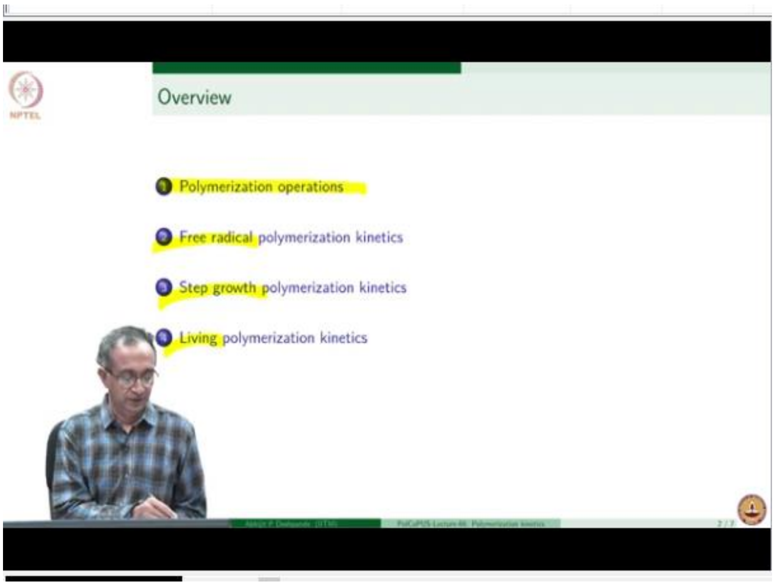
Polymers: Concepts, Properties, Uses and Sustainability
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology-Madras

Week 9
Polymer Processing and Recycling Techniques

Lecture-66
Polymerization Kinetics

Hello, welcome to the course on polymers in which we are looking at concepts and applications as well as looking at properties and sustainability. In this week we are looking at polymer processing and the later part of the lectures will also talk about the recycling techniques and what are the processing techniques which are available when we talk of recycling of macromolecular systems. This particular lecture we will look at polymerization kinetics what we will see is some polymer processing operations there are reactions also. Generally we know that polymerization is done in a synthesis plant and then polymer processing is done. But there are several other contexts in which polymerization is a general phenomenon which is observed. So, therefore we will quickly look at where all polymerization processes are involved. And then try to see some mechanisms associated with these polymerization processes.

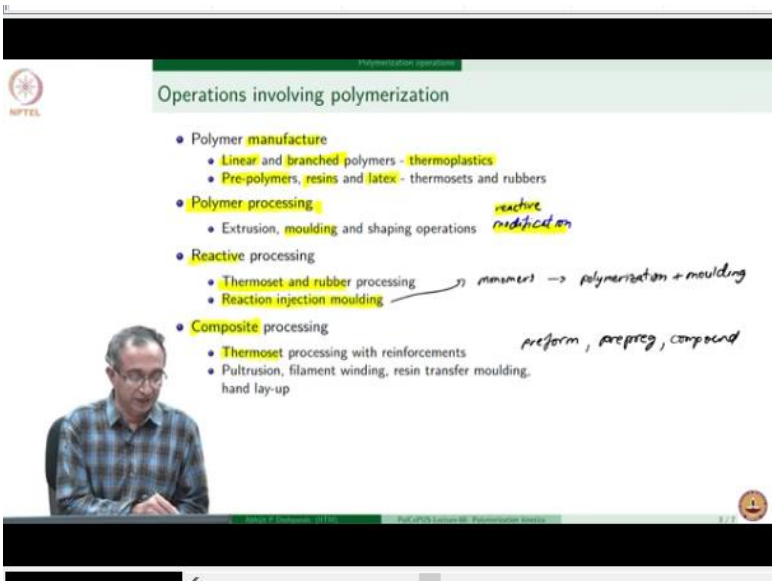
(Refer Slide Time: 01:14)



Overview

1. Polymerization operations
2. Free radical polymerization kinetics
3. Step growth polymerization kinetics
4. Living polymerization kinetics

So, our focus will be on concepts related to polymerization , we will do a survey of where all polymerization are involved and then look at kinetics of 3 different processes, free radical polymerization, step growth polymerization and living polymerization. **(Refer Slide Time: 01:35)**



Operations involving polymerization

- Polymer manufacture
  - Linear and branched polymers - thermoplastics
  - Pre-polymers, resins and latex - thermosets and rubbers
- Polymer processing
  - Extrusion, moulding and shaping operations
- Reactive processing
  - Thermoset and rubber processing
  - Reaction injection moulding
- Composite processing
  - Thermoset processing with reinforcements
  - Pultrusion, filament winding, resin transfer moulding, hand lay-up

reactive modification

monomers → polymerization + moulding

preform, prepreg, compound

So, let us first look at where polymerizations are involved and that is of course in the stage where polymer is getting manufactured or a polymerization industry and this belongs to 2 different classes where we manufacture the overall polymer itself when we are making the thermoplastic and these will be linear or branched polymers and in case of thermosets or rubbers the manufacturers which are creating they will create actually a formulation. They will create what is called either a pre-polymer or a resin or a latex. Latex is a term especially used in case of rubber like materials. Latex also implies that it is a 2 phase system, there is a polymer rich phase and then there is a solvent and so in case of rubbers for example this latex is prepared and then finally where the part is being produced shaping as well as cross linking reactions specifically are carried out.

So, in case of thermosets and rubbers because cross linking reactions will determine the shape, shaping and cross linking has to be done together. So, in that case we prepare only a pre-polymer or what is called a resin. We use resin as a term because viscosity is high but not very high. So, these materials can still flow and are amenable to shaping. So, this is a 2 broad class of polymerization processes. In one case we do the polymerization and then do only processing. In the other case we do some amount of polymerization to make the resin or pre-polymer or latex and then finish the polymerization and cross linking processes during manufacture of the part or fabrication of the part. In then of course we have the polymer processing and in polymer processing generally we only have extrusion molding operations.

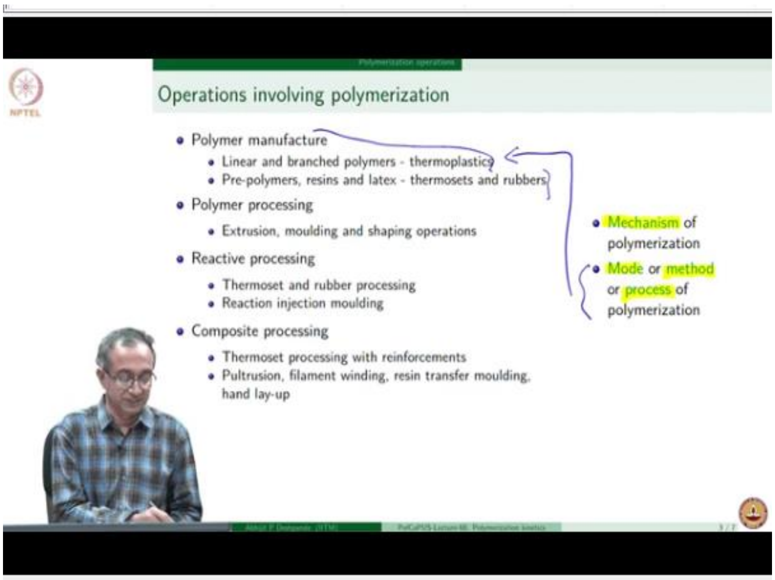
However, we could have modifications being done at this stage. So, we could add a compatibilizer which is a reactive compatibilizer, we could add some amount of branching in a polymer and so some reactive modifications can be done in this case which can lead to some amount of polymerization, some cross linking may also happen, it could be desirable at times but it could be undesirable also. So, depending on especially in the context of recycling of polymers many of these reactions may take place. The other of course is the reactive processing itself. So, as I mentioned for thermoset and rubber processing definitely involves polymerization cross linking reactions. But we also have process such as reaction injection molding. So, injection molding is a generally shaping operation.

And where we only are involved with flow and some amount of reactive modification but reaction engineering injection molding is where we start with monomers and carry out polymerization and molding simultaneously. So, reaction injection molding therefore combines both of these and in case of composites since we have this task of incorporating fibrous preforms into the polymer quite often we do it with thermoset materials. So, again we use free polymers or resins and sometimes we do it in 2 different ways, we first premix the pre-polymer or resin with the reinforcement and then prepare a preform or a prepreg or a compound what is called a compound and then we freeze it, we keep it under low temperature conditions. So, that polymerizations cross linking reactions do not complete and then this prepreg, preform or compound is taken and then finally molding is done. So, that shaping as well as cross linking reactions can happen simultaneously.

Similarly there are various composite processing equipment where we actually will start with the fiber and then dip the fiber in the resin bath and then actually have the coating and then the fiber is wound on something or fiber along with resin is passed through a dye. So, if it is passed through a dye then we call it pultrusion and C sections and I beams and all of those are made very easily using this technique.

Filament winding is where we take the resin fiber together and we wind it as the name suggests. So, there are different types of processes and all of these cases polymerization is essential part of the processing operation to get the final part.

(Refer Slide Time: 06:33)



Operations involving polymerization

- Polymer manufacture
  - Linear and branched polymers - thermoplastics
  - Pre-polymers, resins and latex - thermosets and rubbers
- Polymer processing
  - Extrusion, moulding and shaping operations
- Reactive processing
  - Thermoset and rubber processing
  - Reaction injection moulding
- Composite processing
  - Thermoset processing with reinforcements
  - Pultrusion, filament winding, resin transfer moulding, hand lay-up

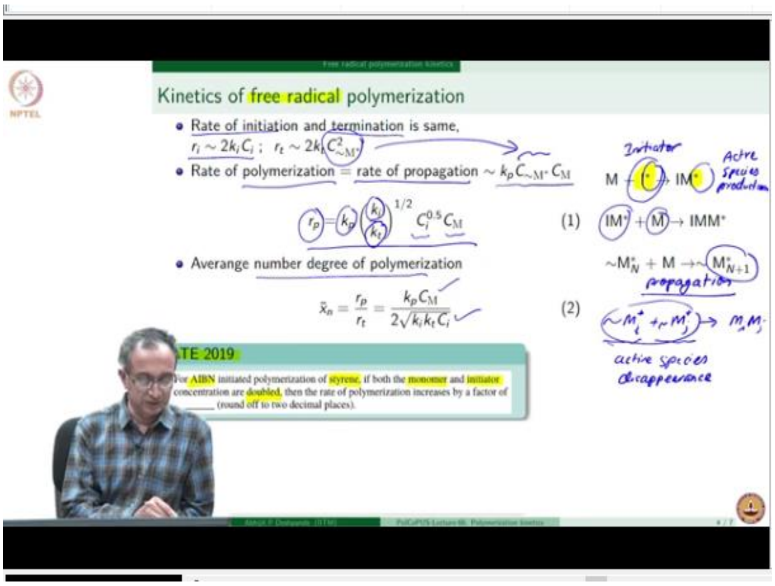
- Mechanism of polymerization
- Mode or method or process of polymerization

In terms of the polymerization process there are 2 aspects which will be of interest to us. One is what is the mechanism of polymerization? Because this mechanism determines how fast or slow the reaction will be, what will be the molar mass distribution and average molar mass that we get? So, it pretty much determines how the polymerization will proceed, but there is also which way the polymerization happens and this is especially valid for this large scale manufacture of polymer. It is also valid for getting the pre polymer and resin.

So, what is the mode or method or process? For example we could do the process what is known as solution polymerization or we could do an emulsion polymerization or maybe a gas phase polymerization. So, each of these will have certain advantages and disadvantages from the point of view of an polymerization operation. We should recall that polymerization is essentially an exothermic process and lot of heat is evolved.

So, management of this heat in terms of it not getting to a stage where it's called a runaway reaction, because when polymerization happens temperature increases, temperature increases polymerization rate increases, polymerization rate increases temperature increases further. So, that is called a runaway reaction so where things can lead to degradation and combustion. So, therefore to avoid such things this mode or method or process is very important because it can determine the stability of overall processing polymerization operation.

(Refer Slide Time: 08:18)



Kinetics of free radical polymerization

- Rate of initiation and termination is same,
  $r_i \sim 2k_iC_i$; $r_t \sim 2k_tC^2_{\sim M^*}$
- Rate of polymerization = rate of propagation $\sim k_pC_{\sim M^*}C_M$

$$r_p = k_p\left(\frac{k_i}{k_t}\right)^{1/2} C_i^{0.5}C_M \quad (1)$$

- Averange number degree of polymerization

$$\bar{x}_n = \frac{r_p}{r_t} = \frac{k_pC_M}{2\sqrt{k_ik_tC_i}} \quad (2)$$

$M + I^* \rightarrow IM^*$

$IM^* + M \rightarrow IMM^*$

$\sim M_N^* + M \rightarrow \sim M_{N+1}^*$

$\sim M_i^* + \sim M_j^* \rightarrow M_iM_j$

TE 2019

For AIBN initiated polymerization of styrene, if both the monomer and initiator concentration are doubled, then the rate of polymerization increases by a factor of ______ (round off to two decimal places).

So, let us do quickly look through the mechanisms that are associated and the kinetics of polymerization, we will first begin with the free radical polymerization and as we have seen the free radical is generated based on an initiator. So, the presence of an initiator is must for this polymerization to proceed and once an active species is formed then it can start attaching with the monomer and then of course the propagation can happen. And so one is interested in knowing the rate of propagation because that is when we are getting a polymer formed in the process. So, rate of polymerization is pretty much equivalent to rate of propagation. However, to analyze what could be the rate of propagation we make an assumption regarding the number of these active species which are there they remain the same.

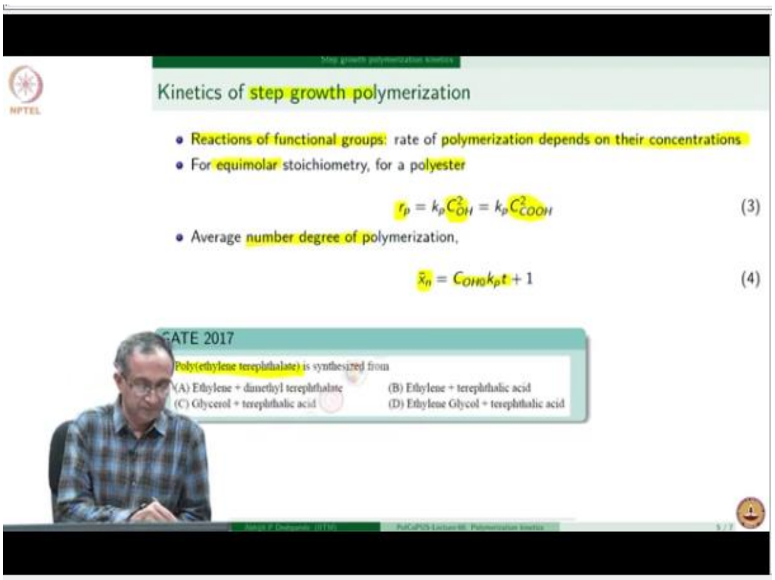
So, **so** that the rate of initiation in which active species gets produced is the same in which we will basically have 2 such active species giving you a terminated polymer. So, this is a reaction in which active species are getting disappearing, so active species disappearance. So, we assume that the rate at which this is happening is equivalent and so rate of initiation which depends on the concentration of the initiator species.

And the rate of termination which depends on how many such species are there. So, therefore c^2 square and basically the composition of the M* polymer chain and k_t and k_i are the rate constants which determine this reaction. So if you equate these 2 reactions and then substitute in the rate of reaction for propagation. So, in this is the unknown. So, this can be substituted from here. And you can come up with the final expression which involves the propagation rate constant, the initiation rate constant and the termination rate constant and the concentration of 2 species with which we start the overall polymerization reaction. We basically start this reaction by taking some amount of initiator and some amount of monomer.

So, this tells us what will be the rate of polymerization given an initial mixture with certain concentration of initiator and certain concentration of monomer.

And based on this we can also calculate the average number degree of polymerization and that again depends on the concentration of monomer and initiator and the rate constants. So, you can see a direct application of this in this exam question where an AIBN initiated polymerization of styrene which happens through this mechanism, the question being asked is if both monomer and initiator are doubled, then what happens to the rate of polymerization? So, looking at the information on the slide you should be quickly able to solve this problem.

(Refer Slide Time: 11:54)



Kinetics of step growth polymerization

- Reactions of functional groups: rate of polymerization depends on their concentrations
- For equimolar stoichiometry, for a polyester

$$r_p = k_p C_{OH}^2 = k_p C_{COOH}^2 \quad (3)$$

- Average number degree of polymerization,

$$\bar{x}_n = C_{OH0} k_p t + 1 \quad (4)$$

GATE 2017

Poly(ethylene terephthalate) is synthesized from

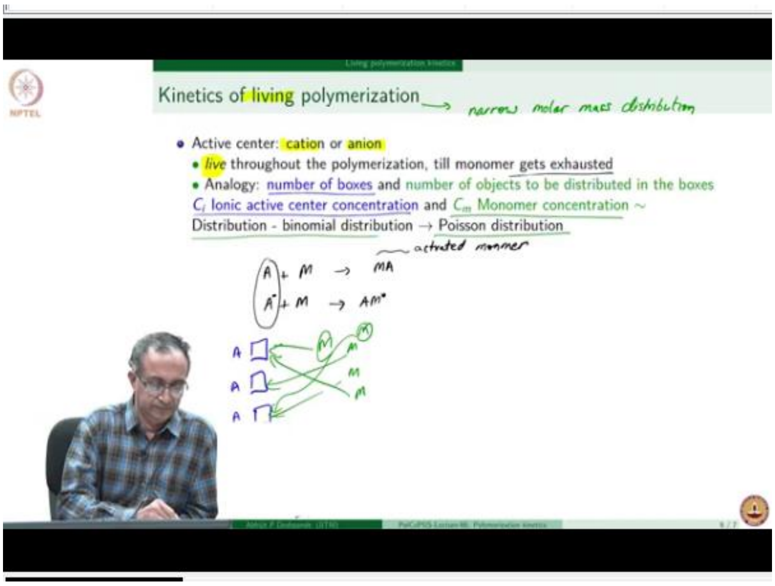
(A) Ethylene + dimethyl terephthalate
(B) Ethylene + terephthalic acid
(C) Glycerol + terephthalic acid
(D) Ethylene Glycol + terephthalic acid

Now let us look at the next type of polymerization where we have a polyester such as PET and this is again an exam question which tries to probe us about you know what are the set of monomers which are used when such a process is carried out in industry. We know for example polyester which means there must be a polyol or diol or a basically a molecule with alcohol groups more than one. So, diol implies 2 alcoholic group and an acid carboxylic acid. So, which of these are those two uh monomers which can lead to PET the polyethylene terephthalate polymer. So, think about it while we discuss. So, step growth is basically reactions of functional groups and the rate of polymerization will depend on how much of these functional groups are there and if we assume that let us say we are starting with the same amount of hydroxyl groups.

And same amount of carboxylic groups which imply equimolar stoichiometry. So, for a polyester the rate of propagation will just depend on the concentration squared because it is basically concentration of OH and concentration of COOH, but since both of those concentrations are equal we could just write the rate as square of each of these concentration and based on this if we calculate the average number degree of polymerization it is actually a linear function of time.

So, as the reaction proceeds the polymer starts growing slowly, that is why we also call this a step growth. It is of course called also condensation polymerization because the reaction between hydroxyl and carboxylic acid groups leaves out water. But it is also a step growth where polymerization happens stepwise and the molecular weight build up the degree of polymerization increases gradually.

(Refer Slide Time: 13:52)



Kinetics of living polymerization → narrow molar mass distribution

- Active center: cation or anion
  - live throughout the polymerization, till monomer gets exhausted
  - Analogy: number of boxes and number of objects to be distributed in the boxes

C_i Ionic active center concentration and C_m Monomer concentration ~

Distribution - binomial distribution → Poisson distribution

activated monomer

$A + M \rightarrow MA$

$A^* + M \rightarrow AM^*$

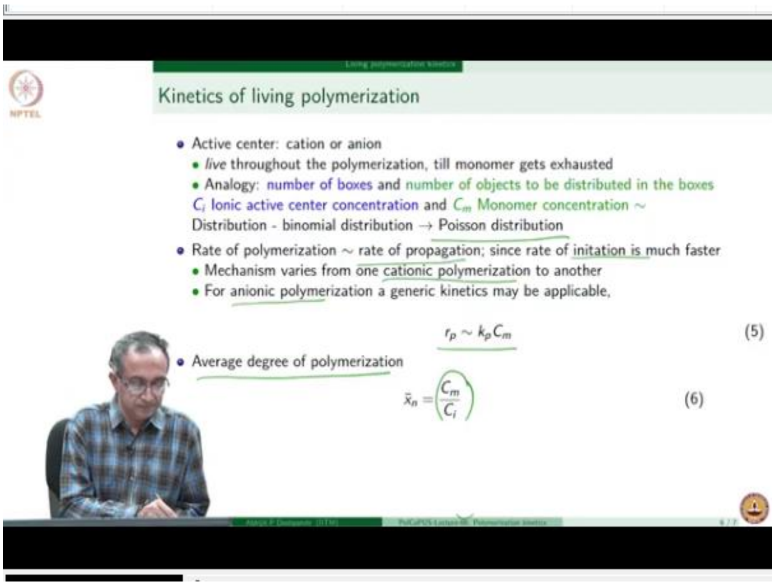
And the other important polymerization mechanism is living polymerization which is based on ionic and so the active center is either a cation or an anion and it is called so because the active center remains live and what that implies is let us say if you have a monomer which is added and then you have this active center. So, this gives you an activated monomer.

So, this is the activated monomer, in this course we have been basically trying to say this kind of a reaction implying star for activated system and so this is the activated monomer. Now what happens in this case is the termination reaction does not happen and so this activated species will remain activated until the monomer in the system gets exhausted. So, if monomer is over no further reaction is possible.

Now this problem is very analogous to basically then saying that the number of boxes depends on how many such activated species are there at time t = 0 and those depend on this cation or anion or whatever is the active center. So, the problem we are solving is the following that we have all these boxes which depend on this activated species. So, that is the number of boxes which are determined based on ionic active center concentration.

And then we have on the other side the monomer concentration. So, each of this monomer which are out there will have to start going and filling these boxes. So, each of them basically will have to fit into a box. So, the problem is the following that we have C_i number of boxes and we have C_m number of monomers, how many different ways can this fitting be done? And so this is a combinatorial problem. And if you work on the distribution of it, it will turn out to be binomial distribution but given that the numbers of boxes are small, I hope you can see why am I saying that numbers of boxes are small. Because our objective is to create a polymer chain which is very long, just imagine if you have just 1 box, then basically we will all the monomers will get combined to form one giant chain. So, of course that is not feasible what we will have is a set of initiators that we are adding which is an ionic initiator and its concentration will determine the number of boxes and then all the monomers start coming and attaching themselves. So, therefore the average number of monomers that get attached to a box or attached to an initiator will depend on this distribution. And at very high number of monomers or less number of these boxes you basically get the Poisson distribution. So, you can go and see how this Poisson distribution is usually narrow distribution compared to binomial or Gaussian or normal distribution and therefore living polymerization always leads to narrow molar mass distribution.

(Refer Slide Time: 17:49)



Kinetics of living polymerization

- Active center: cation or anion
  - *live* throughout the polymerization, till monomer gets exhausted
  - Analogy: number of boxes and number of objects to be distributed in the boxes C_i Ionic active center concentration and C_m Monomer concentration ~ Distribution - binomial distribution → Poisson distribution
- Rate of polymerization ~ rate of propagation; since rate of initation is much faster
  - Mechanism varies from one cationic polymerization to another
  - For anionic polymerization a generic kinetics may be applicable,

$$r_p \sim k_p C_m \quad (5)$$

- Average degree of polymerization

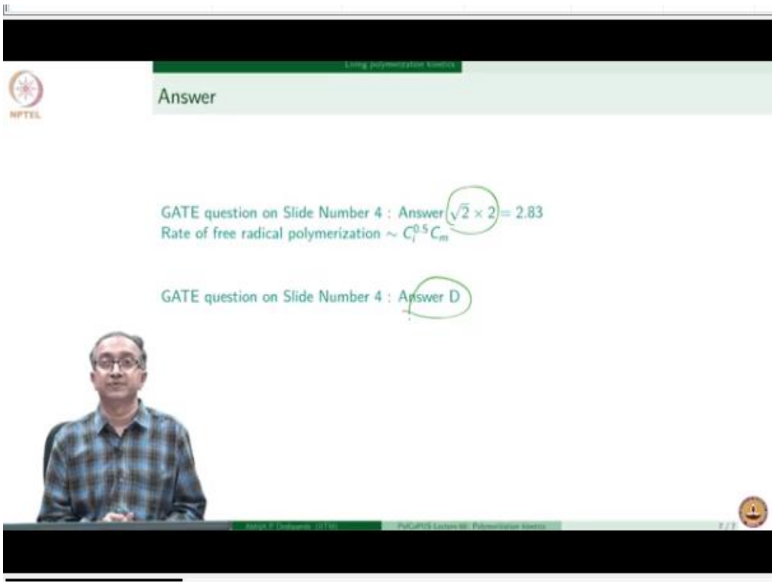
$$\bar{x}_n = \frac{C_m}{C_i} \quad (6)$$

And so the rate of polymerization in this case is again just dependent on rate of propagation because initiation is fast as soon as you put the initiator the boxes get created in which now the all the monomers have to go and fill themselves and of course the detail mechanism is slightly different especially if it is a cationic polymerization and so no generic kinetic model is available. But for anionic polymerization basically the rate of propagation will just depend on how many monomers are there.

Because the active centers or the boxes are already created so that is not the rate determining step at all, there is no termination also. So, that is irrelevant in this case, so the only rate involved is the rate of propagation or rate at which monomers are getting filled in the boxes or monomer is the rate at which monomer is reacting the active center which is present and so it is directly proportional to the amount of monomer present.

And the average degree of polymerization is just the ratio of the 2 concentrations because the problem is that we have m number of balls, we have i number of boxes on average of course m/i will be the average number of box given the i is the total number of boxes. So, this is a straightforward combinatorial problem in which the average degree of polymerization can be found out just by reasoning like what I have given. However the distribution is poisson distribution.

(Refer Slide Time: 19:21)



Answer

GATE question on Slide Number 4 : Answer $\sqrt{2} \times 2 = 2.83$
Rate of free radical polymerization $\sim C_i^{0.5} C_m$

GATE question on Slide Number 4 : Answer D

So, with this we will close this lecture, I hope you will be quickly able to see that if you double the initiator and monomer concentrations the rate of polymerization changes and therefore also the average degree of polymerization will also change and similarly you would be able to identify by doing some search or from your knowledge as to which are the monomers which are present for making PET, thank you very much.