Simple Concepts Related to Single Macromolecules
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Lecture - 09
Polymerization / Depolymerization

Hello and welcome to week 2 of the course on polymers. In this week, we are going to discuss properties of a single macro molecule. Before we get on to doing the discussion of the properties, we are looking at some sustainable aspects of polymeric systems. And we will look at in this lecture at polymerization and depolymerization in the context of sustainability.

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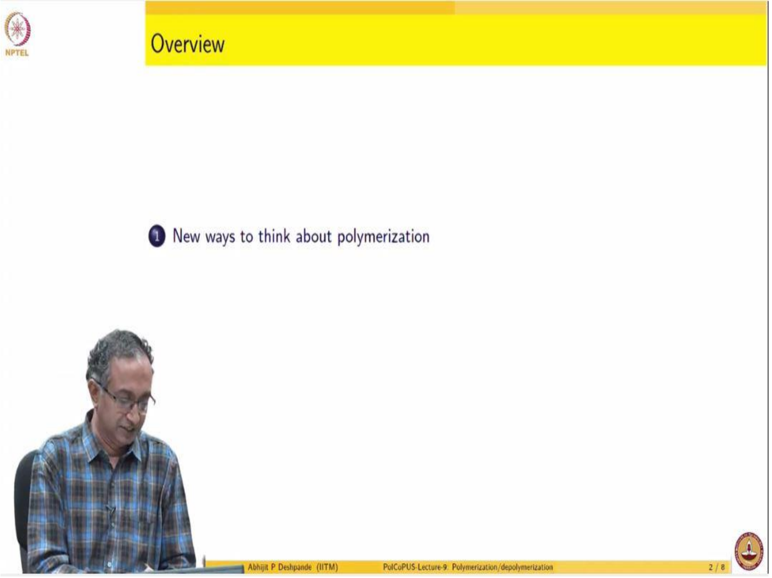

Overview

1. New ways to think about polymerization

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And, this lecture is again also going to be more about thought process and the challenges that are with us and possibilities that can be exploited. So, the focus will be on how do we think in terms of new ways of polymerization and depolymerization.

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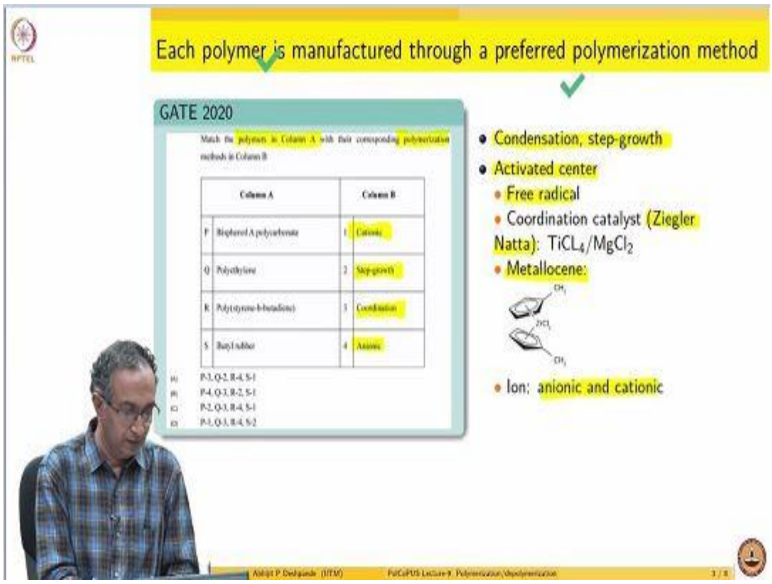

Each polymer is manufactured through a preferred polymerization method

GATE 2020

Match the polymers in Column A with their corresponding polymerization methods in Column B

Column A		Column B	
P	Bisphenol A polycarbonate	1	Cationic
Q	Polyethylene	2	Step-growth
R	Poly(styrene-b-butadiene)	3	Coordination
S	Butyl rubber	4	Anionic

(A) P-3, Q-2, R-4, S-1
(B) P-4, Q-3, R-2, S-1
(C) P-2, Q-3, R-4, S-1
(D) P-1, Q-3, R-4, S-2

- Condensation, step-growth
- Activated center
  - Free radical
  - Coordination catalyst (Ziegler Natta): $TiCL_4/MgCl_2$
  - Metallocene:
  - Ion: anionic and cationic

Just to begin with, let us look at this exam question. In fact, very recent - this year's exam question, where we have to look at a polymer and its corresponding polymerization. So, of course, for each polymer, we have a preferred polymerization method. And this is because, it gives us control over all the aspects that we discussed in earlier lectures in terms of molar mass, molar mass distribution, in terms of molecular architecture, in terms of sequencing, etc.

So, whatever are the features needed in an eventual macro molecule? If they can be achieved using a given polymerization method, then it becomes preferred for that particular polymer. So, in this particular question for example, you can think in terms of the possibilities that are mentioned - coordination polymerization. I hope you can recall what is meant by coordination polymerization. What are examples of coordination polymerization? There are 2 examples of ionic polymerization - cationic and anionic.

And then of course, we spent time in the sixth lecture thinking about step growth polymerization, we looked at an example of polyester, where an acid and alcohol reacted. So, among these polymers which are mentioned, which one might have these reaction where there is a condensation product involved? So, I am sure you can rule out polyethylene and maybe that is why, for example, it is like next to step growth. And so Q 2 is definitely not an option. And so, what are the possibilities that you can think of?

So, ponder over this while the other thing that we have of course classified in the polymerization processes, we said that step growth is an important class of polymerization by which many polymers are made. The other broad class we looked at was in terms of activated center, where a monomer by itself does not react, but in combination with an initiator or a catalyst it does. So, the example of activated species could be free radical or ions or it could be catalytic.

And we have already seen that Ziegler-Natta is very important in terms of making polyethylene and polypropylene and so, it is an important discovery in terms of having good control on polymerization. In the last 20 years or so, we also have Metallocene as an important class of materials which are important for manipulating and having narrow molar mass distribution and controlling branching and so on. And you can see the highlight here that I want you to pick up is in terms of stereochemistry.

In terms of what is the arrangement given a certain set of interactions that are possible with the 3 dimensional structure of this catalyst, then monomers can come only in a particular way and get attached. And therefore, using these catalysts with a coordination catalysts or Metallocene catalyst stereochemistry is managed in such a way that you get very good control on whatever is the polymerization product that is available. So, you get control on the whether branches form or not, whether which type of facticity is obtained and so on.

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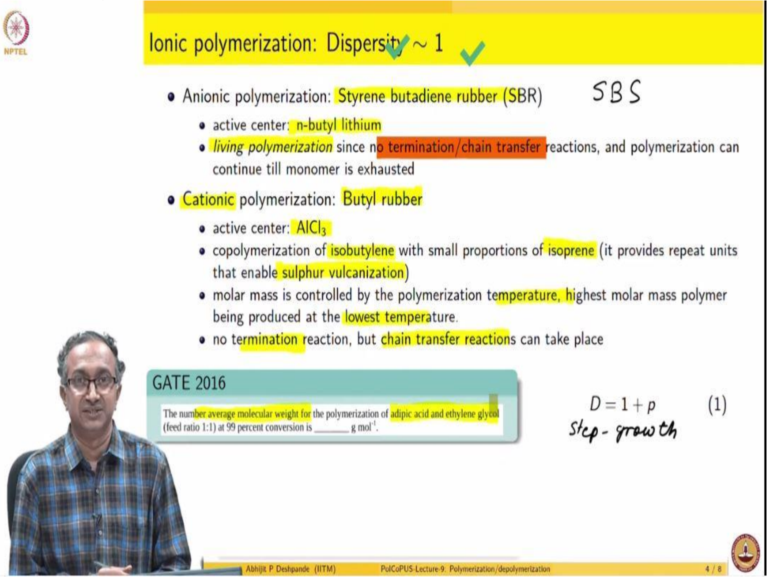

Ionic polymerization: Dispersity ~ 1

- Anionic polymerization: Styrene butadiene rubber (SBR) SBS
  - active center: n-butyl lithium
  - *living polymerization* since no termination/chain transfer reactions, and polymerization can continue till monomer is exhausted
- Cationic polymerization: Butyl rubber
  - active center: $AlCl_3$
  - copolymerization of isobutylene with small proportions of isoprene (it provides repeat units that enable sulphur vulcanization)
  - molar mass is controlled by the polymerization temperature, highest molar mass polymer being produced at the lowest temperature.
  - no termination reaction, but chain transfer reactions can take place

GATE 2016

The number average molecular weight for the polymerization of adipic acid and ethylene glycol (feed ratio 1:1) at 99 percent conversion is _______ g mol^{-1}.

$$D = 1 + p \qquad (1)$$

Step-growth

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So, we will just look at ionic polymerization before we start looking at new ways of thinking about polymerization. The advantage of ionic polymerization is that dispersity which is the ratio of weight average molar mass to number average molar mass can be close to 1, 1.05, 1.07,1.1. Such polydispersity indices are possible when we use ionic polymerization and this is commercially exploited also. So, two most important examples of ionic polymerization are in terms of rubbers.

So, we use for styrene systems, anionic polymerization and it is used for styrene-butadiene rubber, it is also used for another important copolymer of styrene which is SBS. So, there will be minor differences in terms of how the sequencing of monomers is. The monomers here are styrene and butadiene. So, in this case, the active center is through anion which comes from butyl lithium. And this class of polymerization is also called living polymerization.

And in fact, that is the reason why control on molecular weight is so common and dispersity is obtained to be low. What happens in this case is a monomer comes and attaches to the active center and the active center will live as long as monomer is alive the reaction stops in the end active center is still alive, but there is no monomer to react. And also there are no side reactions which can cause the polymer to become a dead end.

So, for example, 2 chains combine which is called a termination step that is not possible here. Or chain transfer - a growing chain suddenly becomes transferred some of its chain mass to another growing active center. So, such chain transfer reactions are also not possible. So, therefore, given that these reactions, which are leading to molar mass distribution, being wider are not there in this case, and secondly, all the monomer can get attached to actives centers we get very good control on molar mass distribution.

The other common example of ionic polymerization in this case cationic polymerization through active center of aluminum chloride is butyl rubber. And in this case, though it is a butyl rubber based on isobutylene for commercial systems, small amounts of isoprene is added. Of course the answer is there on the slide, but, before you look at it think why isoprene is added given that we already discussed about isoprene being part of natural rubber.

And of course, it is because you can cross link it with sulfur. So, in this case, molar mass is controlled by temperature. And depending on temperature, we can get molar mass very high or low. And in this case also, termination reactions are not feasible, but chain transfer reactions can take place and therefore molar mass distribution is not going to be as narrow as in case of anionic polymerization. Just to contrast the kind of dispersity that we get in ionic polymerization, this is the dispersity that you can obtain in step growth.

$$D = 1 + p$$

And if you remember p is the extent of reaction - its the number of functional groups that have reacted to the total number of functional groups that were present initially. So, if you have a 99% reaction D is going to be 1.99. So, you can see that dispersity in this case is going to be close to 2 when the reaction goes to completion. As p approaches 1 reaction goes to completion. So, therefore, D can be 2 when the reaction is complete.

So, therefore, the dispersity in step growth polymerization is always going to be closer to 2, while in ionic polymerization you can get very close to 1 and so, this is one of the advantages of an ionic polymerization. So, this question here from the exam is asking us to calculate the number average molar mass. And so given that, this is the example of PET synthesis. This is based on a very simple theory of Carothers.

Where we can find out quickly what is the molar mass as a function of extent of polymerization. So, I want you to pause here and try to solve this problem before you go further. But this is just to contrast the difference between what is step growth and ionic polymerization.

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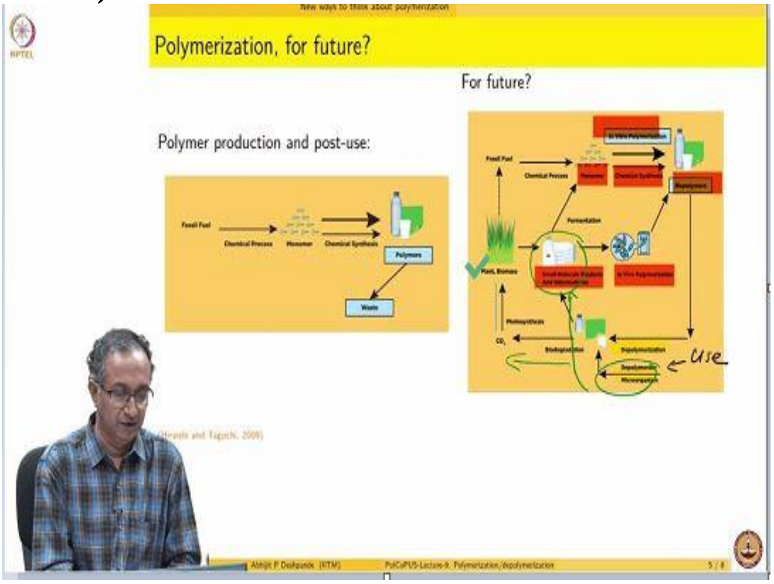

New ways to think about polymerization

Polymerization, for future?

For future?

Polymer production and post-use:

(Hiraishi and Taguchi, 2009)

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Let us look at new ways of thinking about polymerization. Just pause and think what is the current way? How do we do this now? So we currently we use fossil fuel and we use several synthetic processes to get monomers and these monomers are polymerized to get polymerization and several plastics and rubbers and FRP are made. And once the use is over, we end up with lot of waste. So this is the current paradigm that we think is what has led to so many questions being raised about plastics as sustainable material.

So now can we think of a way in which this looks like a cyclic process? And so, this is based on the reference that is cited here at the end of the lecture and also give you the complete reference if you are interested, you can go and look further (Hiraishi and Taguchi, 2009). So, we have plant and biomass as a renewable resource as we discussed in the last class already. So can we not keep that and keep a cyclic process in which from which we first get some small molecules, we could also use these to make monomers.

Then, once monomers are there we could either use in vitro polymerization, which means in a lab with enzymes and other catalysts processes, but not in a bacteria or any other biological resource. And we can use chemical synthesis to get the polymers. And then the other possibilities we can get small molecules and we can also do bacterial synthesis the way we discussed in the previous lecture on renewable resources and again get polymers and once the use is done,

So, once the use is done, post use, we can again very importantly, think in terms of depolymerization using catalyst, such as enzymes, depolymerase or microorganisms. And then what we end up with is smaller fragments of molecules. So, from using these two, we can again get small molecules or we can eventually lead to biodegradation to carbon dioxide and water. And of course, this can again be reused, the carbon dioxide can be again photosynthesize, by and to get plant and biomass, some of the small molecules can again be reused.

So, you can see that now, this is a cyclic process, where, from raw materials to post use we have closed the cycle. So, can we think of many of the polymeric systems that we are using can belong to such a cyclic process? And, that is the challenge that we have in terms of sustainable polymers.

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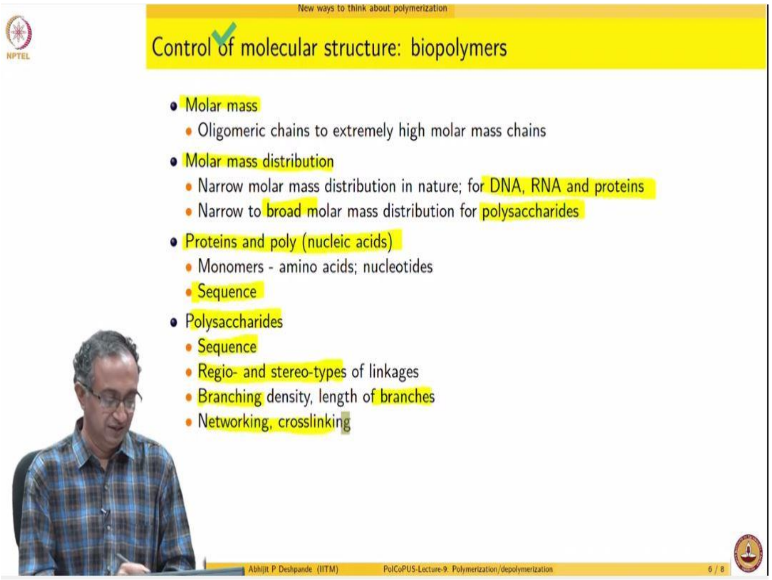

New ways to think about polymerization

Control of molecular structure: biopolymers

- Molar mass
  - Oligomeric chains to extremely high molar mass chains
- Molar mass distribution
  - Narrow molar mass distribution in nature; for DNA, RNA and proteins
  - Narrow to broad molar mass distribution for polysaccharides
- Proteins and poly (nucleic acids)
  - Monomers - amino acids; nucleotides
  - Sequence
- Polysaccharides
  - Sequence
  - Regio- and stereo-types of linkages
  - Branching density, length of branches
  - Networking, crosslinking

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So, just looking at what are the challenges when we think of polymerization processes for biopolymers and natural polymers these are the examples of what are the strategies available in terms of control of molecular structure. So, of course, molar mass itself is controlled and in nature we have examples of oligomeric unit, which means small number of repeating units all the way to extremely high molar mass chains.

So, therefore, synthesis can be done to make very small number of repeating units to extremely large number of repeating units and also there is very nice control on molar mass distributions. And in fact, we get uniform or mono dispersed polymers for various biopolymers. On the other hand, we also have examples of polysaccharides, where broad molar mass distribution is also feasible. We will see that for some of the applications a broader molar mass distribution is desirable.

As I have mentioned this earlier also smaller molar mass present in a sample usually is good for processability from point of view of managing the rheological properties and viscosity in melt conditions. So, therefore, it is from properties point of view narrow molar mass distribution may be always desirable, but from processing point of view sometimes smaller molar mass weight fraction may also be important.

So, as far as proteins and poly nucleic acids are concerned, the control required is in terms of sequence, we have a set of monomers which are amino acids and nucleotides and they have to be stitched together in a particular sequence. When it comes to polysaccharides not only do we have sequence we also have variety of features in terms of geometric linkages. There is a very good diversity and this is something which we will look at later in the course.

There is a diversity of linkages which are possible. If you look at cellulose, starch, pectin - all of these are polysaccharides but they have very different properties. And that is because of the diversity of monomers as well as diversity of linkages, which are present in these kind of polysaccharides. And with polysaccharides, we also have possibility of branching and networking and cross linking. So, therefore, in biopolymer world itself, all the features that we have thought of in terms of synthetic molecule or architecture is present. Now, can this be exploited in terms of polymerization techniques for making new set of polymers? So, that is the question that is broadly in front of us.

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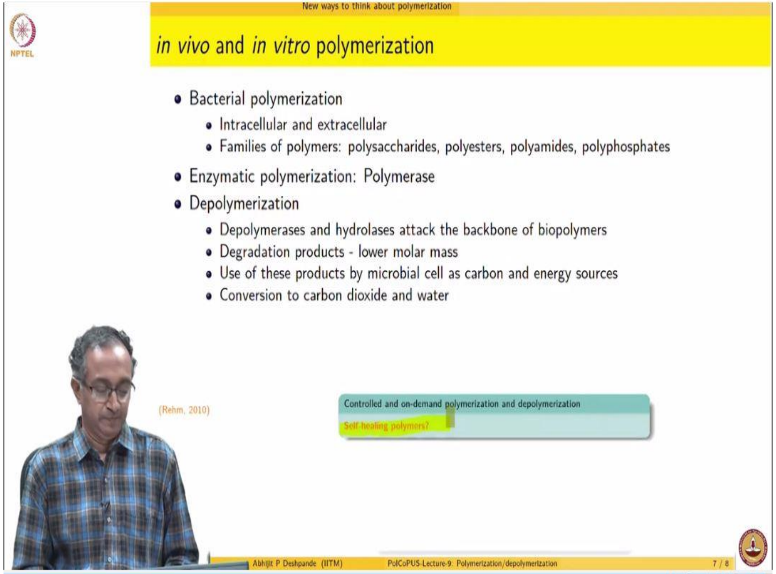

New ways to think about polymerization

in vivo and *in vitro* polymerization

- Bacterial polymerization
  - Intracellular and extracellular
  - Families of polymers: polysaccharides, polyesters, polyamides, polyphosphates
- Enzymatic polymerization: Polymerase
- Depolymerization
  - Depolymerases and hydrolases attack the backbone of biopolymers
  - Degradation products - lower molar mass
  - Use of these products by microbial cell as carbon and energy sources
  - Conversion to carbon dioxide and water

(Rehm, 2010)

Controlled and on-demand polymerization and depolymerization

Self-healing polymers?

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And so, to address that, generally we can think of these 2 sets of techniques in-vivo polymerization in which case we use bacterial polymerization or in-vitro polymerization, in which case we can use some enzymes as the catalyst that can be used for polymerization. And in case of bacterial polymerization, we have polymers produced within the cell also and produced in the cell, but then they are excreted out of the cell - so, extracellular polymers.

And there are 4 families of polymers which are made by bacterial cells. So, polysaccharides is something which we have discussed quite a bit already in this course, polyesters as well, polyhydroxybutyrate - the example that we saw in the last lecture is an example of a bacterial polymer, which is made by using in-vivo polymerization. Bacterias can also make polyamides and polyphosphates.

So, these broad classes of polymers that are made. Of course, remember the challenges. We are talking about synthetic polymers, which are families of polyolefins which are families of polyimides which are families of poly ether. So, we are talking about families which are much larger set of families compared to what these are. Now, the question is can these families of polymers produce a set of properties that are already known to us?

For example, Teflon as a very good engineering material. Can any of the polymers which is made using such techniques become and have properties like Teflon? And now, of course, the answer is no. And that is where the challenge lies. So, the other thing which makes this a cyclic process, these many of these polymers that are made using these strategies is the fact that depolymerization is possible.

And depolymerization is possible because of these enzymes, which attack the macro molecule and lead to chain scission or breakage of macromolecules. And, once the smaller fragments of degradation products are available, these will be lower molar mass in smaller fragments. And so these can be then used by microbial cell as carbon and energy source, just the way glucose or other sugar sources are used by cells, they can use these other smaller fragments, which are coming from degradation of macromolecules.

And once this happens then eventually we have carbon dioxide and water. So, from macro molecule we can go to carbon dioxide and water. So, therefore, in vivo and in vitro polymerization has the capacity to give us macromolecules of a limited set of families presently, but the advantage is that you can close the cycle. Now, can this be done for larger set of polymers? And can we get engineering applications out of such polymers? That is a question to think of.

The other challenging aspect that leads us to research and possibilities is in terms of controlled polymerization and depolymerization. So, on demand, if we can polymerize something or depolymerize something, that is something like natural body. And another important example from body is self healing, when we get a cut or a wound, it heals itself. So, is it not possible in engineering domain that it we get crack on the material can the crack not heal itself?

And so, if we have this ability of on-demand polymerization, it may be possible to develop what are called self healing materials. And there are some examples of demonstrations, but this is a very important area of research in terms of trying to see if we can get self-healing polymers in terms of engineering materials which are very promising to use because of the ability of not leading to catastrophic failure. But, due to self-healing, they can remain functional and eventually we can replace it before a failure or an accident can happen.

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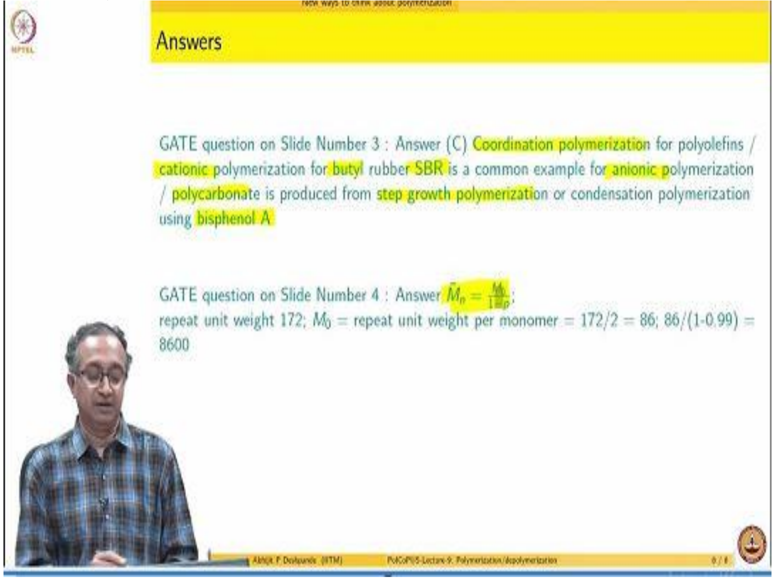

Answers

GATE question on Slide Number 3 : Answer (C) Coordination polymerization for polyolefins / cationic polymerization for butyl rubber SBR is a common example for anionic polymerization / polycarbonate is produced from step growth polymerization or condensation polymerization using bisphenol A

GATE question on Slide Number 4 : Answer $\bar{M}_n = \frac{M_0}{1-p}$;
repeat unit weight 172; M_0 = repeat unit weight per monomer = 172/2 = 86; 86/(1-0.99) = 8600

So, with this thought we can just close this lecture in terms of the questions to the answers that were posed. I hope all of you recognize that Ziegler Natta is an example of coordination polymerization and it is used for polyolefins. SBR is common example of anionic polymer while cationic polymer is butyl rubber and polycarbonate is produced by step growth polymerization using bisphenol-A. So, one of the things that you can think of is, you know, do I have to memorize all of these things?

And my answer would be no you have in terms of develop a judgment and skill in terms of recognizing the patterns. So in case of polyolefins, you have to remember that we think in terms of control of branching, control of isotactic or tacticity. So we talking about some geometric feature, and therefore a coordination catalyst. That is why it is called coordination. So, there is some pattern in the way nomenclature is and what. So, you have to try to remember the underlying ideas of polymerization synthesis.

And it will become natural in terms of what the polymerization technique is. And of course, in terms of step growth polymerization, this is a simple formula to calculate the molar mass average molar mass for a step growth polymerization.

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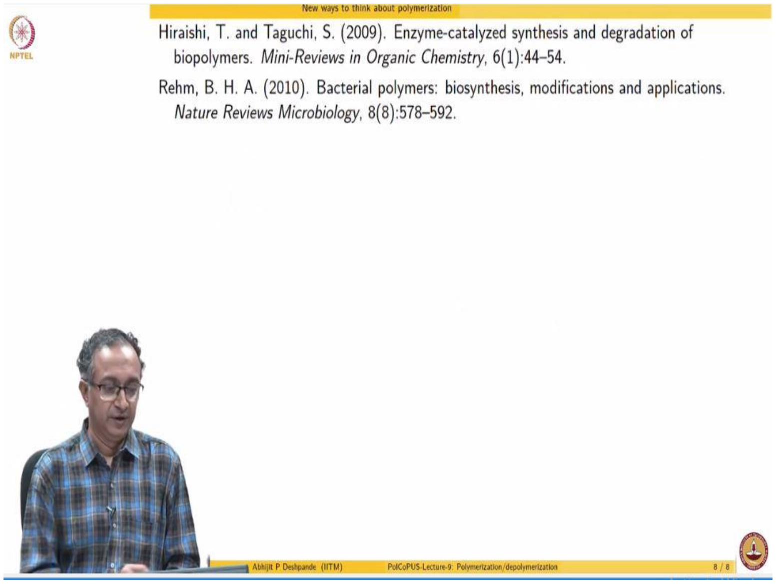

New ways to think about polymerization

Hiraishi, T. and Taguchi, S. (2009). Enzyme-catalyzed synthesis and degradation of biopolymers. *Mini-Reviews in Organic Chemistry*, 6(1):44–54.

Rehm, B. H. A. (2010). Bacterial polymers: biosynthesis, modifications and applications. *Nature Reviews Microbiology*, 8(8):578–592.

So, with this, we will come to a close on this lecture, which is related to thinking about sustainability of polymeric systems. Thank you.