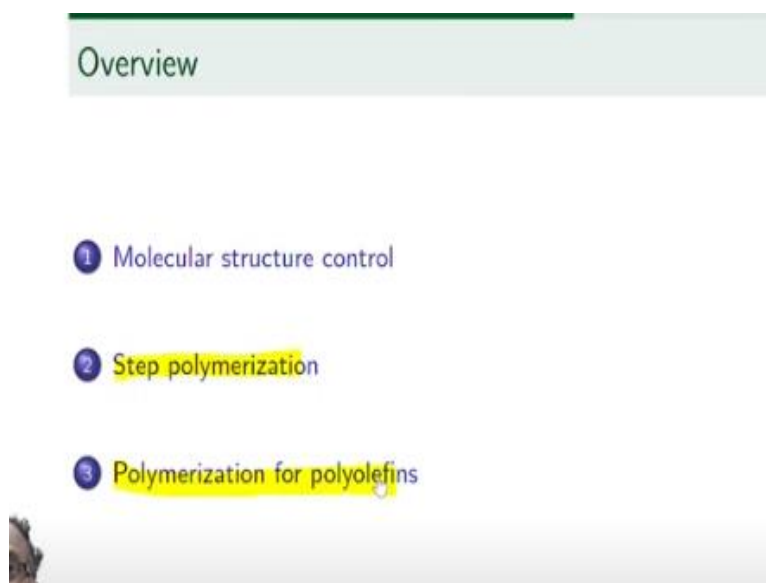


Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 06
Polymerization

Hello, welcome to another lecture on this course on polymers. This is the first week in which we are trying to answer the questions related to polymers and their unique features. In this particular lecture, we will look at some introductory aspects related to polymerization. And the focus in this lecture will be developing a conceptual framework.

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And we will do this by first trying to identify the requirement for structure control, and in this case, the molecular architecture, both qualitatively and quantitatively. And we will also look at two specific examples, which are textbook examples, common examples and they have been around with us for 100 years.

Of course, in the last two, three decades, there are several other types of polymerizations that have become more and more important. And especially from a sustainability point of view, there is a demand on a scientist to develop a set of polymerization which use different raw materials and also give us polymers which are far more precise in terms of molecular structure. But in this particular lecture, we will focus on the preliminary concepts.

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Goal of polymerization - control of molecular structure

- Polymerization of the target set of monomers
- Macromolecules with appropriate
 - Tacticity
 - Chirality
- Control of molecular architecture
 - Sequence
 - Branching, grafting
 - Other architectures - dendrimer, star polymer
 - Networking
- Quantitative control on
 - Molar mass (average), molar mass distribution
 - Segment length (average), segment length distribution
 - Branching density, length of branches
 - Number of generations in a dendrimer
 - Number of star-branches

So let us first look at what is the goal of polymerization and that is essentially, to control the molecular structure, both qualitatively and quantitatively. What do I mean by qualitative? It means, that it we the polymerization should be achieved with a set of monomers that we want polymerization to happen with.

For example, ethylene, propylene if have to be polymerized into a ethylene propylene rubber, then we need to be able to polymerize both ethylene and propylene together. And the macromolecules that we generate, need to have the appropriate amount of tacticity and chirality. In case you are not familiar with these terms, just go and search. And in your initial search itself, you will see lots of images, which explain what is meant by tacticity and chirality. These are related to the position of groups on a chain of macromolecule. And these are very important from the point of view of properties. So when a polymer is made, we need to make sure that it is isotactic, syndiotactic or atactic depending on the application or it needs to have a certain chirality.

We of course, need to be able to control the architecture. And there are several aspects of architecture that we have already discussed. It could be branching or grafting. It could be dendrimer. It could be a cross-link network. And of course, if we have different set of monomers, then the sequence in which the monomers come and so these are all the aspects that have to be controlled by a polymerization technique.

More effective polymerization that we have better control will be on these and of course, that we will quantify using some of the variables that we have already defined. For example, average molar masses or more importantly the distribution itself. And these days, the industrial polymerization process actually run so that we get the target molar mass distribution.

So the molar mass distribution in all its details in terms of number of macromolecules with i repeating units is not just a theoretical exercise to calculate average molar mass. What industries try to do is to calculate this online and then use that in their feedback control strategy, so that they obtain a precise molar mass distribution in their final product. And as we have repeatedly said, molar mass distribution defines the properties of the bulk sample.

In case of cross-linked sample, we will have to look at segment length, average segment length as well as the distribution. In case of branching, the number of branches, how many branches are there and also the length of these branches. Or in case of dendrimer for example, you might have number of generations and so on. So therefore, this is the canvas in which polymerization has to operate and provide us the precise molar mass, sequence, branching and all these features that we talked about.

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The slide is divided into two main sections. The top section, titled "Goal of polymerization - control of molecular structure", lists several objectives in a bulleted format. The bottom section, titled "GATE 2019", contains a multiple-choice question about the catalyst used for isotactic polypropylene.

Goal of polymerization - control of molecular structure

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GATE 2019

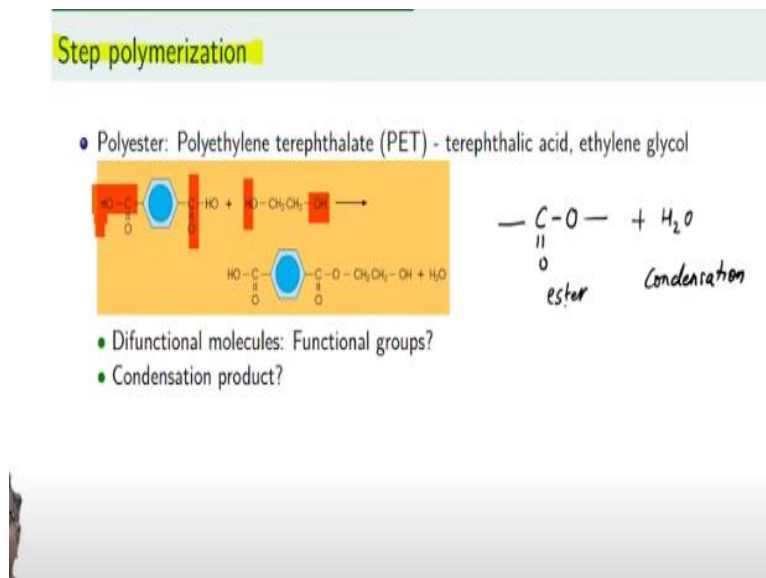
Which one of the following catalysts is used to prepare isotactic polypropylene?

(A) Alkyl lithium (B) BF_3
(C) Ziegler-Natta (D) AIBN

Just so that we are aware of a variety of polymerizations that are present, this question for example, is asking us what is a catalyst which is used for obtaining isotactic polypropylene. In fact, this is quite a significant development in history of polymerization, where the capacity to make isotactic polypropylene came about. I am sure most of you know the answer to this.

But this is to highlight which of the polymerization is needed if you want a specific type of macromolecule with a given qualitative and quantitative control.

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Let us begin by looking at example of step polymerization. Why do we call it step? Because in this case, monomer and monomer react, then a dimer is formed. Then dimer and monomer again react and trimer is formed and so on. So this is a reaction where an n-mer and m-mer is formed to give you n + m. And it is a reaction which happens step by step.

And how does this happen, because we have difunctional molecules. Molecules with two functionalities or two times reaction can happen. And that you can see here in this. There is a carboxylic acid on terephthalic acid, but there are two of them and there is ethylene glycol with two hydroxyl units. So each hydroxyl unit can react with one carboxylic acid.

And so the basic reaction that is happening in this is water molecule is taken out and this you would be familiar with and then an ester bond is form. So this is the ester bond and then the condensation product. So many times this polymerization is also called condensation polymerization. In fact, it was this polymerization based on which the idea of macromolecule was established on a firmer footing.

Can you think why is this? Why is it more difficult to figure out what is the molecular weight of polyethylene and whether ethylene is caught covalently bonded with each other, ethylene molecule and form polyethylene. Why is that more difficult to

establish as compared to polymer in this case or macromolecule where carboxylic acid and hydroxyl keep on reacting?

If you can think of carboxylic acid and titration you might be able to find an answer to this question. So what we have in this case are molecules with some functionality, in this case difunctionality. And these molecules when they react, we form the macromolecule. And it is called step because each time there is a reaction between n-mer and m-mer.

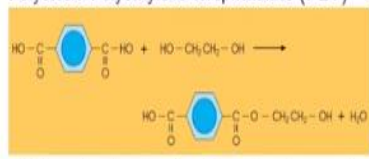
In case of olefinic polymerization or catalytic polymerization, what we will see is an active center is formed, and monomer keeps on getting attached to it. So it is also called a chain polymerization. So once the chain starts, it can keep on growing. But this is called step growth, because every time each monomer and each polymer can react with each other, and they slowly start reacting and building.

In this case, right in the beginning, you cannot have a macromolecule with very long length because monomer has to react with dimer. Dimer has to react with trimer. Trimer has to react with trimer and that is how in steps the molar mass increases. In case of the chain polymerization once an active center is formed, once a catalyst or free radical is formed immediately monomer can start attaching and then form a chain.

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Step polymerization

- Polyester: Polyethylene terephthalate (PET) - terephthalic acid, ethylene glycol



- Difunctional molecules: Functional groups?
- Condensation product?
- Extract from Technical data sheet of SABIC PET PCG 60
a low molecular weight polymer made by continuous melt-phase polymerization process followed by solid-state polymerization. This grade exhibits easy flow ability which benefits thin walled injection molding process.
- Step polymerization with **no condensation product** - polyurethane synthesis

So therefore, the distribution in each and every case depends on the polymerization method. So this is just to highlight how a molar mass distribution and a polymerization method is important and this is taken from a trademark literature from

one of the companies SABIC in this case, where you can see that how they are highlighting what is the different types of polymerization being used.

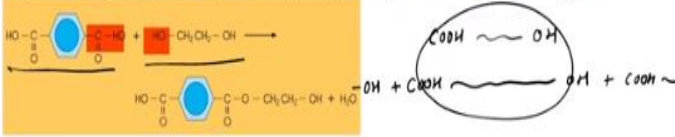
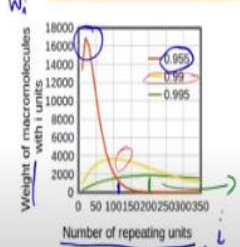
So a melt-phase polymerization followed by solid-state polymerization and therefore, this grade of polyethylene terephthalate that we are discussing it allows easy flow ability. So clearly in this case by manipulation of polymerization techniques, they are able to manipulate and get a target molar mass distribution which can ensure flow ability and therefore good molding characteristics and of course appropriate mechanical properties for the eventual application.

Just to remind you that step polymerization generally has a condensation product, but we also have an example of a condensation step polymerization reaction of polyurethane where there is no condensation product. You can go and look up and find out what is the reaction scheme for polyurethane.

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Step polymerization

- Polyester: Polyethylene terephthalate (PET) - terephthalic acid, ethylene glycol

Slow build-up of higher molecular weight polymers

- Successive reactions of functional groups, hydroxyl and carboxylic
- Analysis in terms of extent of reaction, p

$$p = \frac{\text{Number of functional groups reacted}}{\text{Number of functional groups initially present}} \quad (1)$$

Now this is just to give you an idea of how the molar mass builds slowly. And we already talked about that reaction between carboxylic acid and hydroxyl group is what is taking place and whenever two molecules react in the end, the as soon as this reaction happens one time, what we will get is COOH on one side and the other side OH. And then one more reaction can happen and so on.

So therefore in the end, you will start getting macromolecules which are longer and longer and so the macromolecule can keep on growing. So we can keep track of what is the progress of polymerization by defining a variable called extent of reaction. And this is a ratio of number of functional groups which have reacted to number of functional groups which were initially present.

So if I tell you the number of moles of each of the monomers that were added, then you can know the, what is the number of hydroxyl group added and number of carboxylic group added. And now if the groups are disappearing, which means, the reaction is taking place and you have macromolecules being formed. And therefore, this ratio is very useful.

And as I mentioned in this case, there is a successive reaction of functional group between hydroxyl and carboxylic acid groups and therefore, there is a slow buildup of molar masses. And in this what I have done is plotted the number of repeating units. If you recall from our lecture on molar mass and molar mass distribution, lecture number 5, you know that the x axis is i , the number of repeating units.

And this is now the weight of macromolecules with i unit. Can you identify what was the variable that in the fifth lecture, we have defined this as? You can go back and try to convince yourself that this is W_i . So what you can see is if the reaction has gone up to 95.5% which means, the extent of reaction is 0.955. So the number of functional groups which have reacted is 95.5% and even then, pretty much macromolecules contain only 20 or 30 repeating units largely.

Of course, there are some macromolecules, maybe about 500 weight is there with 120 repeating units and so on. But you can see that it is the smaller fragments are still there. So if the reaction happens for 99%, then we have at least more macromolecules with higher molecular weight. And the green curve here, as you can see, indicate definitely molar masses which are much higher. So in this case, the maximum molar mass is somewhere around 200 repeating units. So you can see that the reaction has to go to 99.5% and then only macromolecules with significantly high molar masses appear. And that is why this is also called a step polymerization.

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Polypropylene/polyethylene polymerization

Active centers: free radical, ion (cation or anion), catalyst site; Activated monomer (M^*)



We will have more time in the lecture on polymerization, depolymerization, upcoming lecture, where we will look at the molar mass distribution in little more detail. Let us look at the other type of polymerization which is for polyolefins. And it is quite commonly used for polypropylene and polyethylene type of polymerization. And we will call them as polymerization in which active center is formed.

So ethylene molecules just being together, do not start polymerizing with each other. In the other case, with carboxylic acid and hydroxyl group, reactions can happen and polyester can form. In this case, ethylene molecule is a molecule which is unreactive. So therefore, it has to be activated and that is what we mean by active center. And activation can happen through multiple means.

There can be a free radical and in fact, some of the earlier discovery of polystyrene or polyethylene is related to formation, accidental presence of free radicals. And oxygen for example is a radical which can be present in many times and so that causing polymerization and a liquefied ethylene or a high pressure styrene giving you a solid mass of polyethylene or polystyrene. These days a lot of polymerizations are done using catalysts. So the active center in this case is a catalyst site. Or we can also have ionic polymerization and both negative ions or positive ions. Anionic polymerization or cationic polymerization are possible. So in each of these case, if M is the monomer, then M^* is the species which is required for polymerization to happen. So a mixture M together as I said, will not polymerize.

So generally, a monomer plus active center give rise to an activated species. And then this activated species can start reacting with other monomers which are present and

the chain can start growing. So basically an active center with N number of monomers can react with another monomer to form and N + 1.

So clearly you can see in this case that as soon as an active center appears, a chain can start building along that active center and there are a lot of monomers which will still be floating around. So even with low extent of polymerization in this case, we can have some high molar mass molecules appearing in the sample.

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Polypropylene/polyethylene polymerization

Active centers: free radical, ion (cation or anion), catalyst site; Activated monomer (M^*)

$$M + \text{Active center} \rightarrow M^* ; M^* + M \rightarrow MM^* ; \sim M_N^* + M \rightarrow \sim M_{N+1}^*$$

- Free radical polymerization
 - Branched polyethylene - Low density polyethylene (LDPE)
 - Atactic polypropylene
- Catalytic polymerization
 - Ziegler Natta polymerization
 - Polyethylene with controlled branching - linear low density polyethylen (LLDPE), high density polyethylene (HDPE)
 - Isotactic polypropylene
 - Metallocene polymerization
 - High density polyethylene (HDPE)
 - Narrow molecular weight distribution

So free radical polymerization generally is used to get branched polyethylene. And in fact, most of the earlier polyethylene which was produced was low density polyethylene. And as we mentioned in our introductory lecture, that this is where branches are much larger and also number of branches are high. And if polypropylene polymerization is done using free radical, then we get atactic polymer.

And properties of atactic polymer are inferior compared to isotactic polymer. And that is why I have said that the ability to polymerize polypropylene into isotactic polypropylene was quite a groundbreaking discovery. And that discovery was using Ziegler Natta catalysis. So Ziegler Natta catalysis can be used to make isotactic polypropylene. It is also useful to make largely linear polyethylene which is high density polyethylene.

Over the last two decades, many commercial polymerization use other sets of catalysts which are called metallocene. And so in this case, very long macromolecules with very high molar masses with polyethylene are possible and also the distribution is quite narrow. And this is something which we will see later on also that if distribution as we said, can be counted as N_i as function of i .

Then this is what I have given an example is a broad molecular weight distribution or molar mass distribution. Alternately, we can also have just this and no other molar masses. So this is a much narrower molar mass distribution. So therefore, narrow or broad molar mass distribution are very important in terms of determining the overall properties of polymer sample. And it is useful to have polymerization method using metallocene which can produce molar mass distribution which is very narrow.

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For further understanding, and knowledge

NPTEL course on
Principles of Polymer Synthesis
by
Prof Rajat K Das

GATE question on Slide Number 3 : Answer (C) Ziegler-Natta



In this particular course, we will spend only couple of lectures on polymerization. But there is a full-fledged course on in NPTEL on polymerization and so those of you who want to learn much more about polymer synthesis and polymerization process should look at the NPTEL course called Principles of Polymer Synthesis.

And this is very useful for getting to know all the details of the catalyst methods, the free radical methods, the other all the methods of polymerization that are useful to produce macromolecules. And just to remind you about the answer about isotactic polypropylene, this is Nobel laureates. In fact, you can go and look up the Nobel Prize winners, which have worked in the area of macromolecules.

And you will see that every decade or so there is always a Nobel Prize winner based on significant achievement in macromolecular science and its application. So with that, we will close this lecture, and we will continue our journey, learning about polymers with lecture number 7 later on. Thank you.