or chemical cross-linking. These are covalent, as we mentioned, and these are fibers or particles held by non-covalent interactions. The short form is NCI.

We have another classification here, which is called metallogels in the medium where the metal is present, in the sense that the metal is linked to the fiber components. The metal here is linked to the fiber components to form gels.

A very straightforward procedure to make the gel is to dissolve it in a warm solution and then allow it to cool below T-gel. A procedure to make gels is to dissolve the substance in a warm solution of a suitable solvent and then cool below T-gel, which is also referred to as the temperature at which the gel forms, the gelation temperature.

And above this temperature, if you heat the substance, it converts into the solution phase, the gel state is lost, and that is referred to as a gel-to-sol transition. But typically, if you want to prepare a gel, you dissolve it in a suitable solvent, warm it up, and then cool it slowly below the gelation temperature, and this leads to the formation of a gel.

And we also have another classification of gel, which is called thixotropic gel. In this case, what happens is that you see a gel substance undergo a gel-to-sol transition when you stir or disturb the gel state.

So, when you apply mechanical agitation to the gelatinous substances, or the gel substance, it undergoes a conversion into the sol state, whether you stir the gel, shake the gel, disturb the gel, or give it some mechanical activation, and the moment you withdraw the external stimuli, it resets itself to the initial state.

It reverses back to the gel state when the stimuli are removed. For example, the paint you see is actually a gelatinous substance, but when you stir the paint solution, it starts flowing freely and converts into a gel substance when it is at rest.

So, paint, is an example of a gel substance that becomes free-flowing, when you mechanically stir it or when you mechanically agitate it. It is free-flowing like water, but again, when you let it rest, it will return to the gel state.

So, these are some of the interesting things about gel, and initially, all the research that was directed towards the identification and discovery of gels was mostly serendipitous.

That means that most of the time, people were trying to crystallize certain organic molecules or metal-ligand complexes, and they observed the formation of this gel-like substance. There is a test referred to as the inversion test, which is performed to ascertain the formation of the gel.

So, once the gel is formed, it practically leads to the immobilization of the liquid. Now you see, you have this white solid, which is dispersed in the solvent, and it forms a kind of viscous mass. It is a viscoelastic material, and this is, say, the top of the container which is covered.

Now, you actually put it upside down. So, this now becomes the top, and now what will happen is that this gelatinous mass will essentially come and stick here; it sticks and does not fall under gravity.

So, this falling under gravity does not take place, telling you that this is a gelatinous state, where there are strong forces of adhesion between the solvent molecules and the jelly-like substance, which actually sticks again to the glass surface, thereby preventing it from falling down freely under gravity, and it is proof of the formation of a gel.

So, this inversion test is interesting for characterizing the formation of gels. And let us now look at some of the important properties of gels.

There are also gels that are very sensitive to temperature. For example, we have the thermoresponsive gels. Let us take an example of a thermoresponsive gel. This is a bis urea compound. It forms a thermoresponsive gel at concentrations below 3 millimolar and is stable up to 100 degrees centigrade.

So, this is an example of a thermoresponsive gel. Now, we can look at the role of external stimuli, such as when you have, for example, a photoisomerizable group, which is present as part of the gelator molecule and undergoes a gel-to-sol phase transition in the presence

of light, converting the gelator substance to an isomer that does not gel. So, let us look at this particular example. We can have this functionality. In the presence of light, it can now convert the cis to the trans geometry.

The cis geometry does not form the gel, but the trans geometry forms the gel-like state. So, this photochemical rearrangement takes place, leading to the formation of the trans geometry, which has the gel state, but the cis geometry does not have one. So, we can actually go from the gel to the sol phase transition, which is triggered by light, that can actually convert a gelator state to a non-gelator state, and vice versa.

So, we can take another example where we have the diazo group, and R is the cholesteryl group; it is a large bulky group. This is a photoresponsive gel, which is a cholesterol derivative, and what happens when you shine light, 330 to 380 nm, is that it converts from the trans to the cis isomer, which does not form a gel state in solution.

So, the gel property of this particular compound is in the trans geometry, but when you irradiate it with 330 to 380 nm light, it loses the gel property when you pass light of different wavelengths. However, when you now pass light of 460 nm, it goes back to the gel state again.

So, this is a reversible process where you can control the process of gelation. So, these two examples talk about the photoisomerizable group being important in gel formation. The next thing we would like to look at is the mechanism by which gel formation is taking place.

So, different models have been proposed, but we will look at some of the models that are responsible for the aggregation of these low molecular weight gelator compounds to form gel-like assemblies.

So, just like you have protein aggregation, which goes from the primary to the secondary to the tertiary structure, the formation of the gel network is also triggered by a hierarchical self-assembly process.

So, for example, let us consider peptide-based gels. First of all, we have these hydrogen bonds. You can see that this is a kind of 1D chain-like structure, around 5 angstroms in length.

These can further aggregate extensively to form these kinds of assemblies of 10-nanometer dimensions, and finally, they can again grow into long fibrils that get entangled.

So, we can have these kinds of fibril structures, which will now get entangled to form this cross-linked network, and these are 10 micrometers in terms of the dimensions, and these form the gel or fibers.

And the morphology can vary from aggregates to fibers to ribbons to sheets to micelles, vesicles, etcetera. So, you have now learned all these things in a previous lecture. So, you can appreciate the formation of these structures that give rise to these gel-like substances.

And there are other ways as well by which these can actually self-assemble with each other. For example, this is one particular type of aggregation that I have talked about. The second one can be where you have this -CO-NH- moiety.

So, what has been proposed is that you now have the polar parts, and you also have the non-polar parts. So, the polar parts can form hydrogen bonds, and the non-polar parts, which actually now get entangled with each other, get cross-linked via this pi...pi stacking, and then the strong hydrogen bonds are mediated by these O-H...O hydrogen bonds.

So, you can have the stacking interactions, and you can have the strong hydrogen bonds, which can actually be formed.

For example, in the case of hydrogels, the water can now solvate the polar regions, and the non-polar regions can now be present within the core, so you have an organization by $\pi...\pi$ stacking, as well as O-H...O hydrogen bonds, which can give rise to the gel-like structure.

And then there is another mode of association, which is favored in the case of anionic substances, where pH plays a very important role. So, we can achieve a gel-to-sol transition, which can be controlled by the pH of the solution. For example, we can have these rod-like fibers, which are present at high pH. Now, when you add protons, you will see that we should represent these anionic species here.

So, these form stacks of anions. And now the protons will go and sit here, protonating these carboxylate groups, and they will actually form this kind of microtubules. And eventually, when you further lower the pH of the solution, which means increasing the acidity of the medium, this will form microcrystals, which are the needles.

The needle formation takes place. So, what happens at the interface is the formation of these hydrogen bonds, which takes place at the interface because you added the proton source, and they now lead to further aggregation from the fibers formed at high pH. Then, they form these microtubes, and finally, they will form the microcrystals.

So, you can control the morphology of the substance, and you can also control this process of supramolecular assembly by tuning the pH of the solution, and this will also change the property. It can go to the crystalline state via the microtubules, starting from the micelle state.

So, these rod-like substances can now eventually convert into microneedles, depending upon the pH of the solution. These are some of the most important processes that take place when we have gel-like substances, and so this gives rise to very fascinating applications of gels.

So, with this, we come to the conclusion of this lecture, and I hope we have been able to appreciate the gel state, the liquid crystal state, and so on and so forth.

Thank you.