Introduction to Polymer Physics

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Lecture-02
Classification of Polymers, Types of Polymerization, Average Molecular Weights and Polydispersity

In the last lecture, we discussed the introduction to the polymer physics course and talked about what exactly polymers are? We discussed the fact that polymers have many confirmations which give rise to molecular flexibility and the motivation towards like studying the physics of polymers. So in this class we will discuss these topics in detail.

Firstly we will discuss very briefly like how polymers are made, unlike polymer chemistry course we will discuss this briefly and then finally move to why study polymer physics? So, firstly how exactly are polymers made?

A polymer chain contains a repeating unit and sequence of repeating units and n denotes the number of repeating unit.

$$\text{--}\,(CH_2 - CH_2 \text{-}\ CH_2 \text{--})_n$$

Polymers are macromolecules but all macromolecules are not polymers what really means is that if you do not have a repeating sequence, we do not typically call that a polymer. For example a protein, protein consist of unique sequence of amino acids but they are non-repeating sequence, so in that case we do not call it a polymer. So, polymers are typically formed by some kind of a monomer which in the case of polyethylene shown above, the monomer in that case is the ethylene molecule ($CH_2{=}CH_2$) this is a monomer. When we combine n monomers- the double bond of monomers is replaced by the single bonds in polymers because the carbon at the ends form a new bond then another carbon. Thus 1 bond of the double bond went to another single bond with different carbon and so on forming a large chain of polymer.

There are 2 major ways to make a polymer-

- Addition polymerisation- It goes like something like this:

$$A + A_n \rightarrow A_{n+1}$$

  So, starting from say a monomer A we will make something like A2, so 2 ethylene will come together form like butane type of molecule then that will come together with another ethylene from like hexane type of molecule and so on and so forth. So, the chain will continue to build as the polymerisation is taking place.

- Condensation polymerisation- In this process we start with 2 polymer chains or small polymer chains which combine together or condense together and form a larger chain.

$$M_x + M_y \rightarrow M_{x+y}$$

So, in the first case we always require a monomer to react, so a monomer to reacts with a growing chain and forms like a bigger chain. In the condensation case there are 2 chains which react and form a larger chain.

So, by looking at the physics aspect of things we observe in the very beginning we have monomers in the system in a beaker or the reactor. These monomers are small monomers and they react, polymerisation is taking place and form a polymer. As we can see when the polymer is being formed by either the addition mechanism or by condensation mechanism it is not happening only at a single place in the beaker, this happening at many places. For example many small polymers are coming together at the same time and form a polymer. So, what you will see in the system is that many polymer chains are start forming and the chain will grow, addition polymerisation is taking place. The key point is that if you have say a beaker or a reactor then in that particular case not only 1 polymer chain is being formed because we may start with a gas of monomers or a liquid of monomers but liquid typically contains moles of monomers and species. So, moles means 10^{23} number of molecules, they are coming together at any given time, and a very large number say 10^{20} or 10^{15} polymers are started forming. It doesn't really have 1 polymer chain but many polymer chains. For example some of the polymer chains maybe more fortunate and they can get like larger as they have found another monomers in the way. On the other hand some polymer chains can be less lucky and found less monomers around them and thus they will grow lesser.

In the end we will have a combination of polymer chains which contain some larger and smaller chains. It is very difficult to have a constant molecular weight or a constant value of this chain. So, whenever a polymer is being sold or bought from a market it never has say n=100 or 200 does not have all the corresponding molecular weight what it has is a molecular what in a given Range. So, for example n can be 100 to 500 or for example 1000 to 5000 or for example 10,000 to 50,000 or any other range. The key point here is that whenever we try to control the polymerisation process we can never have a precise control on the molecular weight or the number of repeating units. So, we end up having in terms of say if I refer to some sort value like capital N that tells me the number of repeating units And again use the same kind of a language from molecular weight as well and if I plot a probability distribution of that now, that means that if I am looking at a polymer, polymerisation reaction that produces polymers in the range of 100 to 500 you will have certain value the N which are more probable and certain less probable. So, in most cases you will have a distribution that looks like a Gaussian distributions.

We will have some sort of an average molecular weight or N. So, N can be for two things here- the number of repeating units & molecular weight.

The key idea is that when N is larger, the polymer becomes larger, and then the width of this distribution curve is referred as polydispersity.

This is the real challenge as a polymer chemist we want to first form polymers of any molecular weight as we can expect as a change the molecular weight they change the N, which means smaller n will have different properties from the higher N values. So, if it is like more polydispersed it is not really very successful polymerisation process. It can vary with the application but the challenge for polymer chemist is to first make polymers of any average molecular weight and then to reduce the amount of polydispersity in the same. There are couple of ways we can define the average molecular and polydispersity.

There are certain ways to define average molecular weight. These are:

n_i = is the number of chains

M_i = molecular weight

M_w= Weight averaged molecular weight

$$M_w = \sum ¿ . mi^2 \div \ni . mi$$

And using these two we can define what is known as polydispersity (PD) - It is the ratio of the weight average molecular weight and the number averaged molecular weight.

When PD = 1 then it is called mono dispersed (which is difficult to achieve and everybody aspires for). The quantity PD away from 1 tells how much polydispersity is. The higher the value more is the polydispersity and thus more polydispersed system.

It can be understood by a very easy example is to demonstrate what really these 2 averages mean. Let us think of a system that contains 1000 ants of weight 1gm and we have 1 elephant of weight say 1000 kg. So, we can write 10^6. Now let's compute the number average molecular weight M_n.

$$M_n = 1000*1+ 1*10^6 / 1000 + 1 = 10^3$$

$$M_w= 1000*1 + 1* 10^{12} / 1000*1 + 1* 10^6 = 1$$

And now we will get something like 10^6, a few things to note here, first of all if I look at the number average molecular weight it tells me it is around 1kg okay just by looking at this number we will not be able to guess that there is an elephant in the sample because the average weight around 1kg. So, every species more or less will have a weight of the order of 1kg in the system.

As ants are much lighter and the elephant is much heavier, on the other hand if we look at an Mw it is close to the weight of an elephant. The key point here is in this particular case Mw by Mn is that PD is around 10^3, thus system is polydispersed as we have 1000 ants and 1 elephant.

If we replace elephant by cat which a much lower weight then the M_w will fall down, thus PD will fall down because of the weight difference between the two species becomes smaller, Further if we replace say elephants with for example bee which have even has like a weight comparable to the ant then in that case the polydispersity will be closer to 1. So the key point is the polydispersity becomes closer to 1 when all the species have start having weights within a small range. So, this way we define the average molecular weight and polydispersity.

Now we will discuss about types or classification of polymers. We can classify the polymers in different ways-

- One way to classify is how they originated i.e. the origin of the polymer- for example natural polymer and the example, for example is cellulose which we find in say trees or cotton. And other is synthetic polymers that really made in an industry from the sources which are not natural typically. For example polyethylene.
- Another classification is by structure- Polymers can be represented in a line as there are many carbons and are called linear polymers which corresponds to a fact that there is only one main chain of carbon. Another possibility is a branching polymer where we have a main chain and then a side chain. It contains 2 different chains of carbon which together form a branch. There is fancy structures called as star polymer- It looks like a star, it can be the excellence structure of polymer chemistry. Then there is hyper branched polymers which will have branches within branches. At last we have something known as a comb polymer and as the name suggest it is like a comb you have branches on both the sides of the polymer chain.

Let us consider an example of dendrimer that has been catching as attention in the recent years for applications drug delivery. Dendrimer is a structure that can start from any point and can make certain number of branches. Let us consider the case of 3 branches. Now from each of these 3branches we will again start 2 new branches and then from each of these new ends, we will again start 2 new branches... This will continue like this, so as you can see the first central one have like 3 branches and after that each of them will have 2 branches and depending on like how many steps we can carry and thus we have dendrimers of different generations depending on the how many steps we wish to continue in this process.

Now we will discuss polymer network As you have seen in the case of rubber band- which is a cross linked polymer which means it really composed of polymer chains which are cross linked at certain points due to some kind of covalent linkage or a physical linkage which combine them together and form a very nice network. Another example which are more useful is the diapers- the baby wears them as it can take of plenty of waters. Diapers are made up of composed polymer networks which enables them to contain lot of water inside those systems.

Then we have other ways of classification, for example by composition, so for example we can have what is known as a homo polymer which will contain only one type of repeating units A's A's A's all that**.** Another is co-polymer which means it contains 2 kinds of repeat units and there can be many possible ways this can happen. For example copolymer that is like ABABAB's and so on. Next one is block copolymer we have certain number of A's follows by certain number of B's again like certain number of A's and so on. And at last we have random or statistical copolymer which is like there is no particular order which means it is not like an alternating one or not like block one it can be for example 2, 3 A's then 1 B, then maybe 2 A's then may with 4B's there is no particular order in how they are arrange together. Then there are other types of copolymer like what is called a graft copolymer that is like you have the main chain of A's and then you have side chains of B's and so on.

There is another classification called terpolymer which will have 3 repeat units. So, finally we have discussed on the basis of classification i.e. Classification by origin, classification by structure and classification by composition.

Now we will look into last classification i.e. classification by phase- If a polymer is a solution, then the chemistry depends on what phase the polymer is present. It can be present as a solution it can be present as a blend, it can be present as a crystal, it can be like a gel and it can be like a melt and which we will discuss in detail what exactly do they mean and what implications they have on the polymer behaviour.

So, in this lecture we discussed about the ways to make a polymer chain, methods to make polymer chains, addition polymerisation and condensation polymerisation, characterize the average molecular weight and polydispersities of polymer chains and then finally we discussed the types and classifications of a polymer.

In the next lecture we will discuss what are the universal aspects which give rise to the polymer physics and what exactly we learn when we do the physics of these polymer. So, I want to conclude here. thank you.