Polymer Process Engineering

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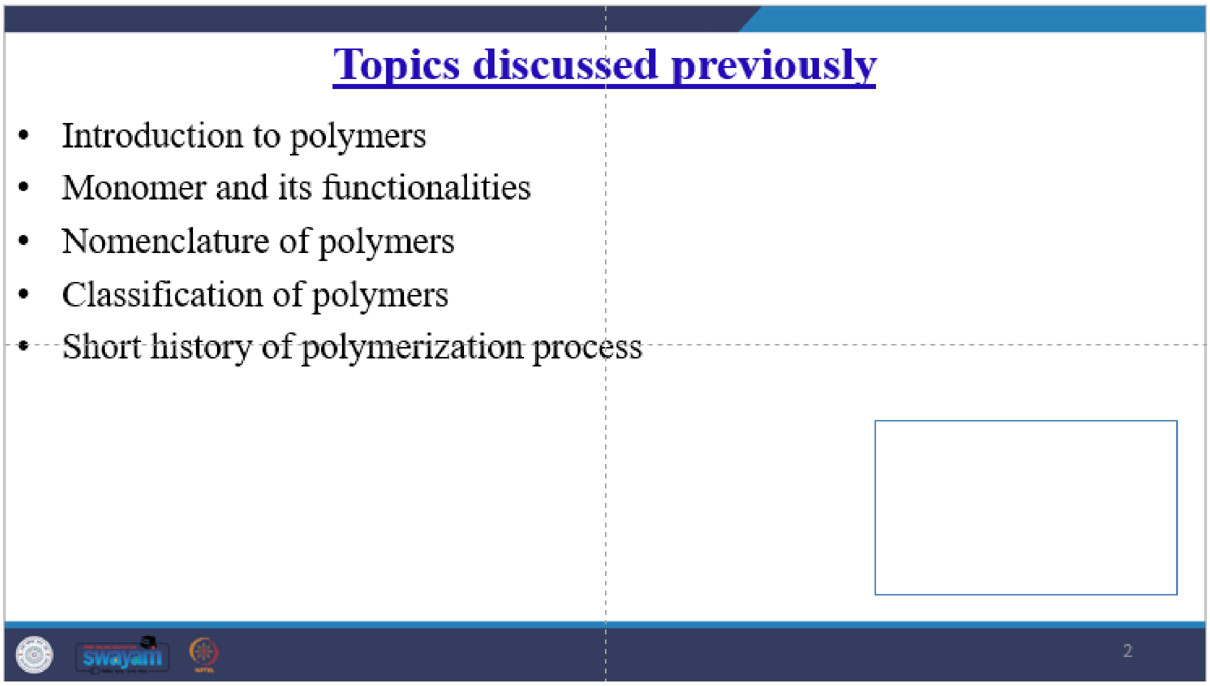
Lecture – 02

Polymers and Polymerization Techniques

Welcome to the next chapter of Polymer Process Engineering. Here we are going to discuss the polymers and polymerization techniques. Now, before we go into the detail of this particular chapter, let us have a look about what we discussed in the previous chapter. We discussed about the introduction of polymers, what different type of the polymers are there. Then we discussed about the backbone of those polymers that is called the monomer and how these monomers can join together to form the polymer. Their functionality, their covalency, their bonding structure, etc.

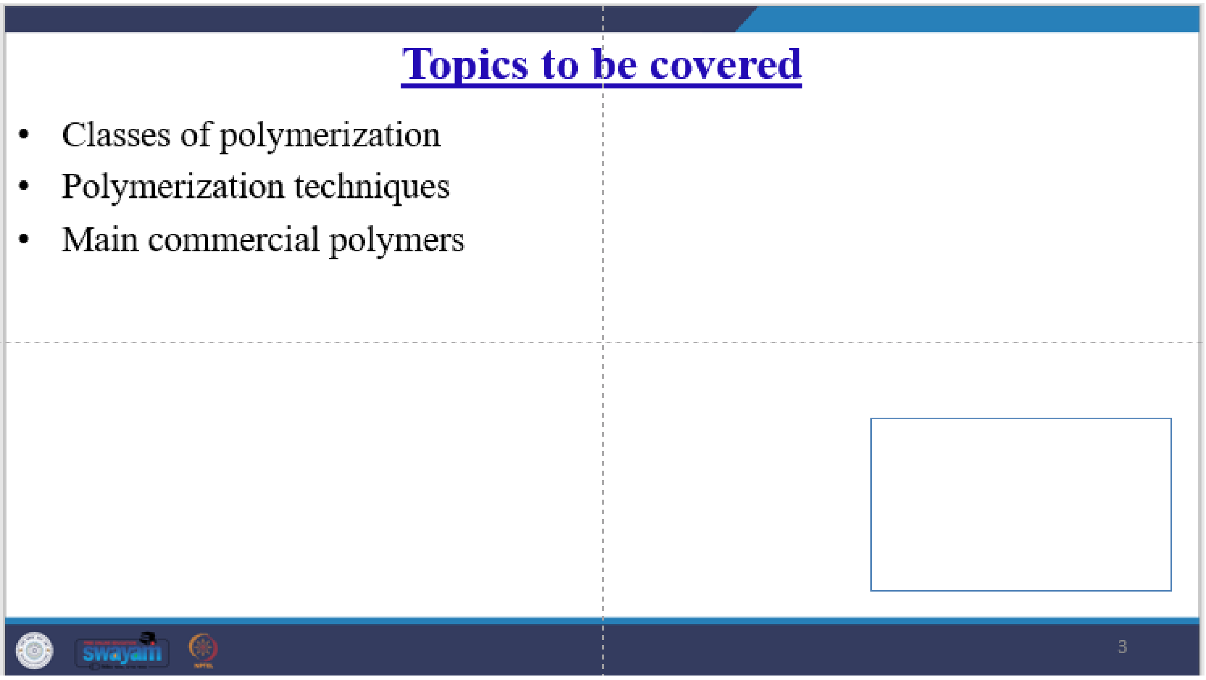


Topics discussed previously

- Introduction to polymers
- Monomer and its functionalities
- Nomenclature of polymers
- Classification of polymers
- Short history of polymerization process

Then we discussed because in due course of time you will find so many different nomenclatures. So, we discussed briefly about different type of a nomenclature scheme of polymers. Then we had a brief discussion about the different type of a classification streams of polymers, how we can classify like based on the source, based on the polymerization process, based on the chemistry, all these things we have discussed. Then it was the duty to discuss about the short history of the polymerization process, because it is very important to know that how this polymerization process evolved over the period of time.

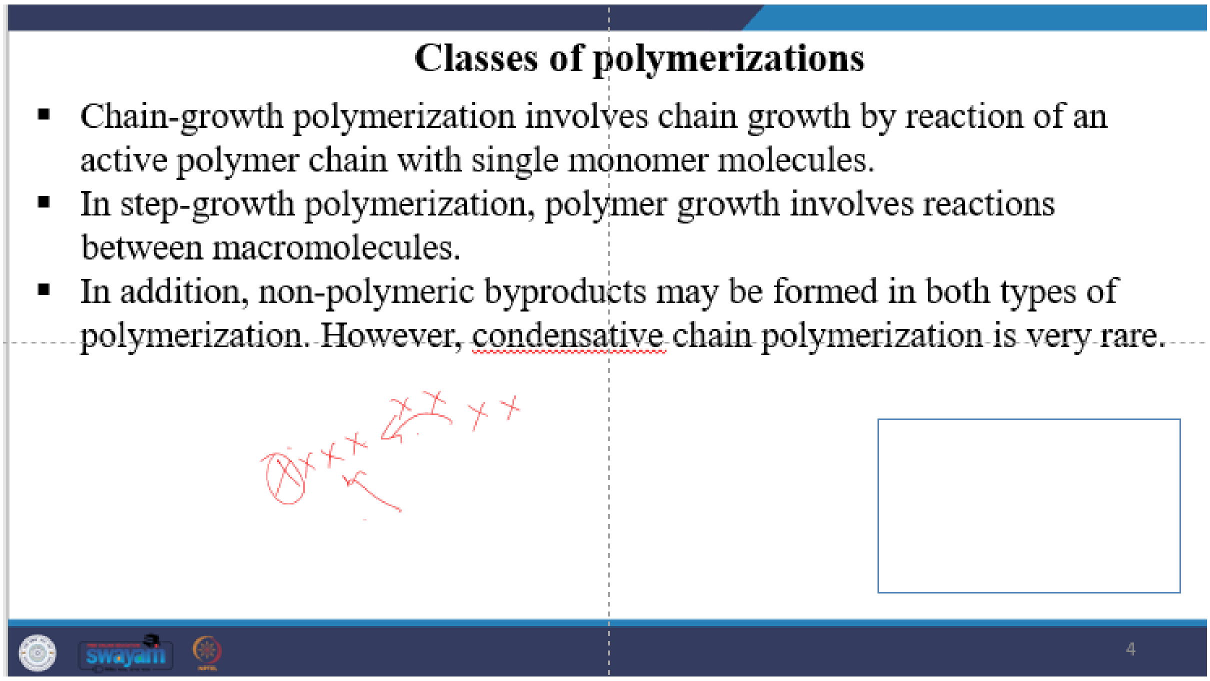
Now, in this particular segment, we are going to discuss the different classes of polymerization. Then we will discuss about the polymerization techniques and we will discuss about the different commercial polymers. So, let us talk about the different classes of polymerization. Now, you see that we discussed about the addition and condensation polymerization. Another class is called the chain growth polymerization.



Topics to be covered

- Classes of polymerization
- Polymerization techniques
- Main commercial polymers

This involves the chain growth by a reaction of an active polymer chain with the single molecule, monomer molecule. Now, just for the sake of an example, this is my chain and over the period of time different monomers this X represents the monomer and different monomers can add on to form the different the chain or growth of the chain. So, this is you can say that this particular polymerization scheme called the chain growth polymerization. Another is the step growth polymerization. This polymer growth involves the reaction between the macromolecules.

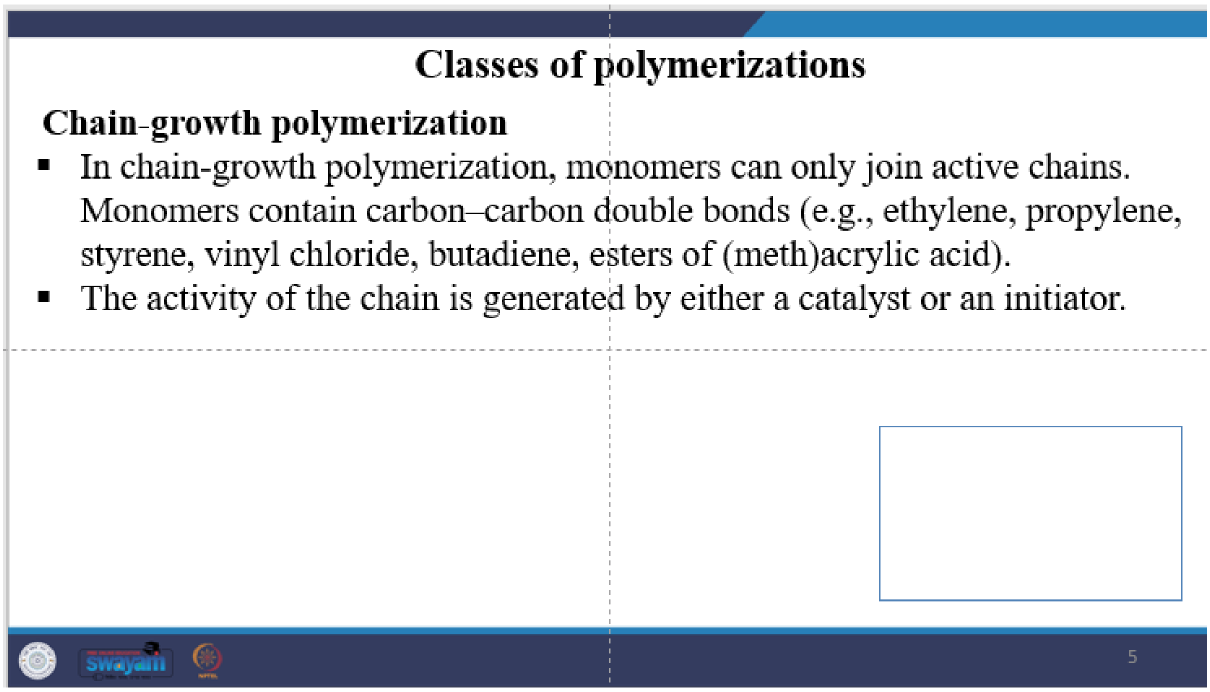


Classes of polymerizations

- Chain-growth polymerization involves chain growth by reaction of an active polymer chain with single monomer molecules.
- In step-growth polymerization, polymer growth involves reactions between macromolecules.
- In addition, non-polymeric byproducts may be formed in both types of polymerization. However, condensative chain polymerization is very rare.

So, the chains can get interacted with different other chains. Now, in addition, the non-polymeric byproducts these may be formed in both types of polymerization. Now, the condensative chain polymerization is very rare. Now, in chain growth polymerization, monomers can only join active chains. Now, what is the definition of active chains? They must either have a double bond or some functional group present over it and simultaneously that similar type of property monomer should possess.

So, the monomer contains the carbon-carbon double bond like ethylene, propylene, styrene, vinyl chloride, butadiene, ester of methylacrylate. All these are the best candidate of this type of chain growth polymerization. The activity of chain is generated by either a catalyst or an initiator because something should be there to trigger the polymerization reaction. Now, several classes of chain growth polymerization, this can be distinguished according to the type of active center. Now, sometimes active centers they are referred as a functional group, sometimes other aspects like coordination polymerization.

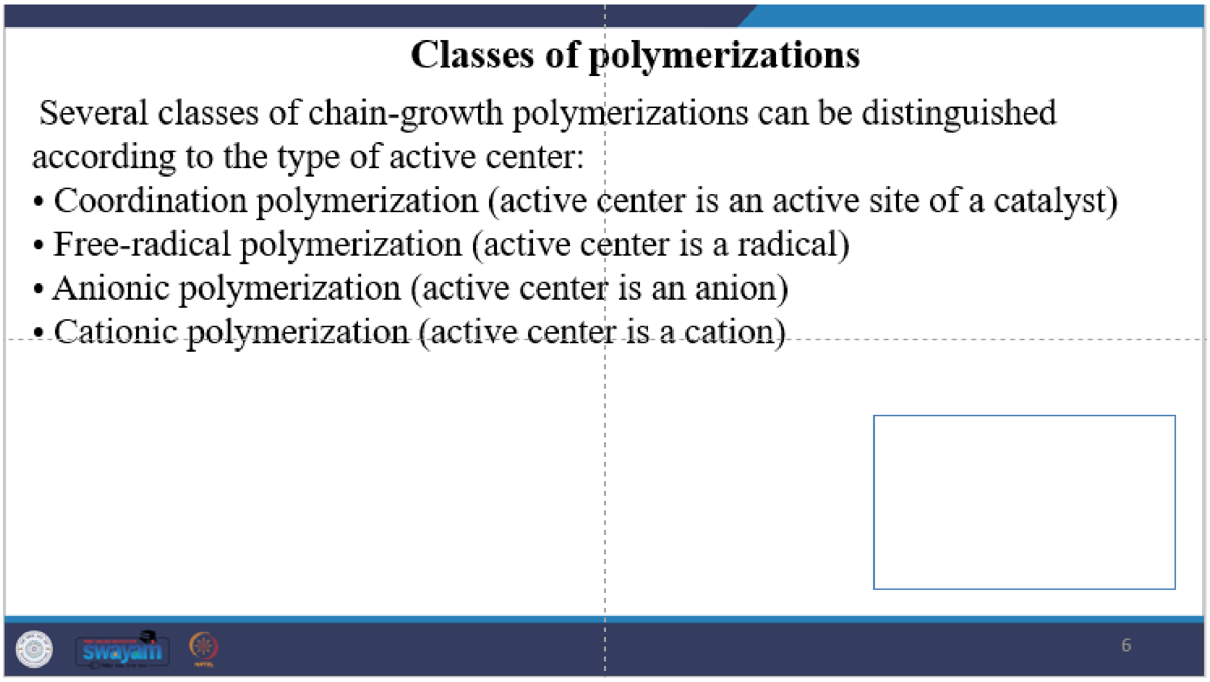


Classes of polymerizations

Chain-growth polymerization

- In chain-growth polymerization, monomers can only join active chains. Monomers contain carbon–carbon double bonds (e.g., ethylene, propylene, styrene, vinyl chloride, butadiene, esters of (meth)acrylic acid).
- The activity of the chain is generated by either a catalyst or an initiator.

The active center is an active site of a catalyst. So, this triggers the polymerization process. Similarly, the free radical polymerization, the essential active part is the radical that means you need to form you need to have free radical in the reaction mass so that you can propagate these polymerization reactions. Similarly, the anionic polymerization, here the active center is anion that means they must possess all the sites must possess anionic structure. Similarly, the cationic polymerization where the active center is a cation.

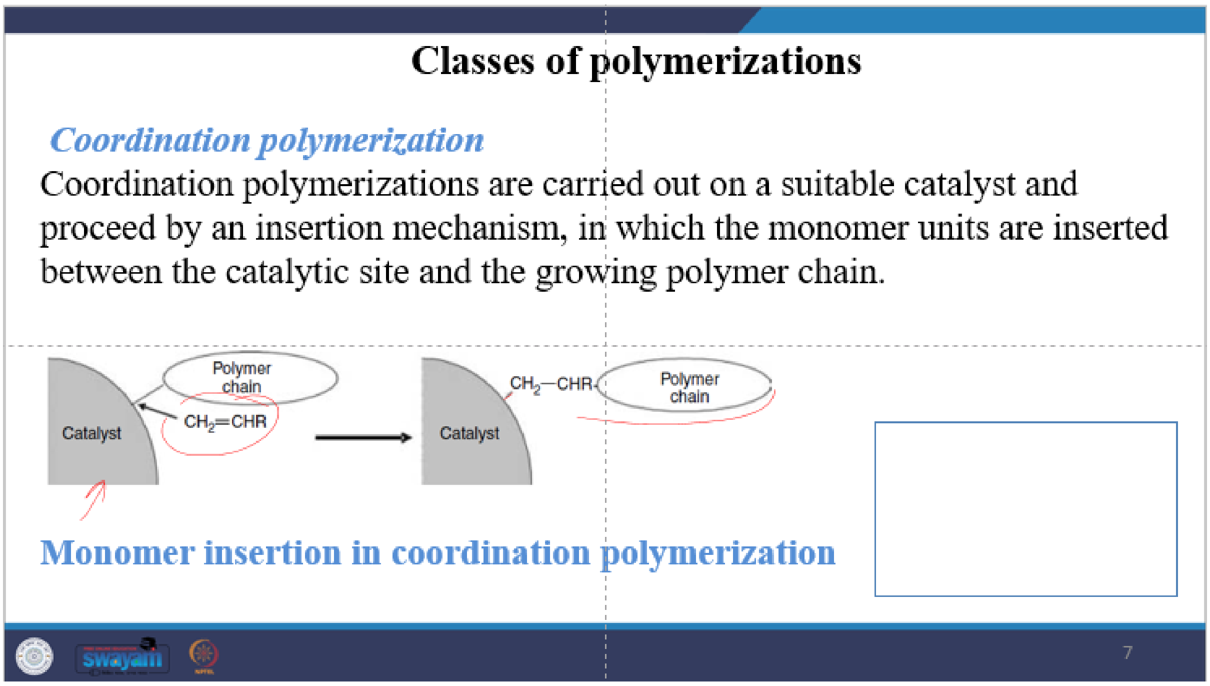


Classes of polymerizations

Several classes of chain-growth polymerizations can be distinguished according to the type of active center:

- Coordination polymerization (active center is an active site of a catalyst)
- Free-radical polymerization (active center is a radical)
- Anionic polymerization (active center is an anion)
- Cationic polymerization (active center is a cation)

Now, let us talk about the coordination polymerization. The coordination polymerization they are carried out in a suitable catalyst and preceded by an insertion mechanism in which the monomer units they are inserted between the catalyst site and growing polymer chain like here you see this is the catalyst and this is the monomer or the polymer chain R represents the chain. Now, here you see that this is the linkage between the catalyst and polymer chain. So, this is called the monomer insertion in coordination polymerization. Now, catalyst for coordination polymerization, this includes the Ziegler-Natta catalyst, we discussed this Ziegler-Natta catalyst in the previous lecture, some sort of a transition metal catalyst and metallocenes.



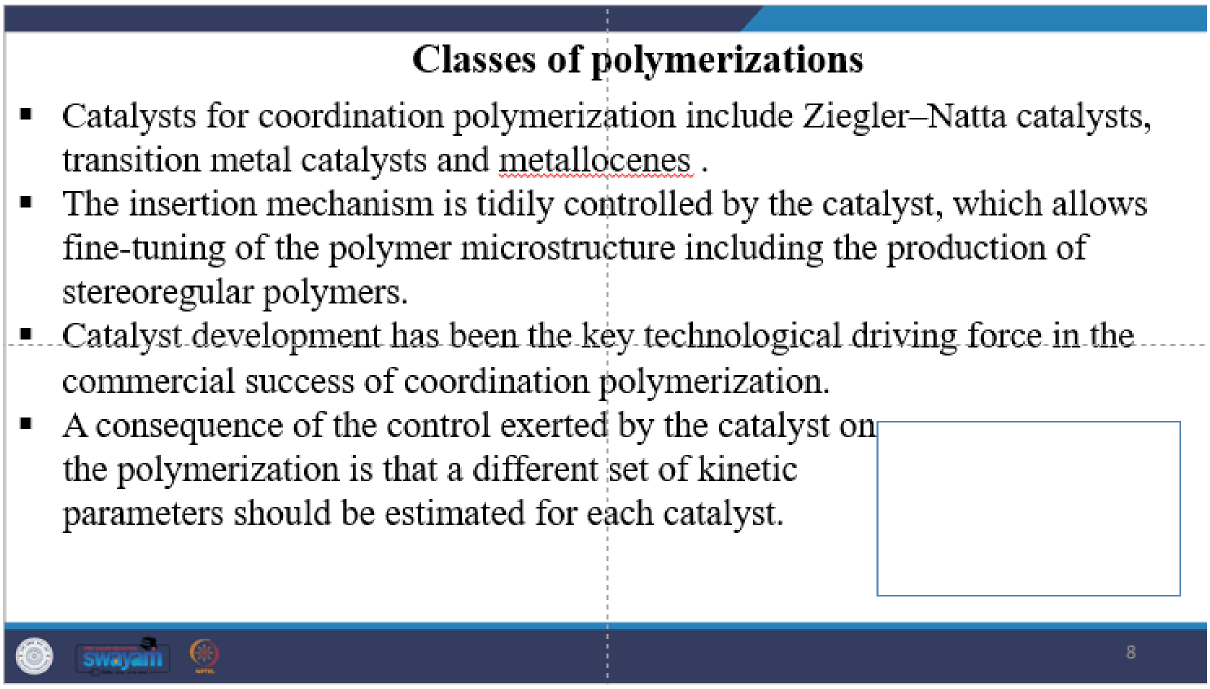
Classes of polymerizations

Coordination polymerization

Coordination polymerizations are carried out on a suitable catalyst and proceed by an insertion mechanism, in which the monomer units are inserted between the catalytic site and the growing polymer chain.

Monomer insertion in coordination polymerization

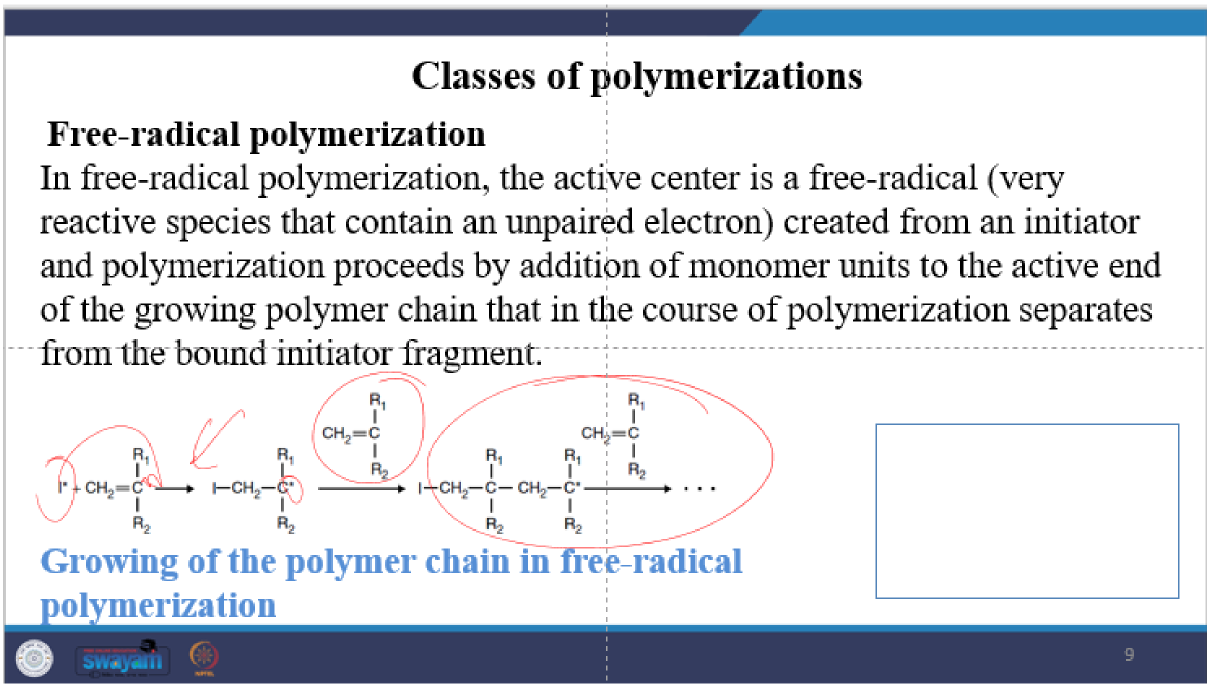
Now, the insertion mechanism is tightly controlled by the catalyst which allows the fine tuning of polymer microstructure including the production of a stereo regular polymers. Now, the catalyst development, this has been a key technological driving force in the commercial success of coordination polymerization. So, you see that the engineering of the catalyst is again a vital role. So, those who are interested in the polymer processes, this is one of the way or arenas where we can work on. The consequence of the control accelerated by the catalyst on the polymerization is that a different set of kinetic parameters should be estimated for each catalyst.



Classes of polymerizations

- Catalysts for coordination polymerization include Ziegler–Natta catalysts, transition metal catalysts and metallocenes .
- The insertion mechanism is tidily controlled by the catalyst, which allows fine-tuning of the polymer microstructure including the production of stereoregular polymers.
- Catalyst development has been the key technological driving force in the commercial success of coordination polymerization.
- A consequence of the control exerted by the catalyst on the polymerization is that a different set of kinetic parameters should be estimated for each catalyst.

So, that is why the polymer reaction engineering, study of polymer reaction engineering is important. Let us talk about the free radical polymerization. Now, in free radical polymerization, the active center is the free radical and this free radical is a very reactive nature and a very reactive species that contains an unpaired electron which always involved to form a pairing. Now, this can be created from an initiator and the polymerization process by addition of monomer units to the active and end of the growing polymer chain that is in course of polymerization this separates from the bond initiator fragment. Now, here you see that this is the initiator and by this way, this free radical is shifted to here.



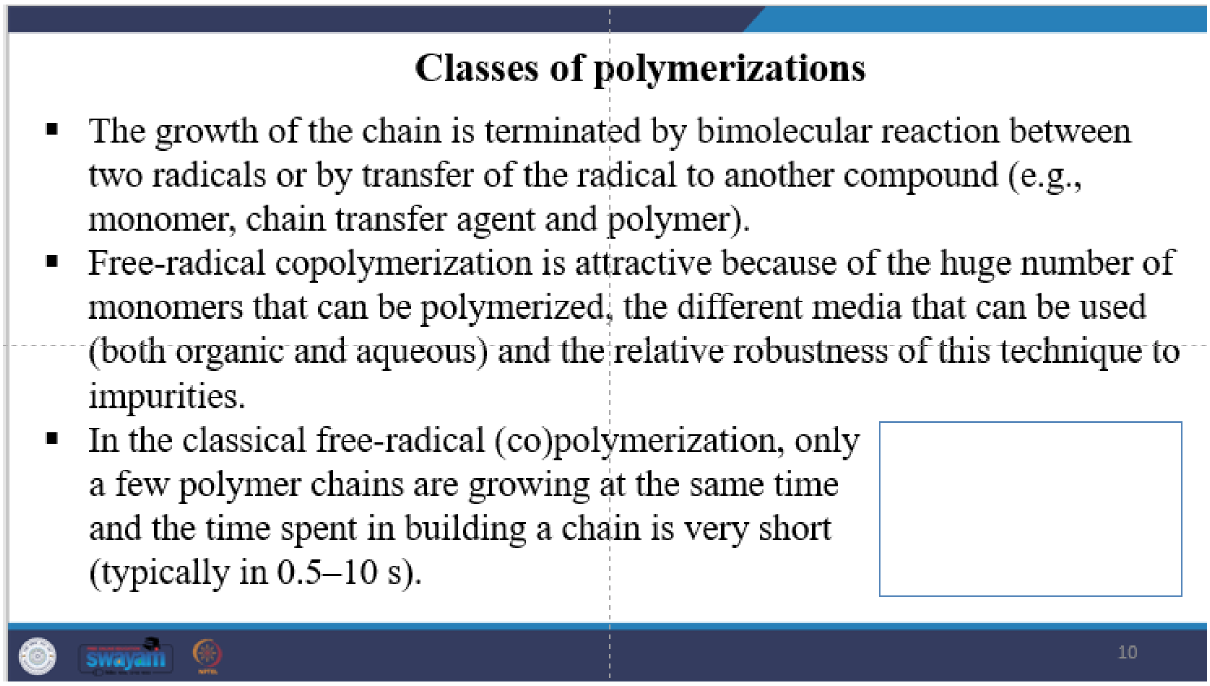
Classes of polymerizations

Free-radical polymerization

In free-radical polymerization, the active center is a free-radical (very reactive species that contain an unpaired electron) created from an initiator and polymerization proceeds by addition of monomer units to the active end of the growing polymer chain that in the course of polymerization separates from the bound initiator fragment.

Growing of the polymer chain in free-radical polymerization

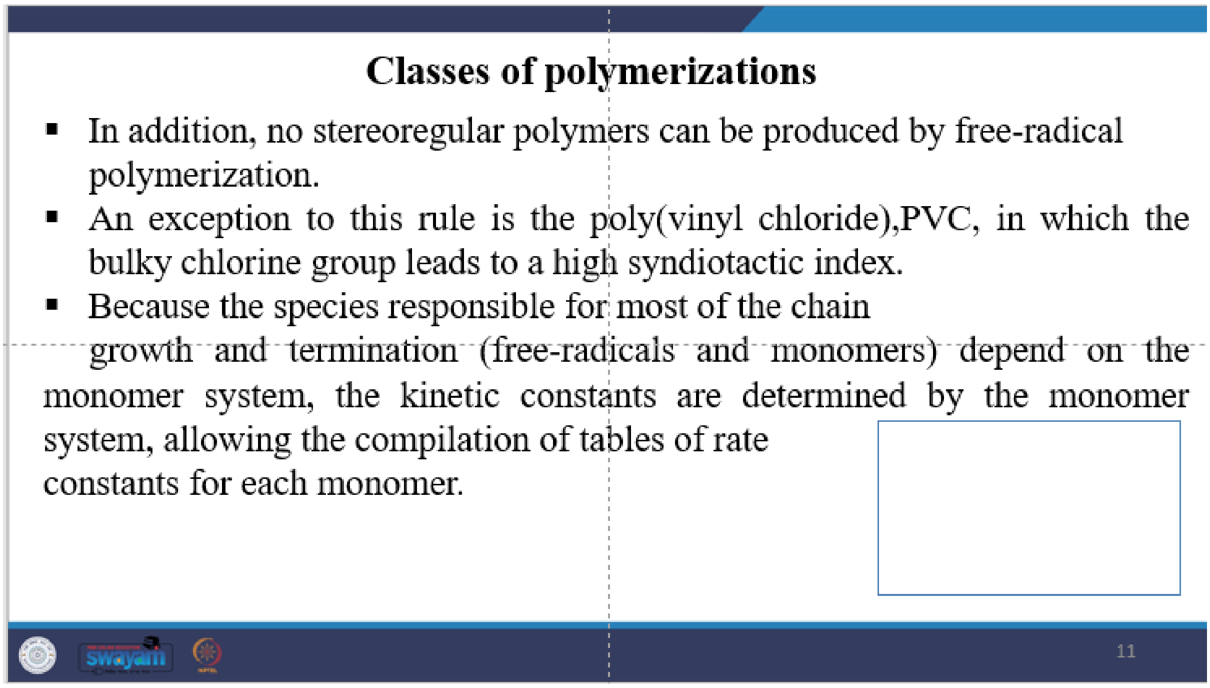
Now, it can become a functional site for the further polymerization process. Now, here this can be attached and this by this way, they can form the growing chain of polymer or the growing of the polymer chain. This is in the free radical polymerization. Now, the growth of the chain is usually terminated by the bimolecular reaction between the two radicals or transfer of the radical another component that is the monomer chain transfer agent or a polymer. Now, see the truncation is very important because when this particular polymerization process starts may be triggered by the various approaches, then all these chains or monomers they can agglomerate and this reaction is called the propagation reaction.



Classes of polymerizations

- The growth of the chain is terminated by bimolecular reaction between two radicals or by transfer of the radical to another compound (e.g., monomer, chain transfer agent and polymer).
- Free-radical copolymerization is attractive because of the huge number of monomers that can be polymerized, the different media that can be used (both organic and aqueous) and the relative robustness of this technique to impurities.
- In the classical free-radical (co)polymerization, only a few polymer chains are growing at the same time and the time spent in building a chain is very short (typically in 0.5–10 s).

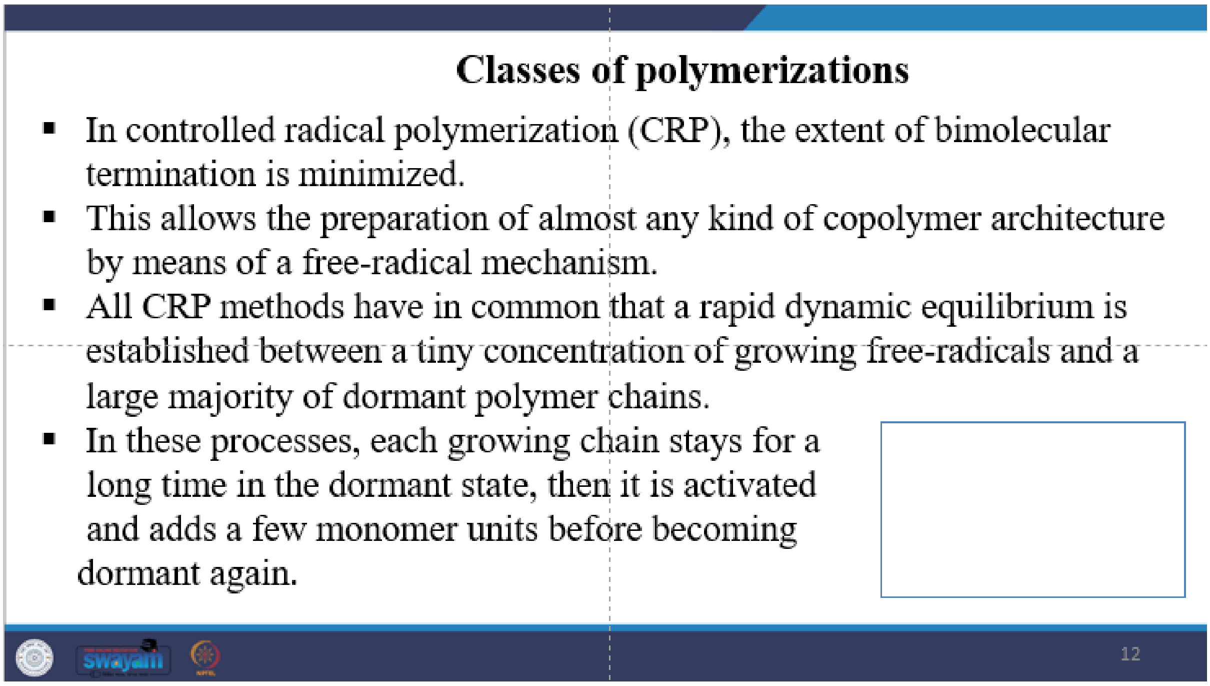
So, first start is this one is the initiation and then propagation. Now, the termination why it is important because if you keep on growing all these chains, then definitely the molecular weight of your polymer mass will become more and more or it can be on the higher side. Now, once it is in higher side, then definitely the properties which you are targeting may not cover. So, that is why the truncation of these polymerization reaction is very important. Now, free radical copolymerization is attractive because large number of monomers that can be polymerized.



Classes of polymerizations

- In addition, no stereoregular polymers can be produced by free-radical polymerization.
- An exception to this rule is the poly(vinyl chloride),PVC, in which the bulky chlorine group leads to a high syndiotactic index.
- Because the species responsible for most of the chain growth and termination (free-radicals and monomers) depend on the monomer system, the kinetic constants are determined by the monomer system, allowing the compilation of tables of rate constants for each monomer.

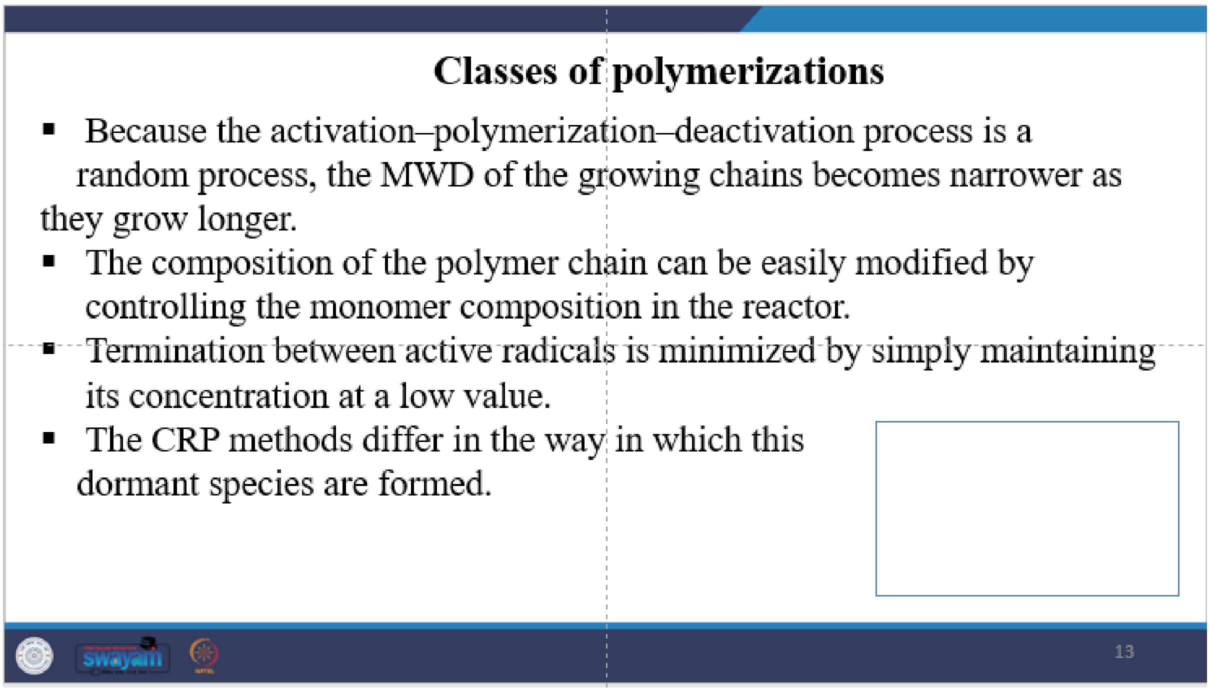
So, the different media that can be used both organic and aqueous and the relative robustness of this technique to impurities. In the classical free radical copolymerization, the only a few polymer chains are growing in the same time and time spent in building a chain is very short typically you can say a fraction of second to 10 seconds. Now, in addition, no stereo regular polymers can be produced by the free radical polymerization. So, it is a very selective in nature. An exception for this particular rule is the PVC in which the bulky chlorine group leads to a highly syndiotactic index.



Classes of polymerizations

- In controlled radical polymerization (CRP), the extent of bimolecular termination is minimized.
- This allows the preparation of almost any kind of copolymer architecture by means of a free-radical mechanism.
- All CRP methods have in common that a rapid dynamic equilibrium is established between a tiny concentration of growing free-radicals and a large majority of dormant polymer chains.
- In these processes, each growing chain stays for a long time in the dormant state, then it is activated and adds a few monomer units before becoming dormant again.

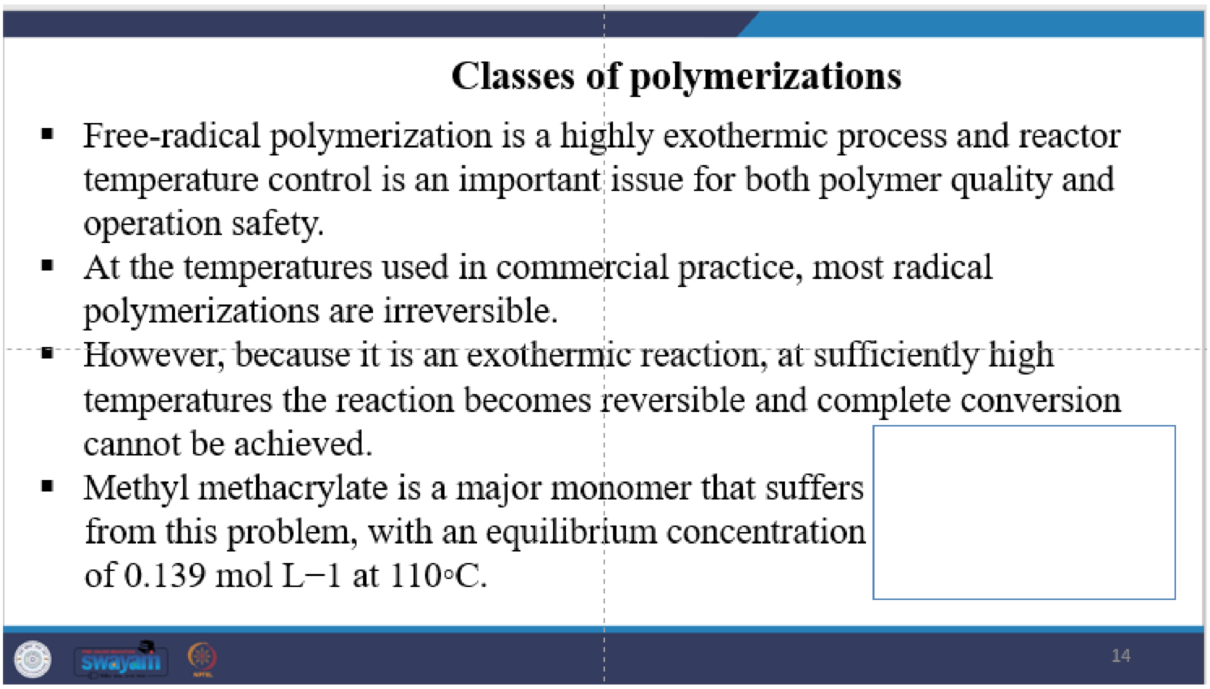
Now, the because of the special species responsible for the most of the chain growth and termination, the free radical and monomer this depends on the monomer system. The kinetic constants they are determined by the monomer system and allowing the compilation of different table of rate constants for each monomer. So, this is a very attractive aspect of polymer reaction studies. Now, in controlled radical polymerization sometimes referred as a CRP, the extent of Y molecular termination is minimized. Now, this allows the preparation of almost any kind of copolymer architecture by means of a free radical mechanism.



Classes of polymerizations

- Because the activation–polymerization–deactivation process is a random process, the MWD of the growing chains becomes narrower as they grow longer.
- The composition of the polymer chain can be easily modified by controlling the monomer composition in the reactor.
- Termination between active radicals is minimized by simply maintaining its concentration at a low value.
- The CRP methods differ in the way in which this dormant species are formed.

So, all controlled radical polymerization methods they are having in common that a rapid dynamic equilibrium is established between a tinny concentration of growth-free free radicals and a large majority of dormant polymer chains. Now, in this process, each growing chain stays for a long time in the dormant state, and then it is activated and adds a few monomer units before becoming dormant again. So, in this way, you can control the molecular mass of those polymers. Now, because of the activation polymerization or deactivation process, this is a random process; the molecular weight distribution of growing chains becomes narrower as they grow larger or longer in size. So, the distribution or range becomes narrower and narrower over the period of time, because, over the period of time, the nascent monomers may get depleted over the period of time.



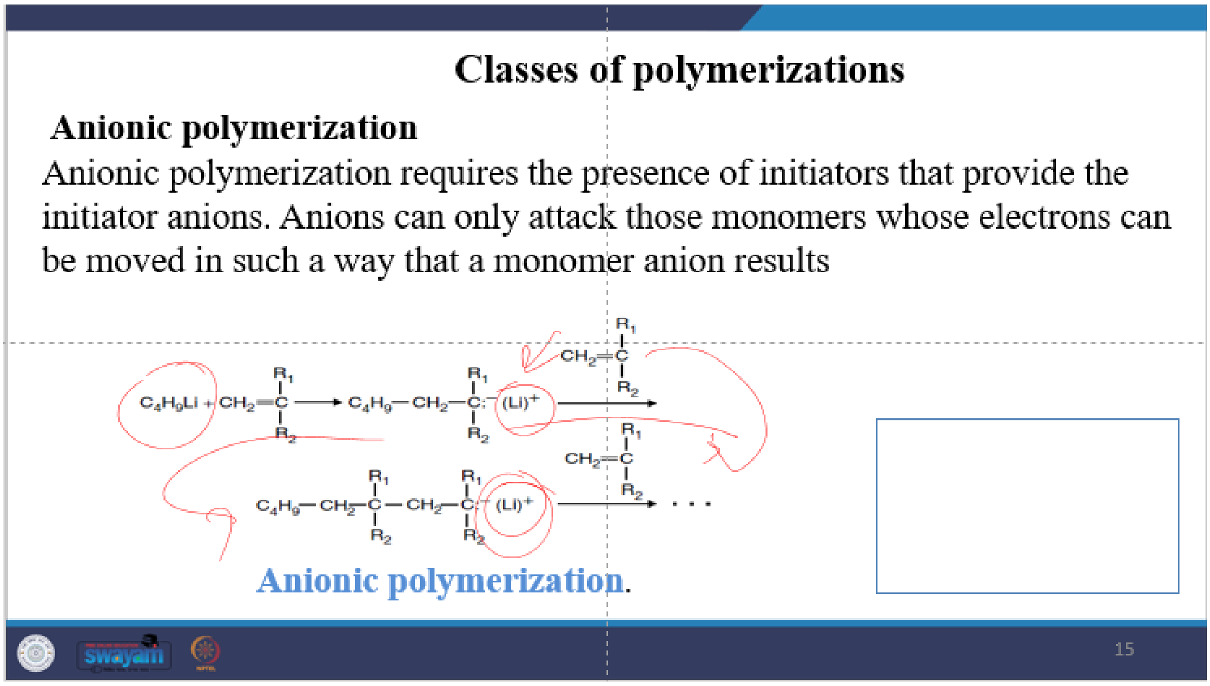
Classes of polymerizations

- Free-radical polymerization is a highly exothermic process and reactor temperature control is an important issue for both polymer quality and operation safety.
- At the temperatures used in commercial practice, most radical polymerizations are irreversible.
- However, because it is an exothermic reaction, at sufficiently high temperatures the reaction becomes reversible and complete conversion cannot be achieved.
- Methyl methacrylate is a major monomer that suffers from this problem, with an equilibrium concentration of 0.139 mol L−1 at 110°C.

Now, the composition of the polymer chain can be easily modified by controlling the monomer composition in the reactor. The termination between the active radicals is minimized by simply maintaining its concentration at a low value because the termination is very crucial at the right time when you need to truncate the growth of the polymer chain. So that is why the concentration of these active radicals is very important. So, in case if you have a high value in that case, this termination reaction would be very difficult, and the CRP methods are different in the way in which these dormant species are formed. Now, these free radical polymerizations are highly exothermic, and reactor temperature control is a very important aspect.

Otherwise, this rise in temperature may trigger further polymerization, and sometimes, this polymer polymer mass may get charred. So, temperature control is very important to maintain polymer quality and operational safety. Now, at the temperatures used for commercial practice, most radical polymerizations are irreversible. Now, because this is an exothermic reaction at a sufficiently high temperature, the reaction becomes reversible, and complete conversion cannot be achieved. This is irony in the polymerization process that complete conversion is a difficult task.

Methyl methacrylate is a major monomer that suffers from this problem with an equilibrium concentration of 0.139 moles per liter at 110 degrees Celsius. Another class of polymerization is anionic polymerization. As the name or the class implies, this requires the presence of an initiator that provides the initiator anions. Now, this anion can only attack those monomers whose electrons can be moved in such a way that a monomer anion results.



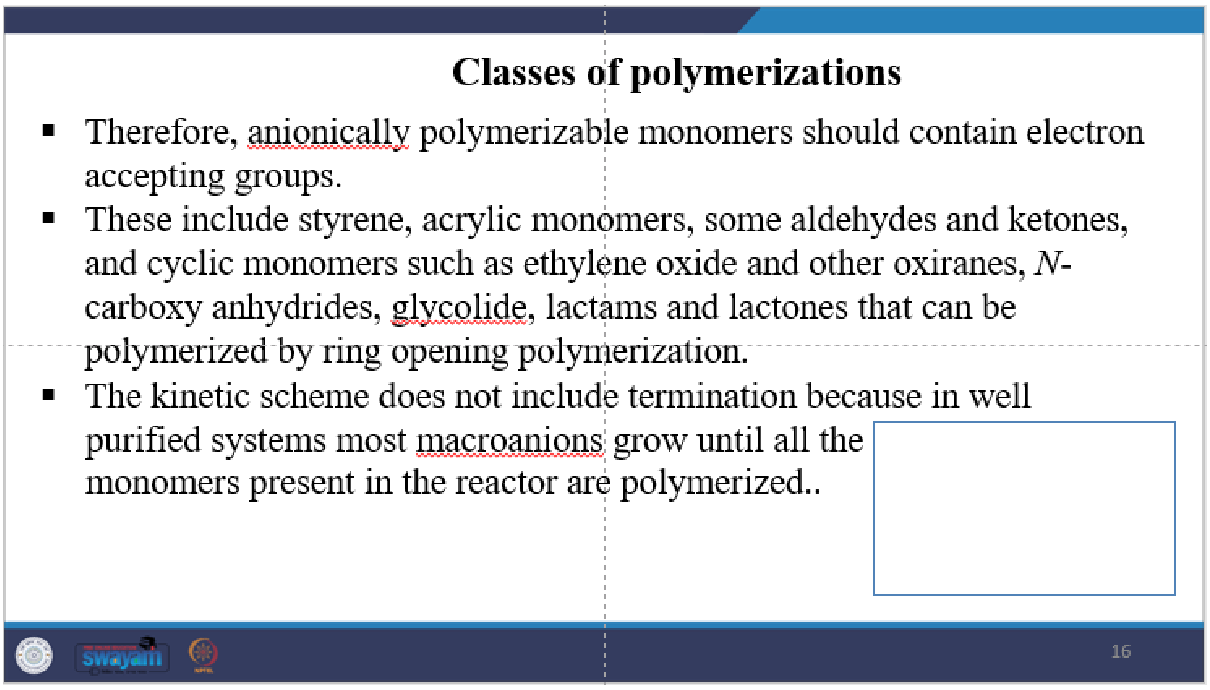
Classes of polymerizations

Anionic polymerization

Anionic polymerization requires the presence of initiators that provide the initiator anions. Anions can only attack those monomers whose electrons can be moved in such a way that a monomer anion results

Anionic polymerization.

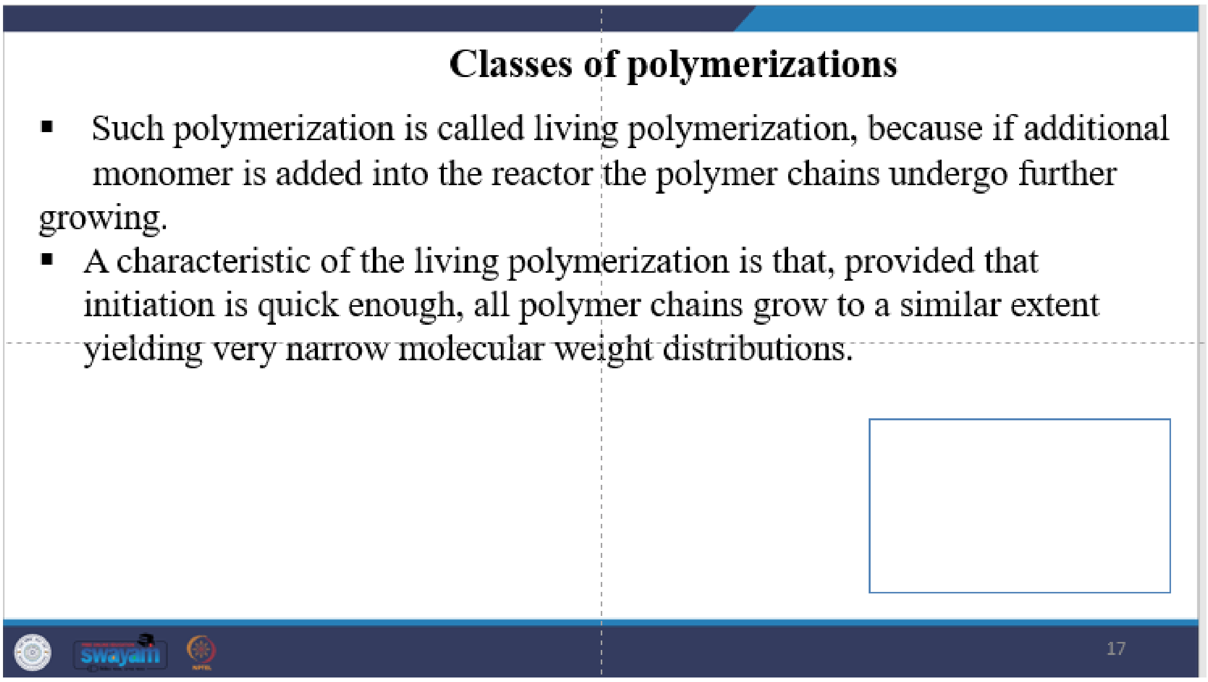
You see in this particular structure, now this is the initiator and this forms this anion and this further propagates the anionic polymerization reaction. So, you see that everywhere, you will find this anionic polymer or anionic monomer. Now, anionically polymerizable monomers they should contain electron-accepting groups. Now, this includes the styrene, acrylic monomer, some aldehydes and ketones and acyclic monomers such as ethylene oxide and other oxidants, the carboxylic anhydrides, glycolides, lactams, lactones that can be polymerized by the ring-opening polymerization. So, it gives enough opportunity for the polymerization process.



Classes of polymerizations

- Therefore, anionically polymerizable monomers should contain electron accepting groups.
- These include styrene, acrylic monomers, some aldehydes and ketones, and cyclic monomers such as ethylene oxide and other oxiranes, *N*-carboxy anhydrides, glycolide, lactams and lactones that can be polymerized by ring opening polymerization.
- The kinetic scheme does not include termination because in well purified systems most macroanions grow until all the monomers present in the reactor are polymerized..

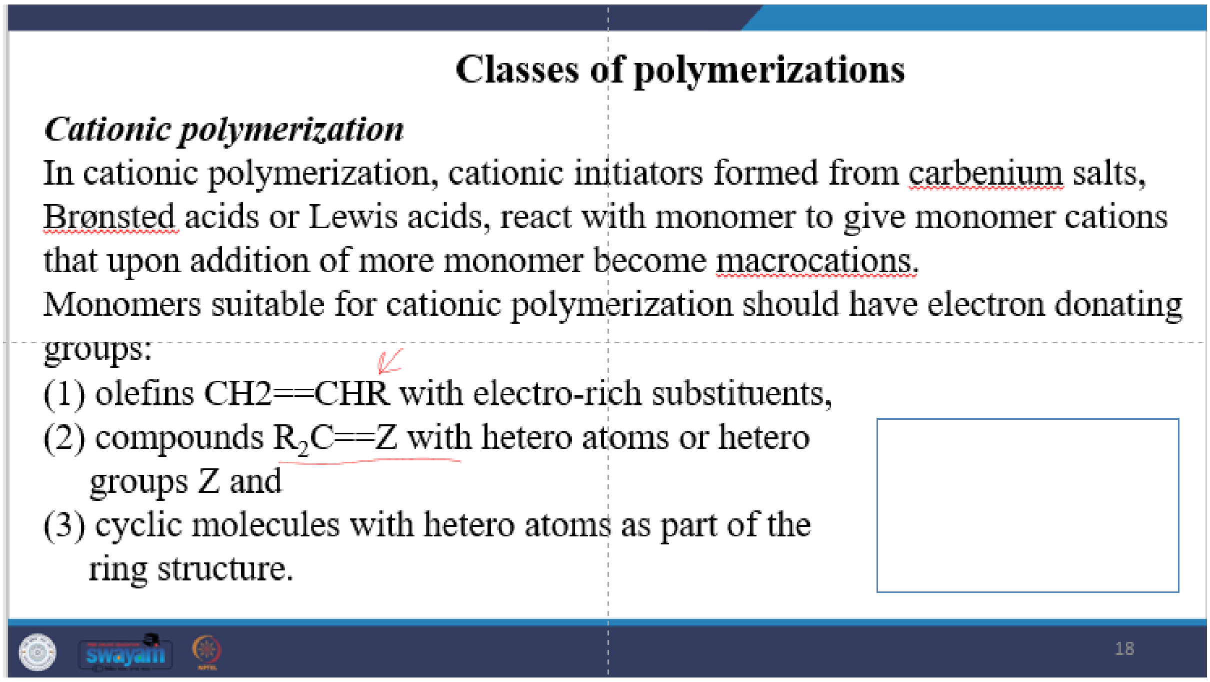
Now, the kinetic stream does not include the termination because in a well-purified system, most macro ions grow until all the monomers present in the reactor are polymerized. It is a plus way and a minus way because it can purify the reaction mass, but simultaneously, the control mechanism should be robust. Now, such polymerization this they are called leaving polymerization because if an additional monomer is added to the reactor of the polymer chain, this undergoes further growth. A characteristic of these leaving polymerization is that they provided the initiation is quick enough all polymer chains grow to a similar extent, yielding a very narrow molecular weight distribution. Let us talk about cationic polymerization.



Classes of polymerizations

- Such polymerization is called living polymerization, because if additional monomer is added into the reactor the polymer chains undergo further growing.
- A characteristic of the living polymerization is that, provided that initiation is quick enough, all polymer chains grow to a similar extent yielding very narrow molecular weight distributions.

Now, in cationic polymerization, the cationic initiator is formed from the carbenium salt. Now, the bronsted acid or Lewis acid reacts with the monomer to give the monomer cations. Now, upon the addition of more monomer becomes macro cations. Now, monomers suitable for the cationic polymerization should have electron donating groups like olefin, CH2, CHR, and R representing the chain with electro-rich substitutes for the compound R2CZ with the heteroatoms or heterogroups called Z and cyclic molecules with the heteroatom as a part of the ring structure. Now, there are many more cationically polymerizable monomers than anionically polymerizable ones.



Classes of polymerizations

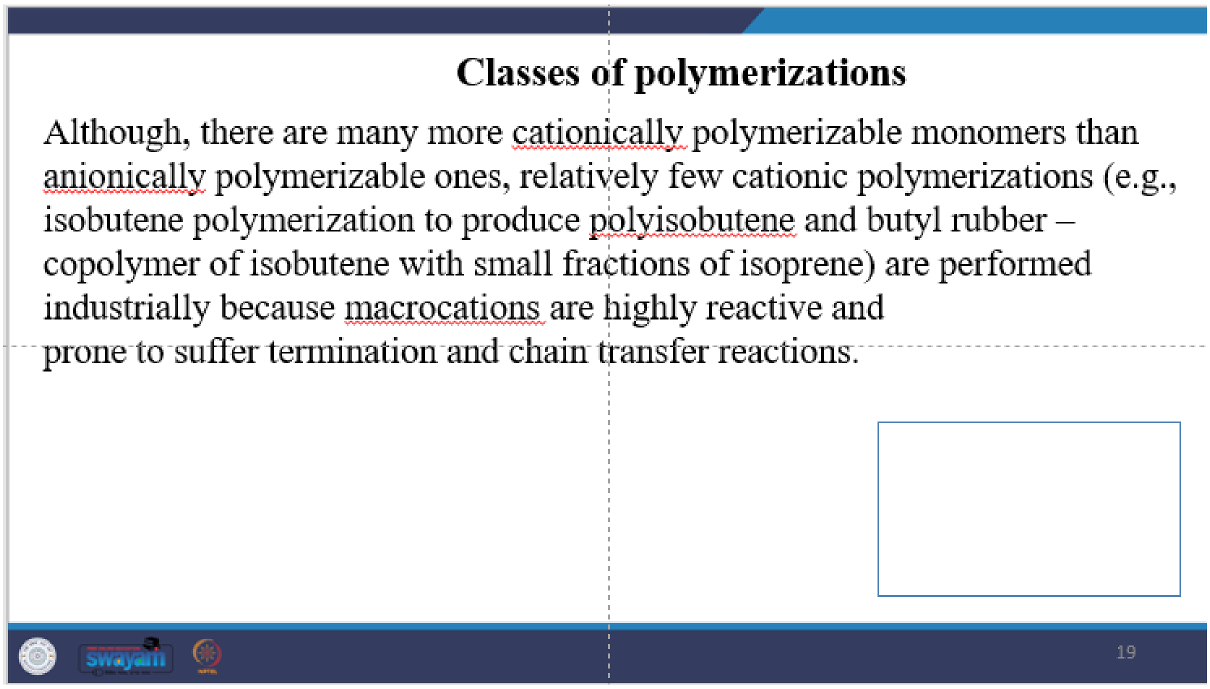
Cationic polymerization

In cationic polymerization, cationic initiators formed from carbenium salts, Brønsted acids or Lewis acids, react with monomer to give monomer cations that upon addition of more monomer become macrocations.

Monomers suitable for cationic polymerization should have electron donating groups:

(1) olefins CH2==CHR with electro-rich substituents,
(2) compounds R_2C==Z with hetero atoms or hetero groups Z and
(3) cyclic molecules with hetero atoms as part of the ring structure.

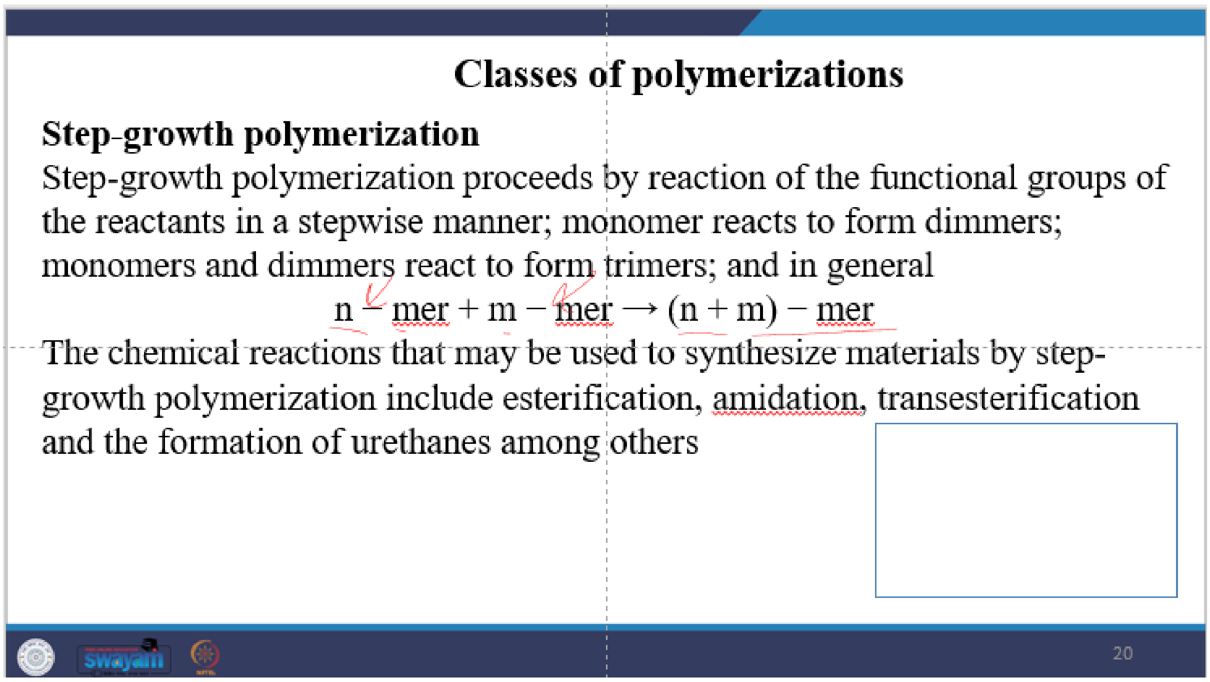
Now, there are very few cation polymerizations like isobutene polymerization to produce the poly isobutene and butyl rubber copolymer of isobutene with a small fraction of isoprene they are performed industrially because macro cations are highly reactive and prone to suffer termination and chain transfer reaction. So, controlling the reaction or propagation of the reaction is very important. In the previously the termination was important here the propagation is important. Let us talk about the step growth polymerization. This step growth polymerization this proceed by the reaction of a functional group of the reactants in stepwise manner and the monomer reacts to form the dimers monomers, trimers, dimers react for the trimers in general like different type of they form the different type of a mers like this monomer, this monomer they form this one like dimers, trimers like this.



Classes of polymerizations

Although, there are many more cationically polymerizable monomers than anionically polymerizable ones, relatively few cationic polymerizations (e.g., isobutene polymerization to produce polyisobutene and butyl rubber – copolymer of isobutene with small fractions of isoprene) are performed industrially because macrocations are highly reactive and prone to suffer termination and chain transfer reactions.

Now, the chemical reaction that may be used to synthesize a material by step growth polymerization this includes esterification, amidation, transesterification, and the formation of urethanes, among others. So, all step growth polymerization fall into two groups depending on the type of monomers employed; the first one implies the use of at least two bifunctional and polyfunctional monomer each one possessing a single type of active group. The monomers involved in this type of reaction are often represented as AA or BB, where A and B are the different reactive groups. An example of this particular reaction is the formation of a polyester from the diols and diacid. So, here you see diols and diacid, and they form this polymer.



Classes of polymerizations

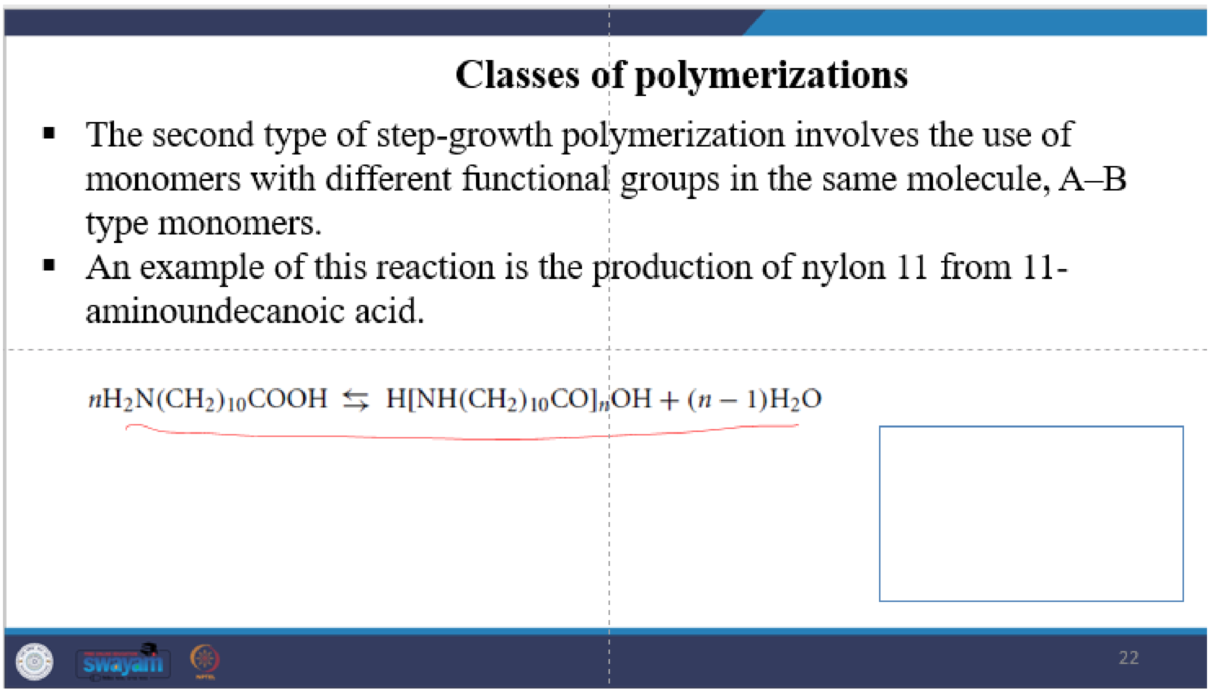
Step-growth polymerization

Step-growth polymerization proceeds by reaction of the functional groups of the reactants in a stepwise manner; monomer reacts to form dimmers; monomers and dimmers react to form trimers; and in general

$$n - \text{mer} + m - \text{mer} \rightarrow (n + m) - \text{mer}$$

The chemical reactions that may be used to synthesize materials by step-growth polymerization include esterification, amidation, transesterification and the formation of urethanes among others

Now, the second type of step is growth polymerization, which involves the use of monomers with different functional groups in the same molecule A B type of a monomer. An example of this reaction is the production of nylon from one amino daconic acid here; you see this in the amino and daconic acid. Now, the bifunctional monomers such as AA BB or AB yield the linear polymers, branch, and cross-linked polymers that are obtained from the polyfunctional monomers. So, this is the difference between these two classes. Now let us take the example of polymerization of formaldehyde with phenol this may lead to the complex architecture.

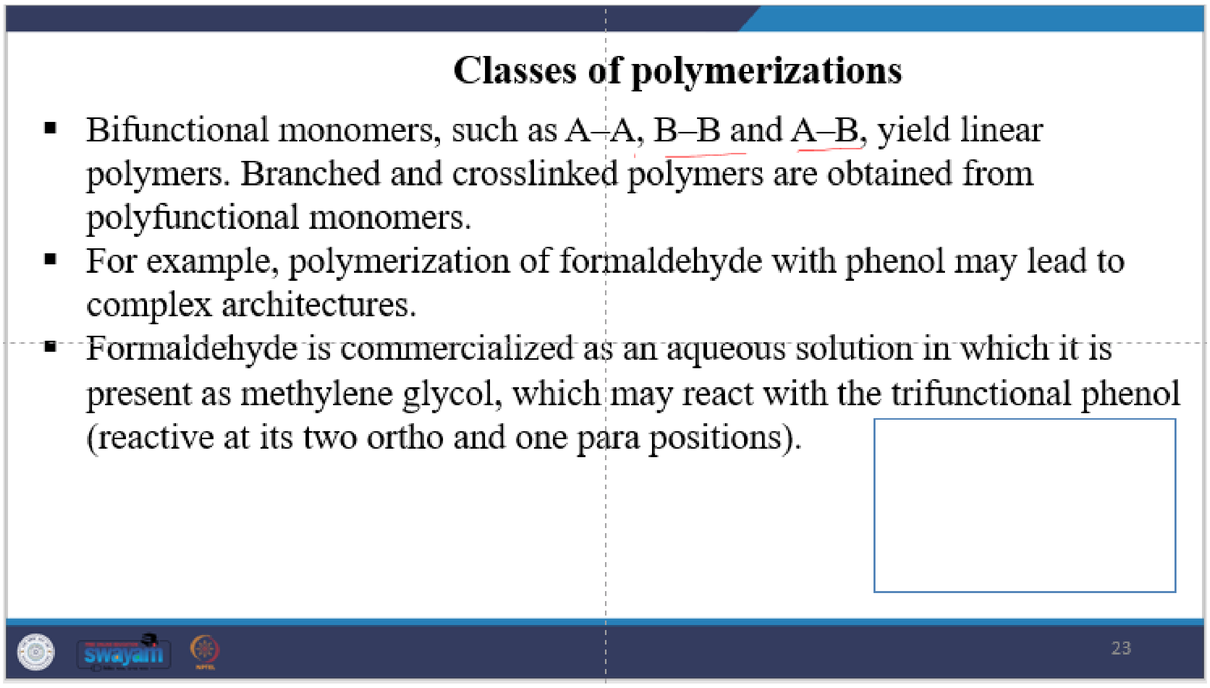


Classes of polymerizations

- The second type of step-growth polymerization involves the use of monomers with different functional groups in the same molecule, A–B type monomers.
- An example of this reaction is the production of nylon 11 from 11-aminoundecanoic acid.

$$n\text{H}_2\text{N(CH}_2)_{10}\text{COOH} \leftrightarrows \text{H[NH(CH}_2)_{10}\text{CO]}_n\text{OH} + (n - 1)\text{H}_2\text{O}$$

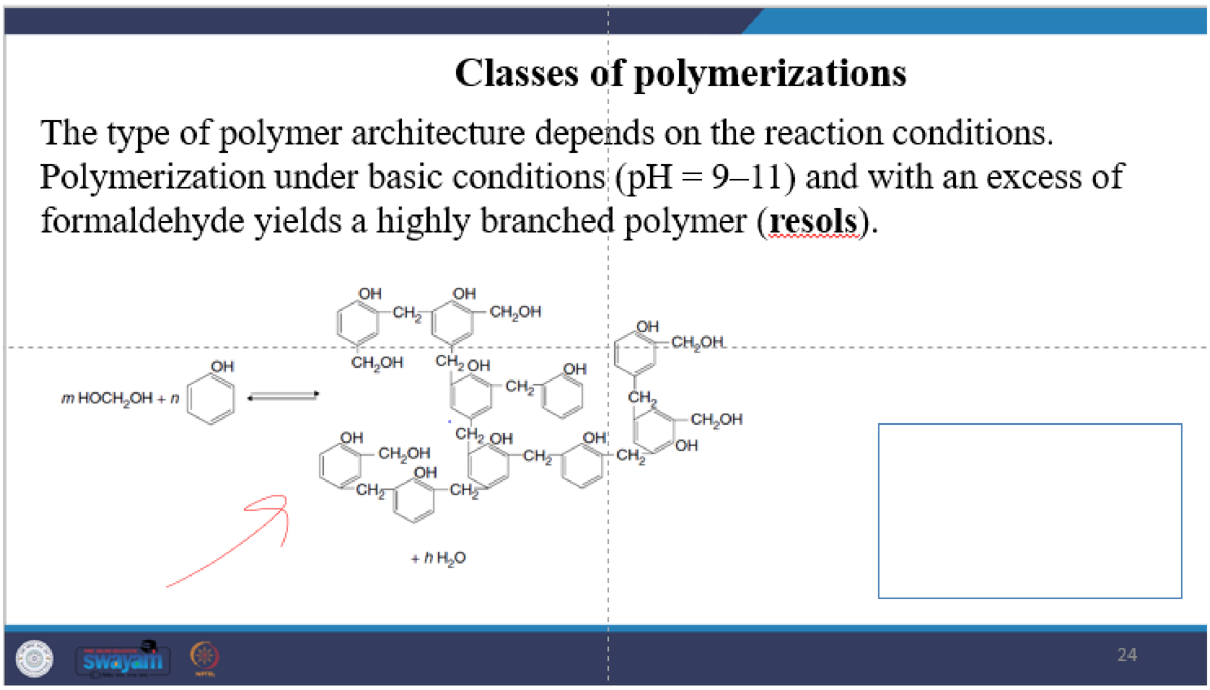
Now, formaldehyde is commercialized as an aqueous solution in which it is presented as a methylene glycol, which may react with the tri-functional phenol the reactive at its two ortho and 1 para positions. Now, this type of polymer architecture depends on the reaction conditions. Now, the polymerization under the basic conditions where you can maintain the pH from 9 to 11 with an excess of formaldehyde yields the highly branched polymer results you see over here. In this case, the polymerization is stopped when the polymer is still liquid or in a soluble phase. The formation of the final network, which is called the curing is achieved during the application part which is like in a foundry or binders to make the cores and mold for the cost of steel, iron, and non-ferrous.



Classes of polymerizations

- Bifunctional monomers, such as A–A, B–B and A–B, yield linear polymers. Branched and crosslinked polymers are obtained from polyfunctional monomers.
- For example, polymerization of formaldehyde with phenol may lead to complex architectures.
- Formaldehyde is commercialized as an aqueous solution in which it is present as methylene glycol, which may react with the trifunctional phenol (reactive at its two ortho and one para positions).

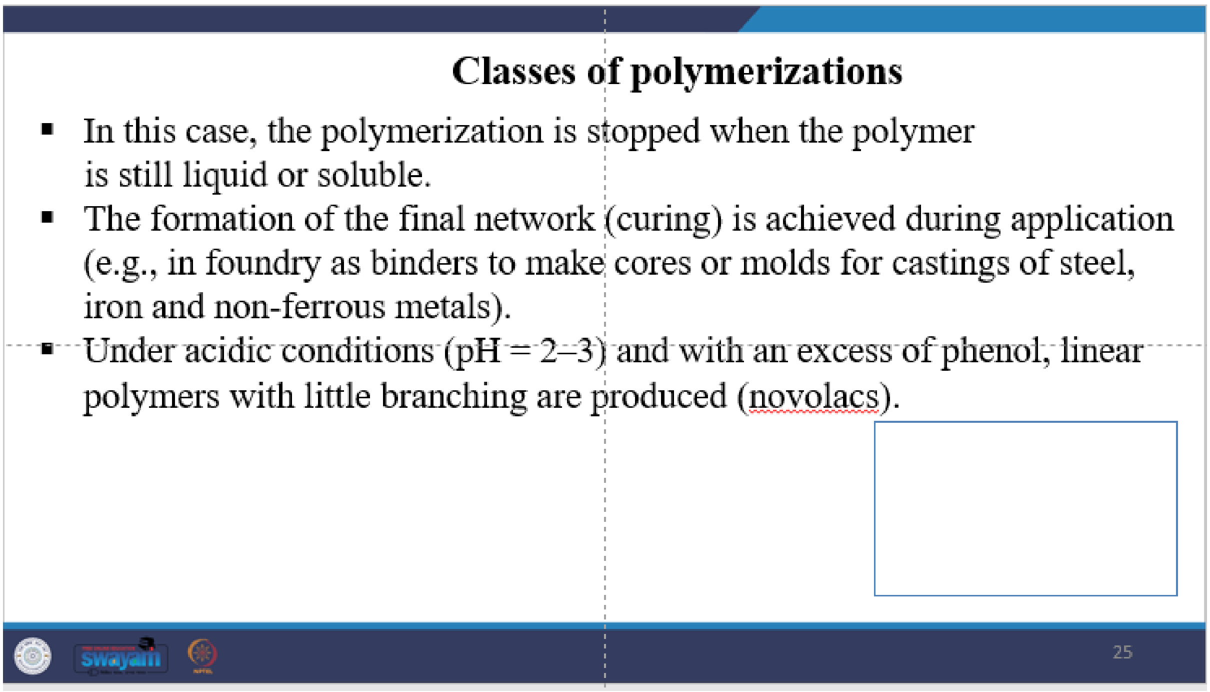
That means the termination it takes place during the course of the application. Now, under the acidic condition, when the pH is maintained between 2 and 3 with an excess of phenol linear polymer with a little branching, they are produced, and these are called the NOVLEX. Now, in a step-growth polymerization, the molecular weight continuously increases with the times and the formation of polymers with a sufficiently high molecular weight for practical application. Now, this requires a very high conversion of the reactive groups, sometimes more than 98 to 99 percent. Now, this requirement imposes stringent conditions on the formation of the polymers by step polymerization.



Classes of polymerizations

The type of polymer architecture depends on the reaction conditions. Polymerization under basic conditions (pH = 9–11) and with an excess of formaldehyde yields a highly branched polymer (**resols**).

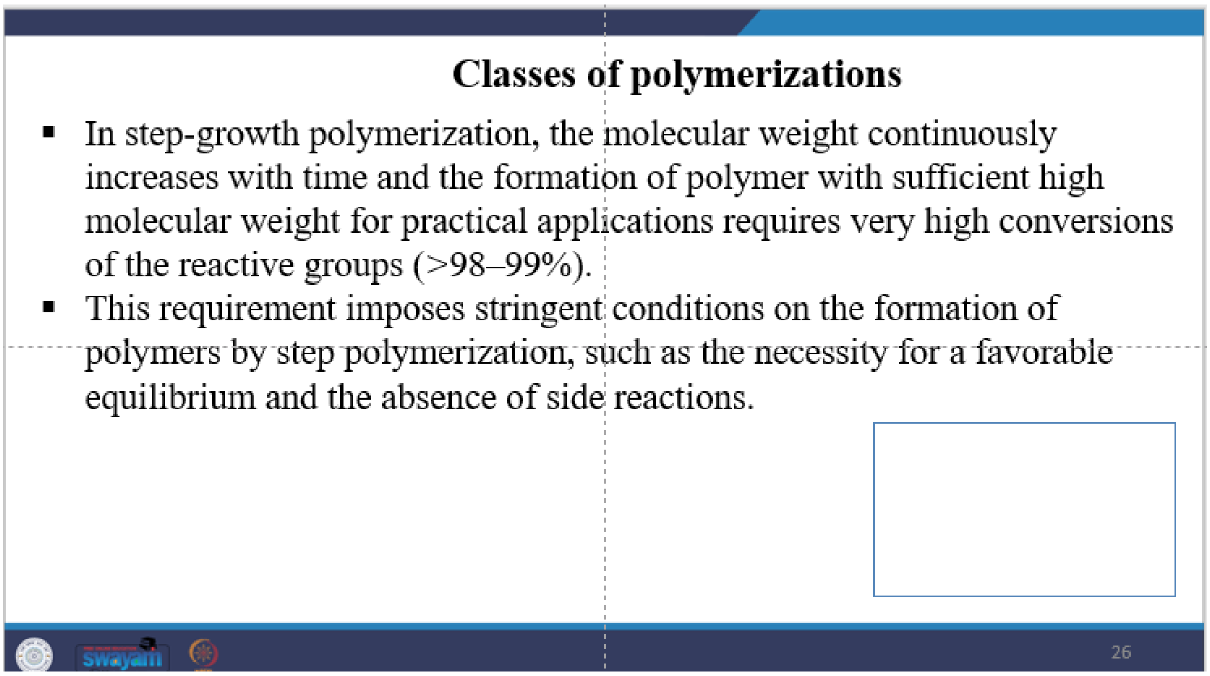
Now, such as the necessity for a favorable equilibrium and absence of side reactions. Now in a batch system, the equilibrium conversion is such that only oligomers are formed. In practice, these are the reactors from which the by-product, like water in the esterification process, is continuously removed by using a vacuum and or inner gases. Now, this allows the shifting of equilibrium in the forward direction, hence achieving the high conversion and high molecular weight because the chains are continuously reacting with the monomers or themselves.



Classes of polymerizations

- In this case, the polymerization is stopped when the polymer is still liquid or soluble.
- The formation of the final network (curing) is achieved during application (e.g., in foundry as binders to make cores or molds for castings of steel, iron and non-ferrous metals).
- Under acidic conditions (pH = 2–3) and with an excess of phenol, linear polymers with little branching are produced (novolacs).

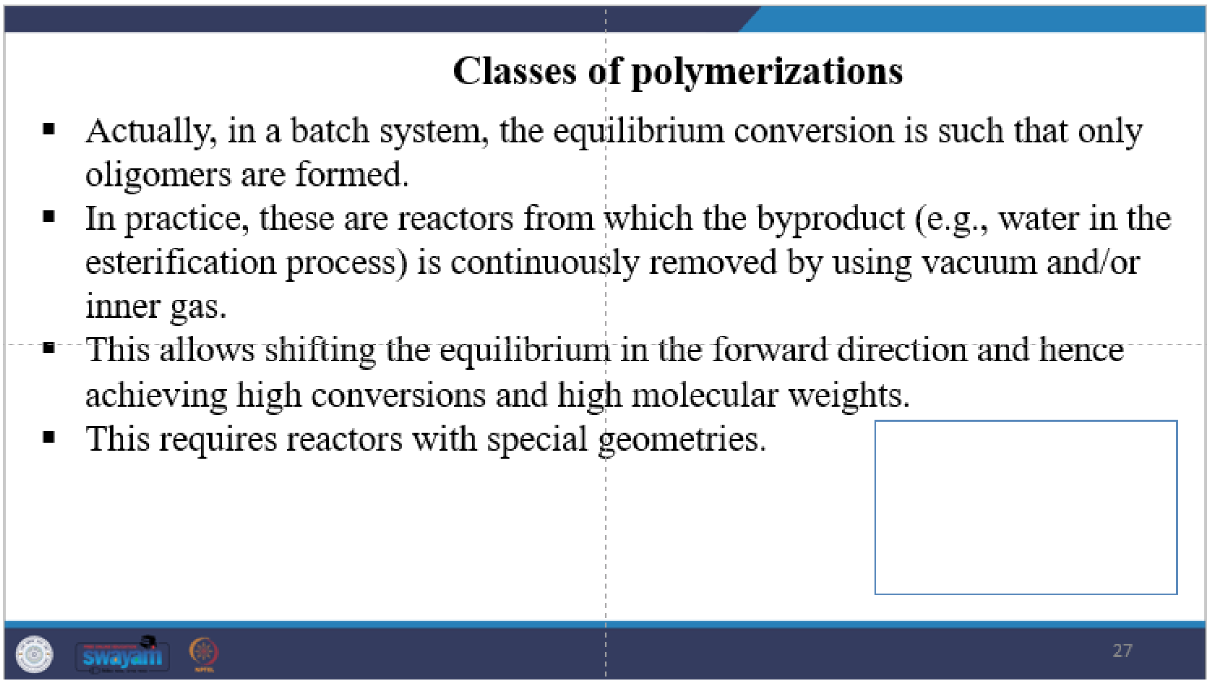
So, in that case, you can anticipate the high molecular weight. Now, this requires a reactor with special geometrics or geometry. Now, different types of polymerization classes which we discussed, can be implemented in several ways like bulk polymerization, solution polymerization, gas phase polymerization, slurry polymerization, suspension polymerization, and emulsion polymerization. Now in bulk polymerization, the only components of the formulation are the monomer and the catalyst or initiator.



Classes of polymerizations

- In step-growth polymerization, the molecular weight continuously increases with time and the formation of polymer with sufficient high molecular weight for practical applications requires very high conversions of the reactive groups (>98–99%).
- This requirement imposes stringent conditions on the formation of polymers by step polymerization, such as the necessity for a favorable equilibrium and the absence of side reactions.

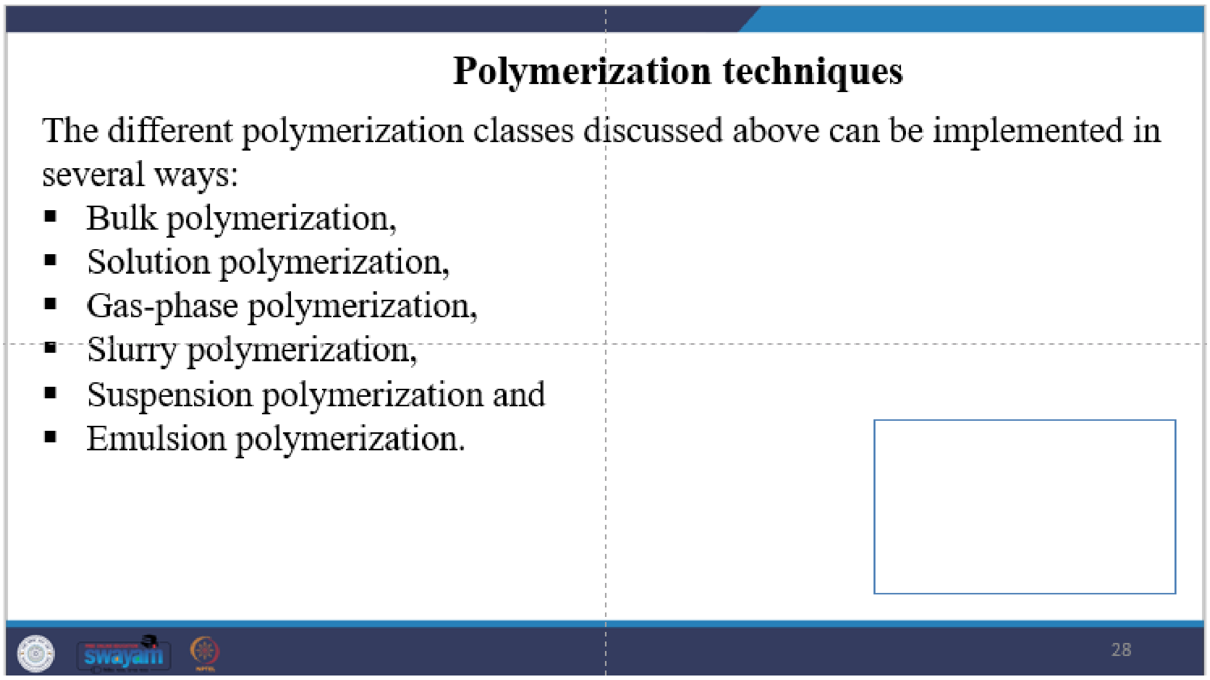
So these things are essential. Now when the polymer is soluble in the monomer the reaction mass remains homogeneous for the entire process. Examples of homogeneous bulk polymerization are the production of low-density polyethylene, referred to as LDPE. The general-purpose polystyrene and polymethyl methacrylate PMMA are produced by this free radical polymerization and in the manufacture of many polymers they are produced by step-growth polymerization. This includes the PET polyethylene terephthalate, polycarbonate, and nylons. The main advantage of bulk polymerization is that they are very pure polymers produced at a very high production rate per unit volume of the reactor.



Classes of polymerizations

- Actually, in a batch system, the equilibrium conversion is such that only oligomers are formed.
- In practice, these are reactors from which the byproduct (e.g., water in the esterification process) is continuously removed by using vacuum and/or inner gas.
- This allows shifting the equilibrium in the forward direction and hence achieving high conversions and high molecular weights.
- This requires reactors with special geometries.

But there are certain drawbacks also attributed to this process is that the removal of polymerization heat is extremely difficult because of the high viscosity of the reaction mass. This is associated with the high concentration of polymers. See when these chains, polymeric chains are entangled each other so the viscosity will be very high. So, you need to control the temperature it is very difficult. The thermal control of the reactor is more difficult in free radical polymerization than in step-growth polymerization.

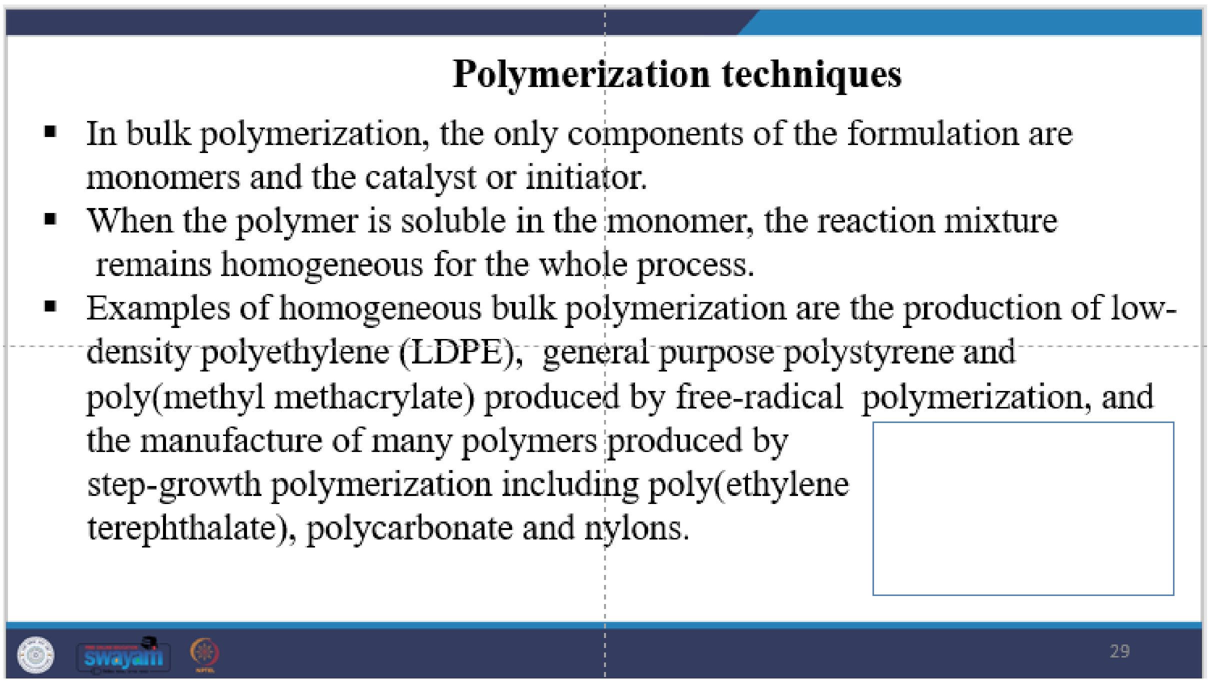


Polymerization techniques

The different polymerization classes discussed above can be implemented in several ways:

- Bulk polymerization,
- Solution polymerization,
- Gas-phase polymerization,
- Slurry polymerization,
- Suspension polymerization and
- Emulsion polymerization.

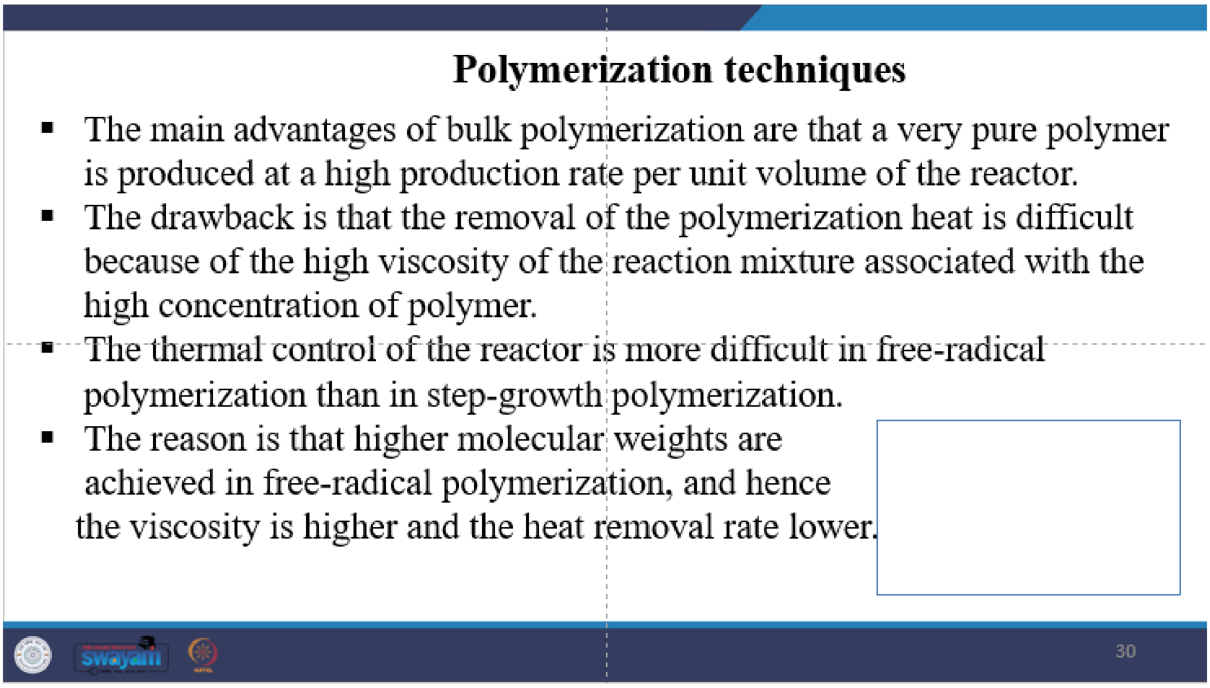
The reason is that the high molecular weight is achieved in free radical polymerization. Hence, the viscosity is higher, and the heat removal rate is lower. The way of achieving good thermal control and avoiding the use of solvent is to use suspension polymerization. So, this is another class. And this process, drops of monomer containing the initiator are suspended in water like this. This is a chamber, and here you see that the monomer contains the initiator, and this they are dropped in the water.



Polymerization techniques

- In bulk polymerization, the only components of the formulation are monomers and the catalyst or initiator.
- When the polymer is soluble in the monomer, the reaction mixture remains homogeneous for the whole process.
- Examples of homogeneous bulk polymerization are the production of low-density polyethylene (LDPE), general purpose polystyrene and poly(methyl methacrylate) produced by free-radical polymerization, and the manufacture of many polymers produced by step-growth polymerization including poly(ethylene terephthalate), polycarbonate and nylons.

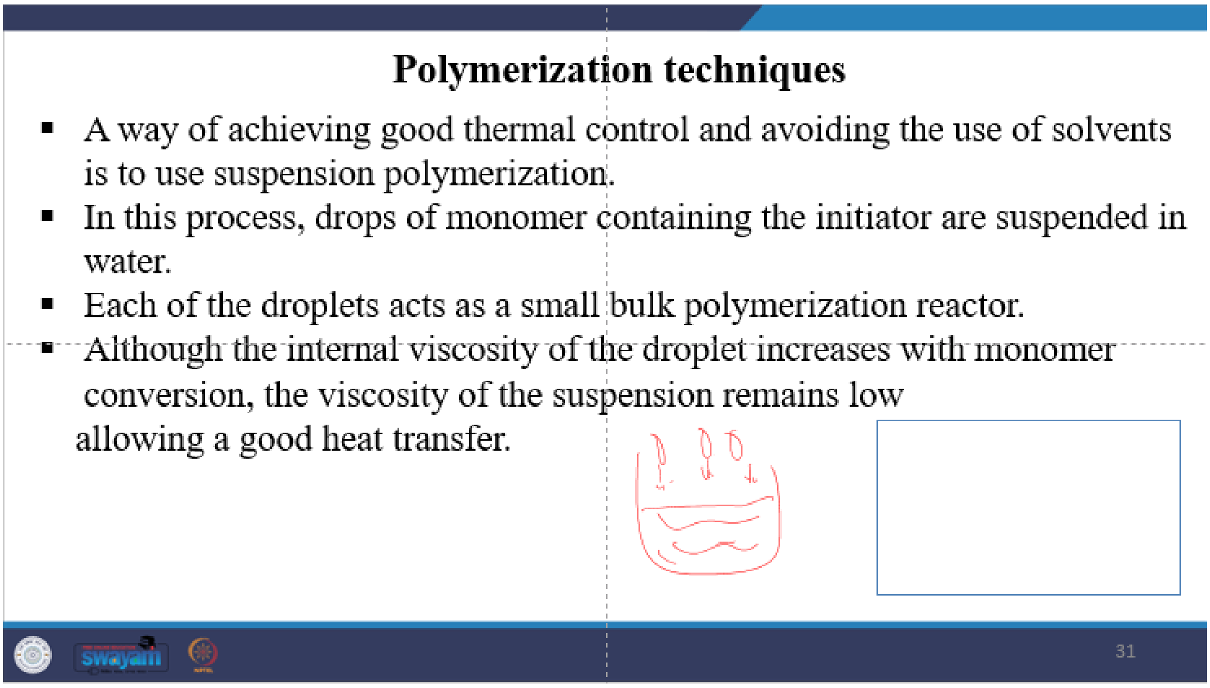
Each droplet acts as a small bulk polymerization reactor. The internal viscosity of the droplet increases with the monomer conversion, and the viscosity of the suspension remains low, allowing good heat transfer. So, you see that the water can act as a heat transfer agent. Now, suspension stability and the particle size distribution are controlled by the agitation and the type and concentration of the suspension agent. A particular product with a diameter ranging from 10 micrometres to 5 mm can be obtained easily. Now, these particles contain the suspension agents although some removal is possible, the final product inevitably contains some amount of suspension agents.



Polymerization techniques

- The main advantages of bulk polymerization are that a very pure polymer is produced at a high production rate per unit volume of the reactor.
- The drawback is that the removal of the polymerization heat is difficult because of the high viscosity of the reaction mixture associated with the high concentration of polymer.
- The thermal control of the reactor is more difficult in free-radical polymerization than in step-growth polymerization.
- The reason is that higher molecular weights are achieved in free-radical polymerization, and hence the viscosity is higher and the heat removal rate lower.

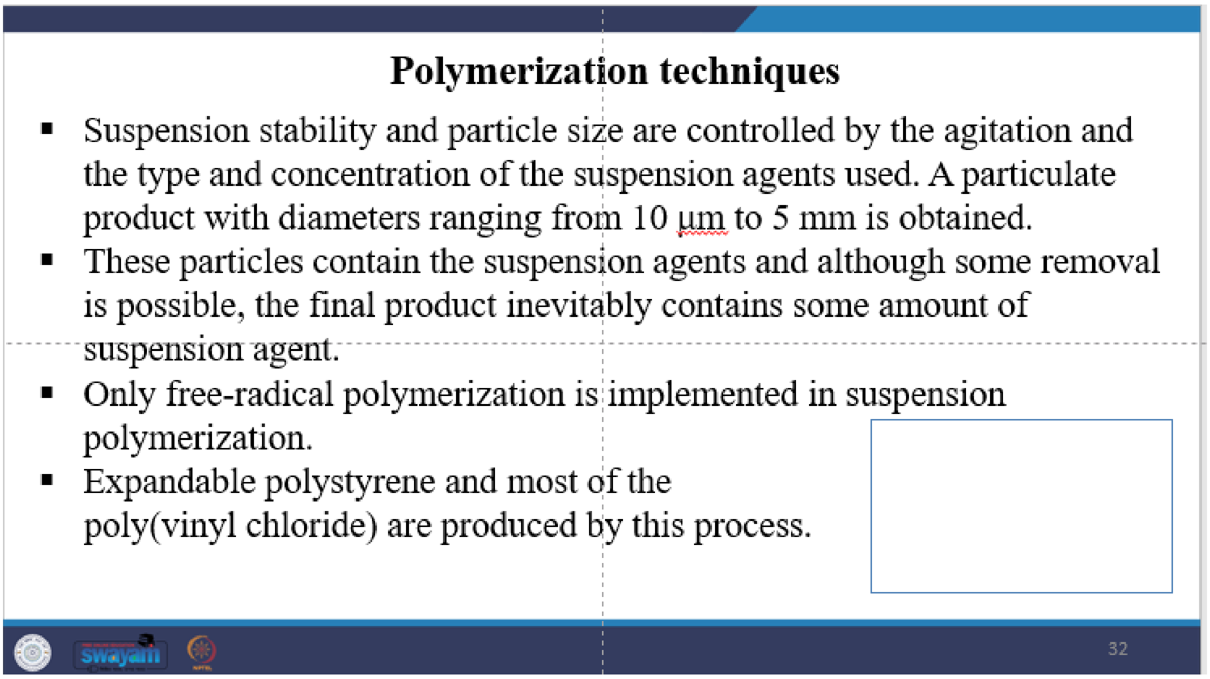
So, free radical polymerization is implemented only in suspension polymerization. Expendable polystyrene and PVC products are produced by this process. Emulsion polymerization is the polymerization technique leading to polymer finally dispersed particle diameters usually ranging from, say, 80 to 500 nanometers in a continuous medium and this medium is sometimes like water. Now, this product is frequently called latex. Now, only free radical polymerization has been commercially implemented in emulsion polymerization.



Polymerization techniques

- A way of achieving good thermal control and avoiding the use of solvents is to use suspension polymerization.
- In this process, drops of monomer containing the initiator are suspended in water.
- Each of the droplets acts as a small bulk polymerization reactor.
- Although the internal viscosity of the droplet increases with monomer conversion, the viscosity of the suspension remains low allowing a good heat transfer.

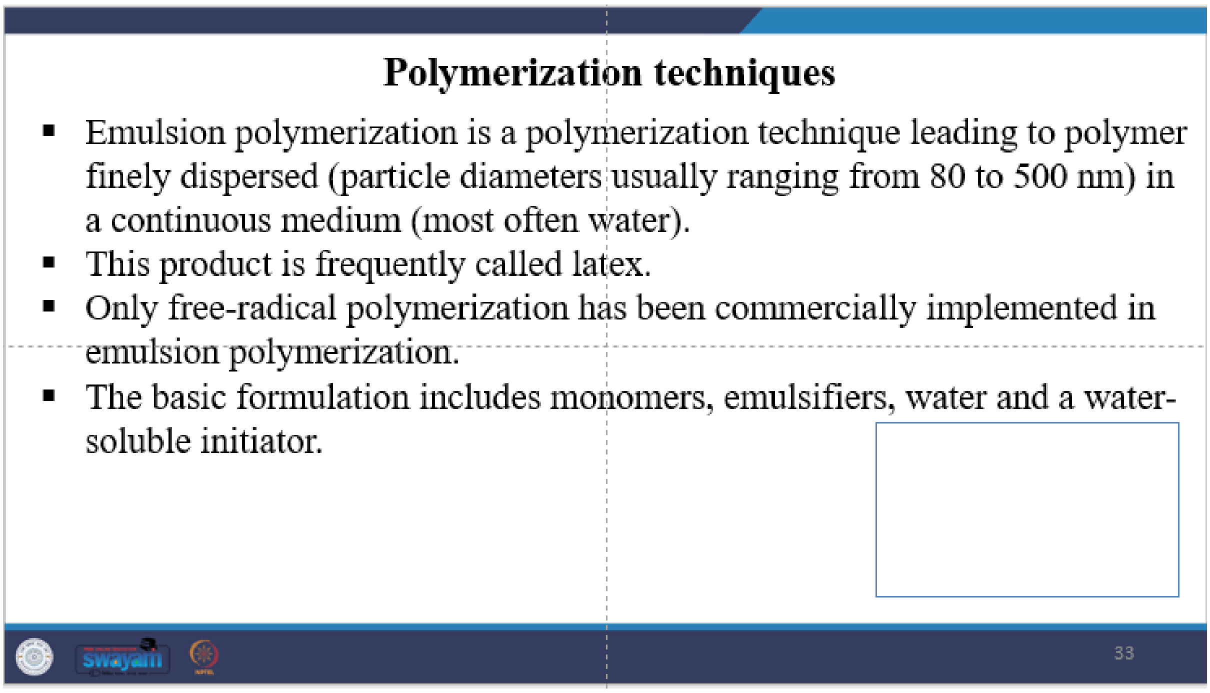
The basic formulation includes the monomer, emulsifier, water, and a water-soluble initiator. Usually, these monomers are dispersed in 10 to 100 micrometer droplets under agitation. The amount of emulsifier is enough to cover these droplets and to form a large number of micelles. Radicals formed by the decomposition of the initiator start the polymerization in the aqueous phase. The oligomer formed enters in though the micelles are precipitate in the aqueous phase in both cases forming the tiny polymer particles.



Polymerization techniques

- Suspension stability and particle size are controlled by the agitation and the type and concentration of the suspension agents used. A particulate product with diameters ranging from 10 μm to 5 mm is obtained.
- These particles contain the suspension agents and although some removal is possible, the final product inevitably contains some amount of suspension agent.
- Only free-radical polymerization is implemented in suspension polymerization.
- Expandable polystyrene and most of the poly(vinyl chloride) are produced by this process.

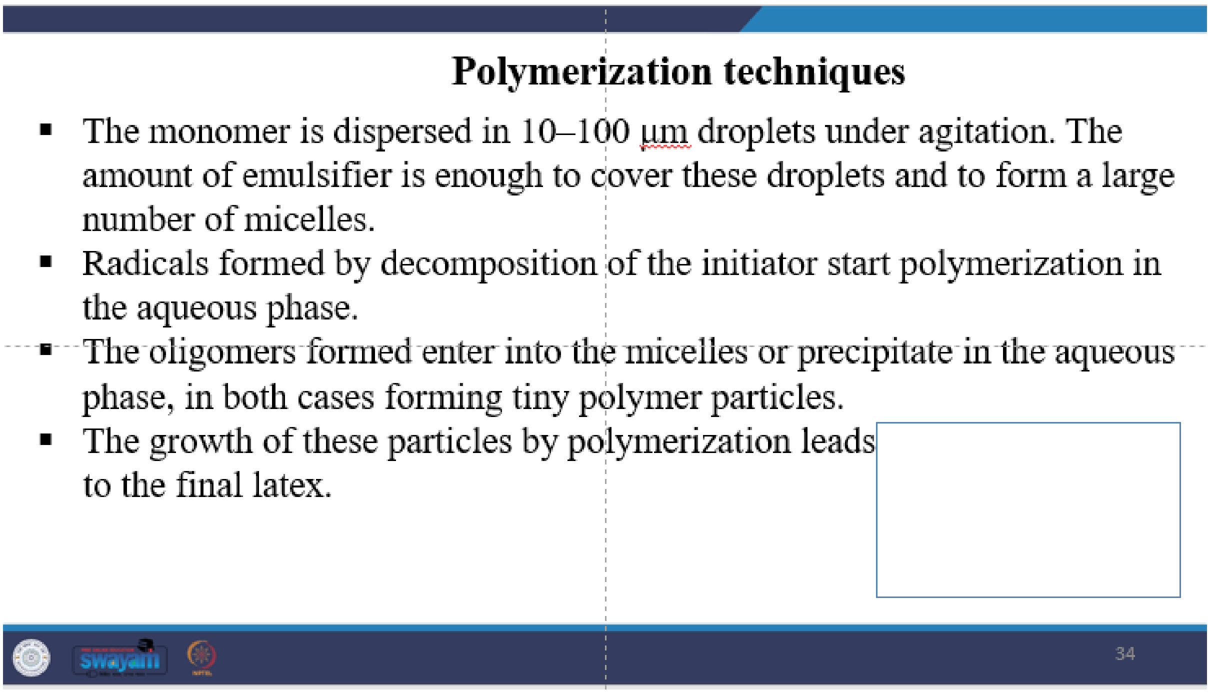
So, the growth of these particles by the polymerization leads to the final latex. And the monomer droplets act as a monomer reservoir and almost no polymerization occurs in them. So, this is the beauty of this particular technique. The particle size of the latex is not determined by the size of the monomer droplet but by the number of particles formed.



Polymerization techniques

- Emulsion polymerization is a polymerization technique leading to polymer finely dispersed (particle diameters usually ranging from 80 to 500 nm) in a continuous medium (most often water).
- This product is frequently called latex.
- Only free-radical polymerization has been commercially implemented in emulsion polymerization.
- The basic formulation includes monomers, emulsifiers, water and a water-soluble initiator.

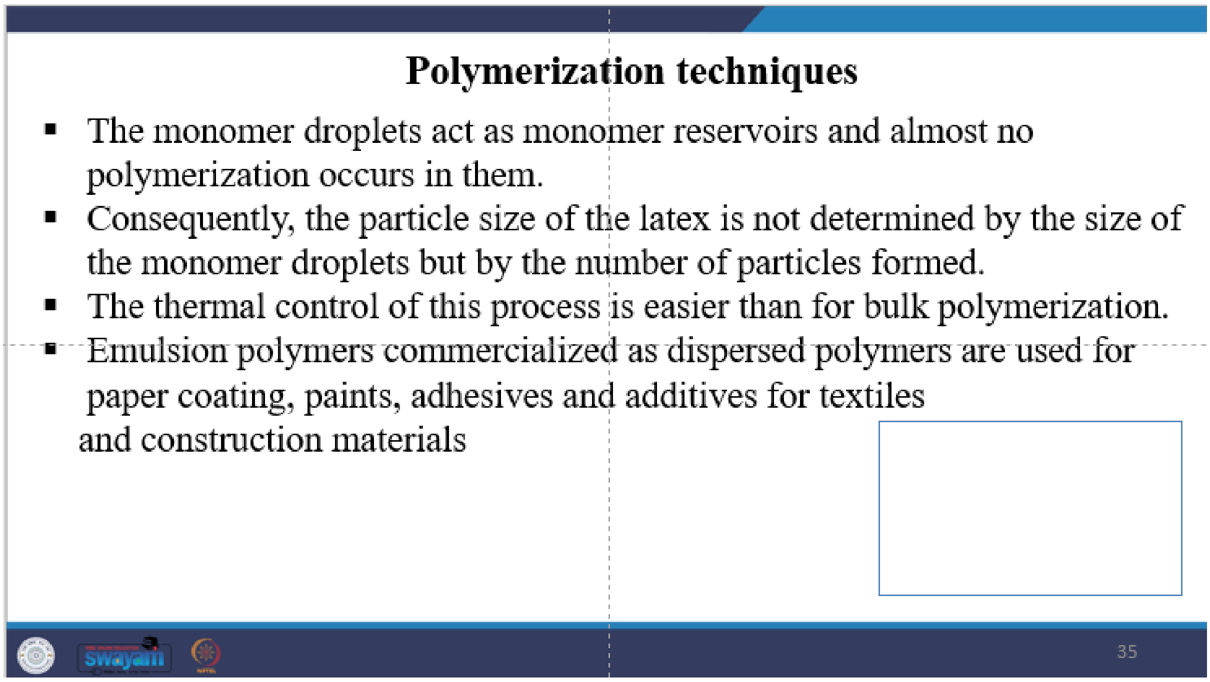
So, the size of the monomer does not matter. Now, the thermal control of these processes is easier than bulk polymerization and emulsion polymerization commercializes the dispersed polymers that are used for paper coating, paint, adhesive, and additives for textiles and construction materials. So, the polymerization of ethylene is often carried out in a gas phase using the heterogeneous coordination catalyst, and the polymer is formed on the active sides of the catalyst, forming an expanding catalyst polymer particle. So, the gaseous monomer diffuses through the pores of the particles and through the polymer to reach the active sides. Slurry polymerization is often used in the manufacture of polyolefin. Similarly, the reaction system consists of the catalyst dispersed or dissolved as in the case of soluble metallocene catalyst in a continuous medium which may be a diluent in which the monomer is dissolved or pure monomer and the polymer is insoluble in the continuous medium.



Polymerization techniques

- The monomer is dispersed in 10–100 µm droplets under agitation. The amount of emulsifier is enough to cover these droplets and to form a large number of micelles.
- Radicals formed by decomposition of the initiator start polymerization in the aqueous phase.
- The oligomers formed enter into the micelles or precipitate in the aqueous phase, in both cases forming tiny polymer particles.
- The growth of these particles by polymerization leads to the final latex.

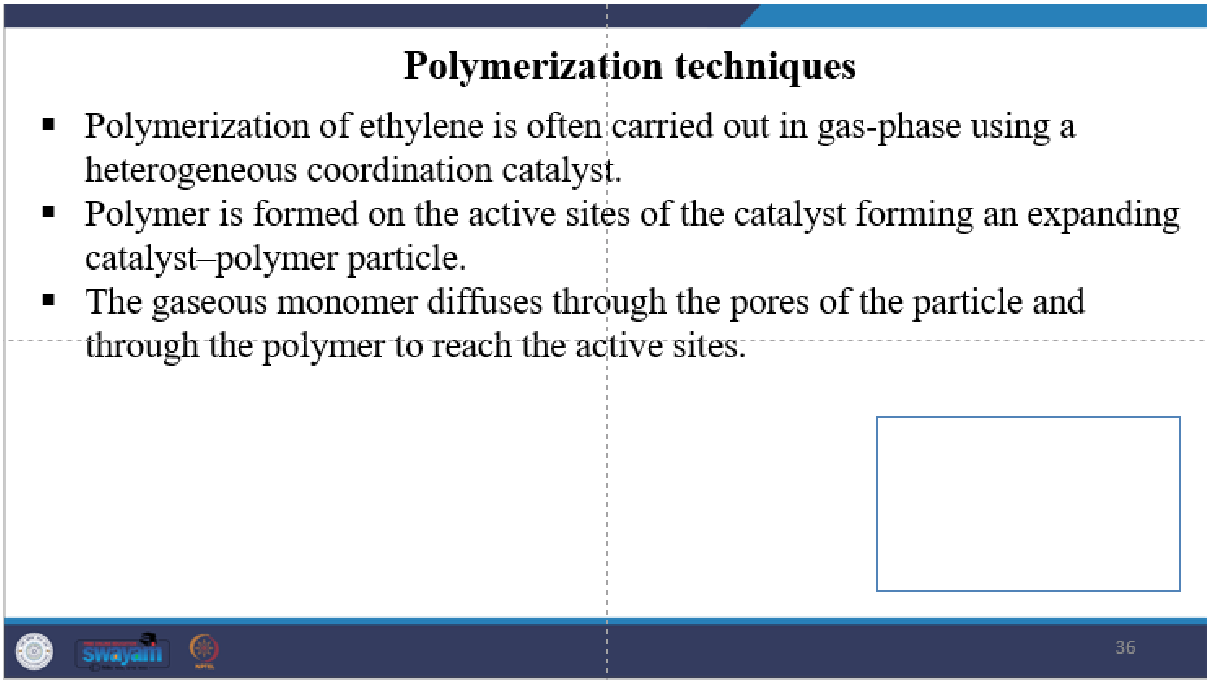
Therefore, it precipitates on the catalyst, forming slurry. HDPE is produced in a slurry of isobutene called the Chevron Phillips process. Now, let us have a brief discussion about the main commercial polymerization. Now yearly world production of synthetic polymer exceeds almost 200 million metric tons, and about half of this amount corresponds to polyolefins. Now here you see that 17 percent polypropylene is attributed to the world polymer market HDPE 16, LLDP 11 percent, LDP 8 percent likewise, different polymers contribute to the world polymer market. Now the main commercial polymers are polypropylene, HIPPE is the composite polymer composed of the soft ethylene-propylene copolymer dispersed in the matrix of polypropylene.



Polymerization techniques

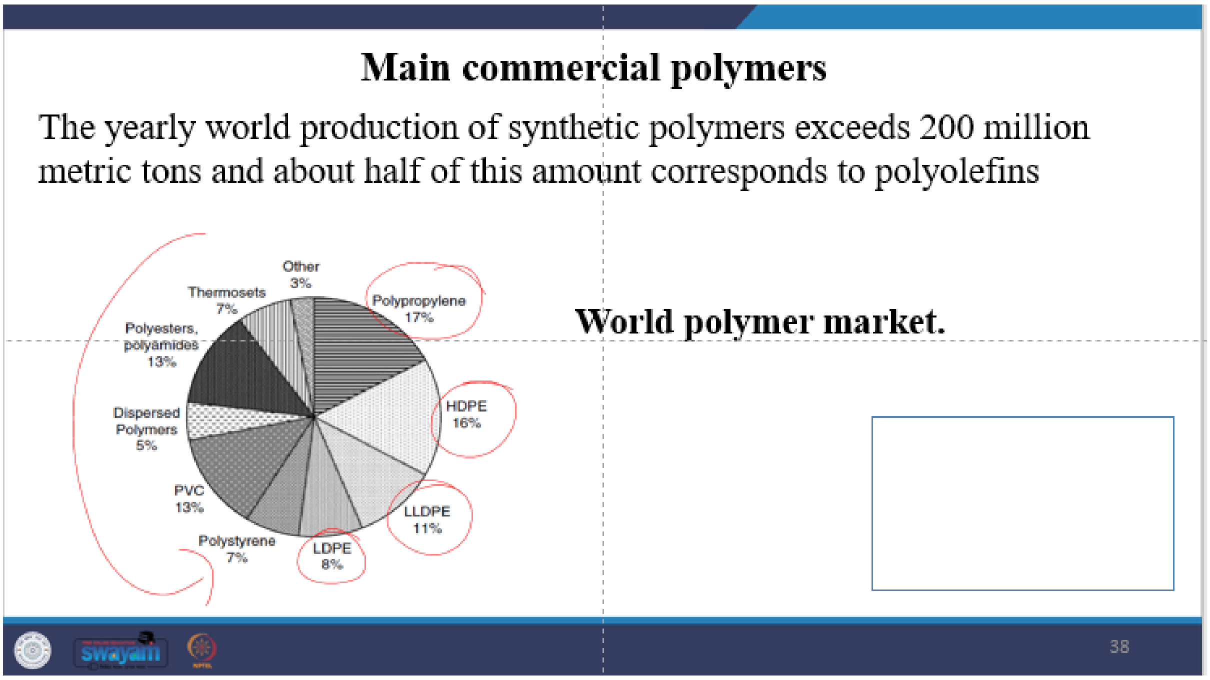
- The monomer droplets act as monomer reservoirs and almost no polymerization occurs in them.
- Consequently, the particle size of the latex is not determined by the size of the monomer droplets but by the number of particles formed.
- The thermal control of this process is easier than for bulk polymerization.
- Emulsion polymers commercialized as dispersed polymers are used for paper coating, paints, adhesives and additives for textiles and construction materials

Now, the main use of polypropylene is fiber, filament, carpets, raffia bags, netting, cordage, clothing, nonwoven fabrics, etc. Films like food packaging are sometimes used as stationary, automotive parts, appliances, rigid packing, and general consumer products. Polyethylene includes HDPE, LLDPE, and LDPE the main difference among all these polymers is referred to in this particular thing the chain architecture. Here you see that this is the HDPE, and more branch chains are there in LLDPE, and you see that this architecture of LDPE branched with a large number of short branches. Now, HDPE is a linear polymer with almost no branches LLDPE is a linear polymer with varying amounts of short branches, and LDPE has long branches in its basket with a large number of short branches. Now melted linear polyethylene chain crystallizes upon cooling, yielding a semi-crystalline polymer with about 60 percent crystallinity.



Polymerization techniques

- Polymerization of ethylene is often carried out in gas-phase using a heterogeneous coordination catalyst.
- Polymer is formed on the active sites of the catalyst forming an expanding catalyst–polymer particle.
- The gaseous monomer diffuses through the pores of the particle and through the polymer to reach the active sites.

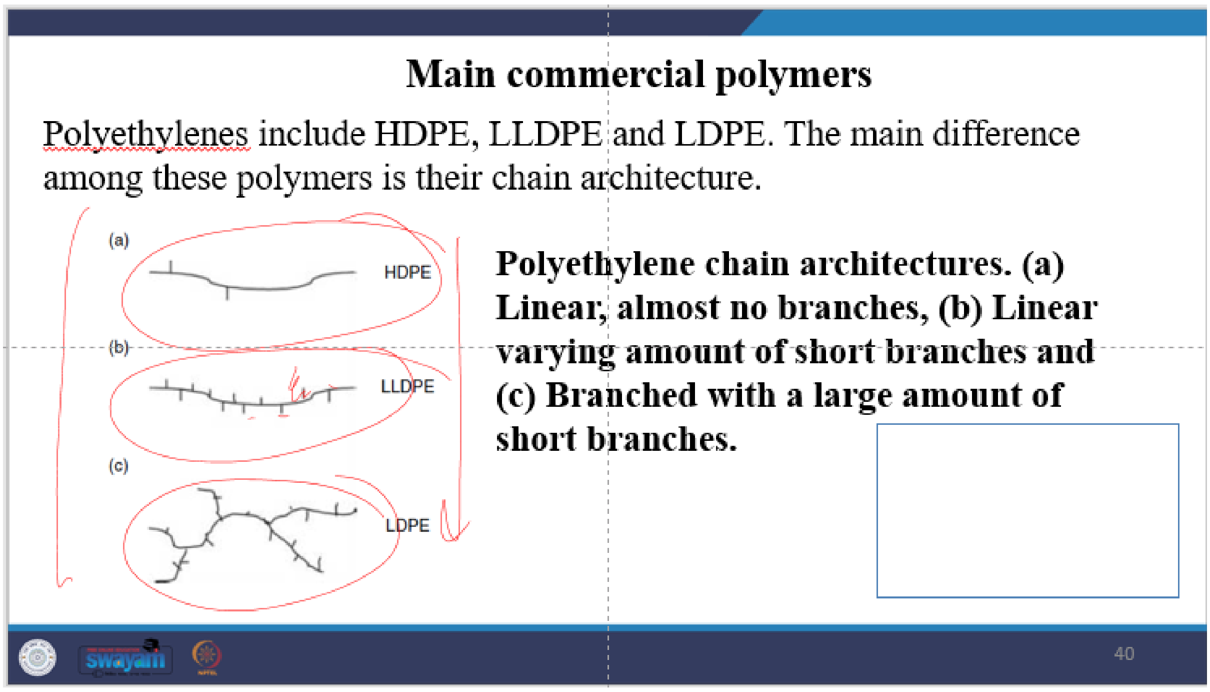


Main commercial polymers

The yearly world production of synthetic polymers exceeds 200 million metric tons and about half of this amount corresponds to polyolefins

World polymer market.

Now, the crystalline fraction decreases as the branching increases, and LLDPE and LDPE are the amorphous polymers. Now, if we compare with the LDPE produced by the free radical polymerization, the LLDPE exhibits a higher melting point this object can be used at higher temperatures it is stiffer, thinner walls can be used and the presence of this presents higher tensile and impact strength. So, the physical property as well as the chemical property all these things are essential. So, they are more resistant films. The processability of LLDPE is worse than the LDPE for a variety of reasons and the way to improve processability is to produce the bimodal molecular weight distribution.

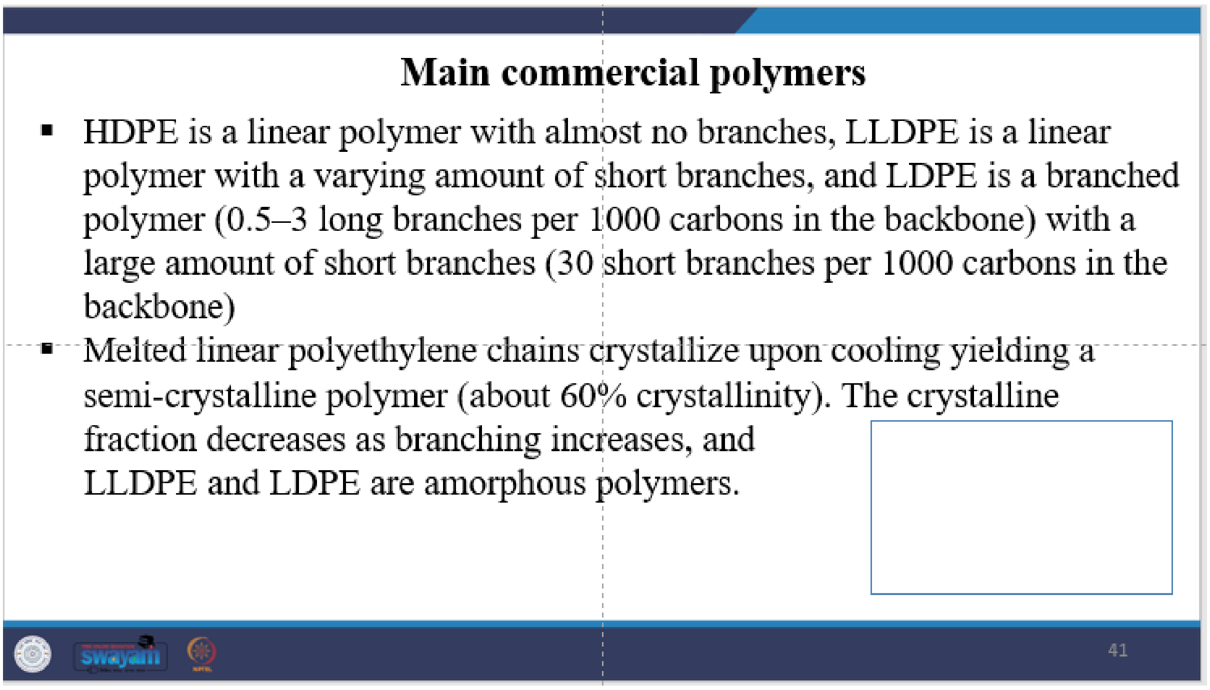


Main commercial polymers

Polyethylenes include HDPE, LLDPE and LDPE. The main difference among these polymers is their chain architecture.

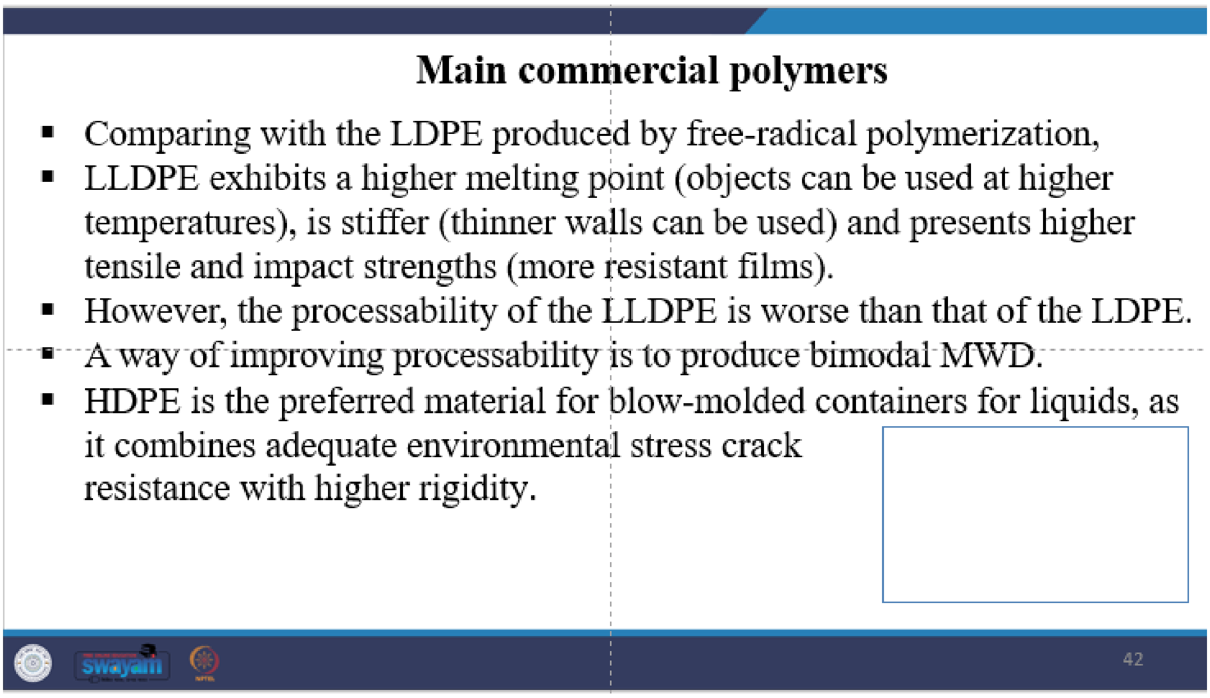
Polyethylene chain architectures. (a) Linear, almost no branches, (b) Linear varying amount of short branches and (c) Branched with a large amount of short branches.

HDPE is a preferred material for blow molding containers we will discuss this later on this is for the liquids as it combines the adequate environmental stress crack resistance with high rigidity. Styrenic polymers, now the Styrenic polymers include the general-purpose polystyrene HIP expendable polystyrene, styrene-acrylonitrile, sometimes referred to as SAN and ABS copolymers. The mechanical properties of general-purpose polystyrene are mainly determined by the molecular weight and this molecular weight ranges from 1,50,000 to 4 lakhs. The strength and the resistance to heat distortion increase, and this increases the molecular weight but the melt viscosity increases making the process more and more difficult. Lubricants like butyl stearate can be added to decrease the viscosity, but they are also lowering the softening point of the polymers.



Main commercial polymers

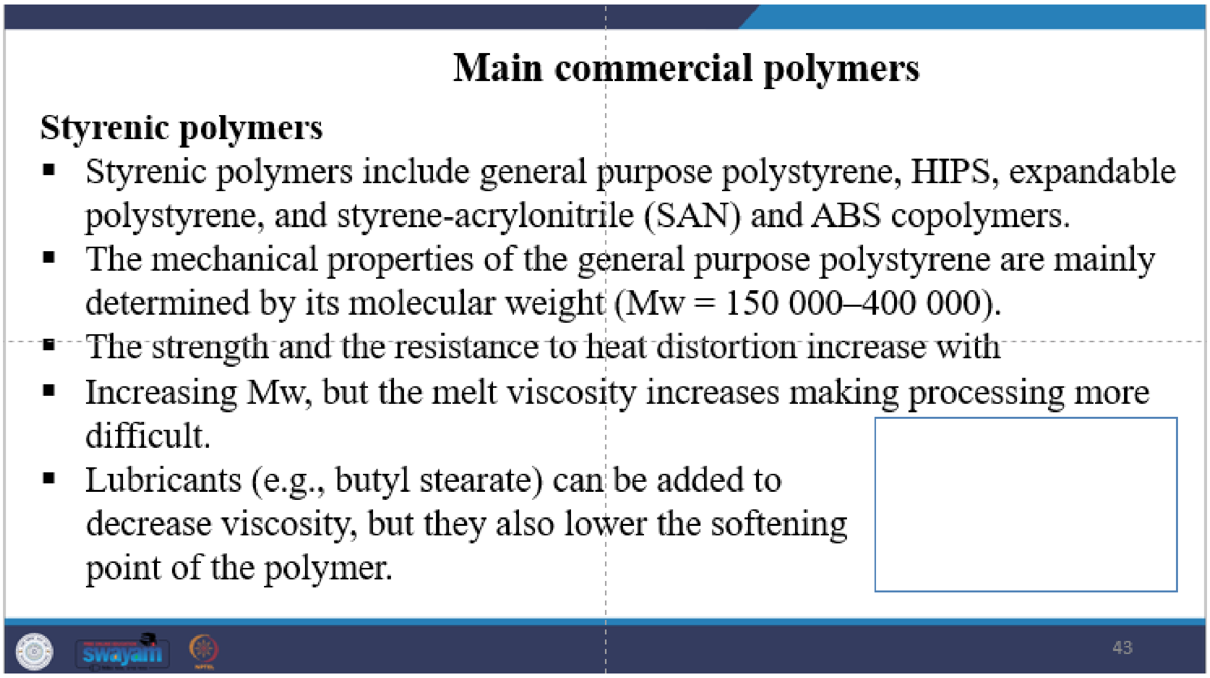
- HDPE is a linear polymer with almost no branches, LLDPE is a linear polymer with a varying amount of short branches, and LDPE is a branched polymer (0.5–3 long branches per 1000 carbons in the backbone) with a large amount of short branches (30 short branches per 1000 carbons in the backbone)
- Melted linear polyethylene chains crystallize upon cooling yielding a semi-crystalline polymer (about 60% crystallinity). The crystalline fraction decreases as branching increases, and LLDPE and LDPE are amorphous polymers.



Main commercial polymers

- Comparing with the LDPE produced by free-radical polymerization,
- LLDPE exhibits a higher melting point (objects can be used at higher temperatures), is stiffer (thinner walls can be used) and presents higher tensile and impact strengths (more resistant films).
- However, the processability of the LLDPE is worse than that of the LDPE.
- A way of improving processability is to produce bimodal MWD.
- HDPE is the preferred material for blow-molded containers for liquids, as it combines adequate environmental stress crack resistance with higher rigidity.

Now, the low viscosity or low molecular weight grades are used for injection molding, whereas the high molecular weight grades are used for the extrusion of film and sheets. Now, during the processing of melt polystyrene, this is forced to the narrow nozzle, and because of the high shear, the polymer chain orientation parallel to the flow cooling is usually fast, and orientation is often maintained to in the solid polymer, leading to anisotropy in the polymer properties. The properties of HIPs are mainly determined by their complex 3-phase morphology composed by rubbery polybutadiene cellular particles dispersed in a polystyrene matrix, and the polybutadiene particles contain the inclusion of polystyrene. The rubbery domain allows the distribution of the stress concentration in a large volume toughening the material. Therefore, the impact resistance of this polymer is much higher than that of general-purpose polystyrene.

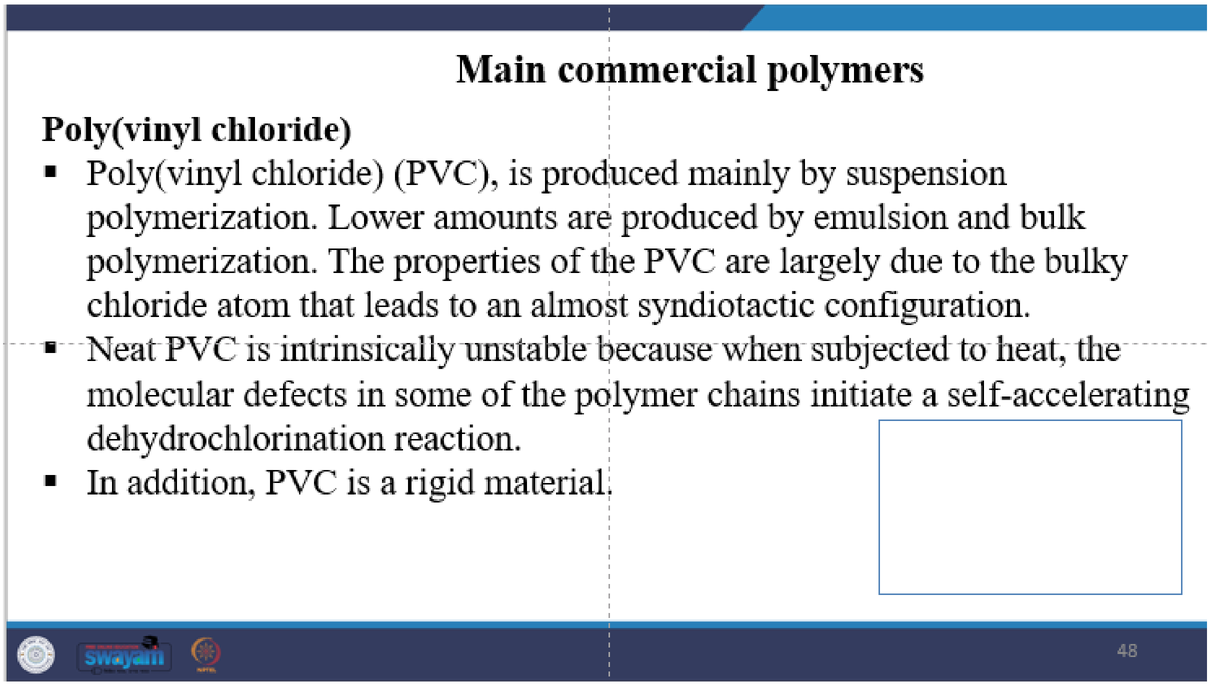


Main commercial polymers

Styrenic polymers

- Styrenic polymers include general purpose polystyrene, HIPS, expandable polystyrene, and styrene-acrylonitrile (SAN) and ABS copolymers.
- The mechanical properties of the general purpose polystyrene are mainly determined by its molecular weight (Mw = 150 000–400 000).
- The strength and the resistance to heat distortion increase with
- Increasing Mw, but the melt viscosity increases making processing more difficult.
- Lubricants (e.g., butyl stearate) can be added to decrease viscosity, but they also lower the softening point of the polymer.

Expendable polystyrene is the raw material fabricated to expand polystyrene. It is produced in the form of small polystyrene beads and swollen with 4 to 7 weight percent of blowing agent molded expanded polystyrene manufactured by the expansion and subsequent steam molding of expandable polystyrene. The main markets are the packaging, insulation, flotation, geofoam, etc. Most of the properties of the expanded polystyrene depend on the apparent density. Lower density leads to poorer mechanical properties and higher water absorption and permeation rates, so the durability may be on the lower side. Expendable polystyrene foams have applications in thermal insulation, impact soundproofing, foam work elements for concrete in the building industry, insulation of the cold storage depot, and storage molded part of packaging.

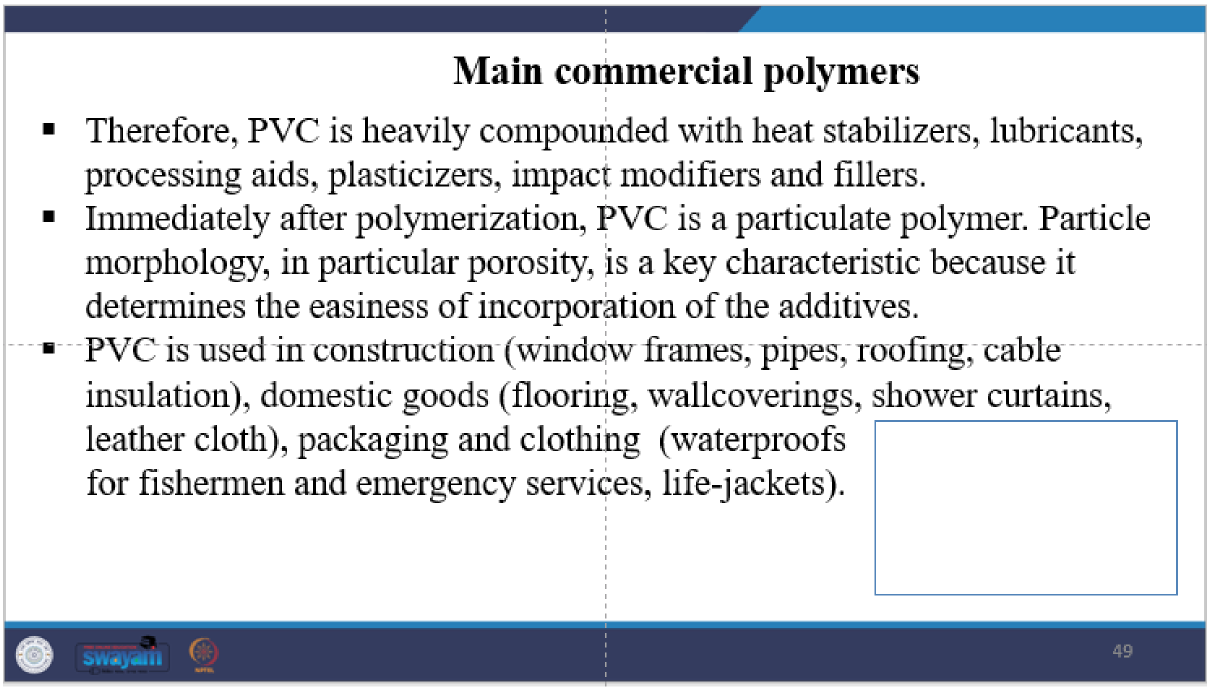


Main commercial polymers

Poly(vinyl chloride)

- Poly(vinyl chloride) (PVC), is produced mainly by suspension polymerization. Lower amounts are produced by emulsion and bulk polymerization. The properties of the PVC are largely due to the bulky chloride atom that leads to an almost syndiotactic configuration.
- Neat PVC is intrinsically unstable because when subjected to heat, the molecular defects in some of the polymer chains initiate a self-accelerating dehydrochlorination reaction.
- In addition, PVC is a rigid material.

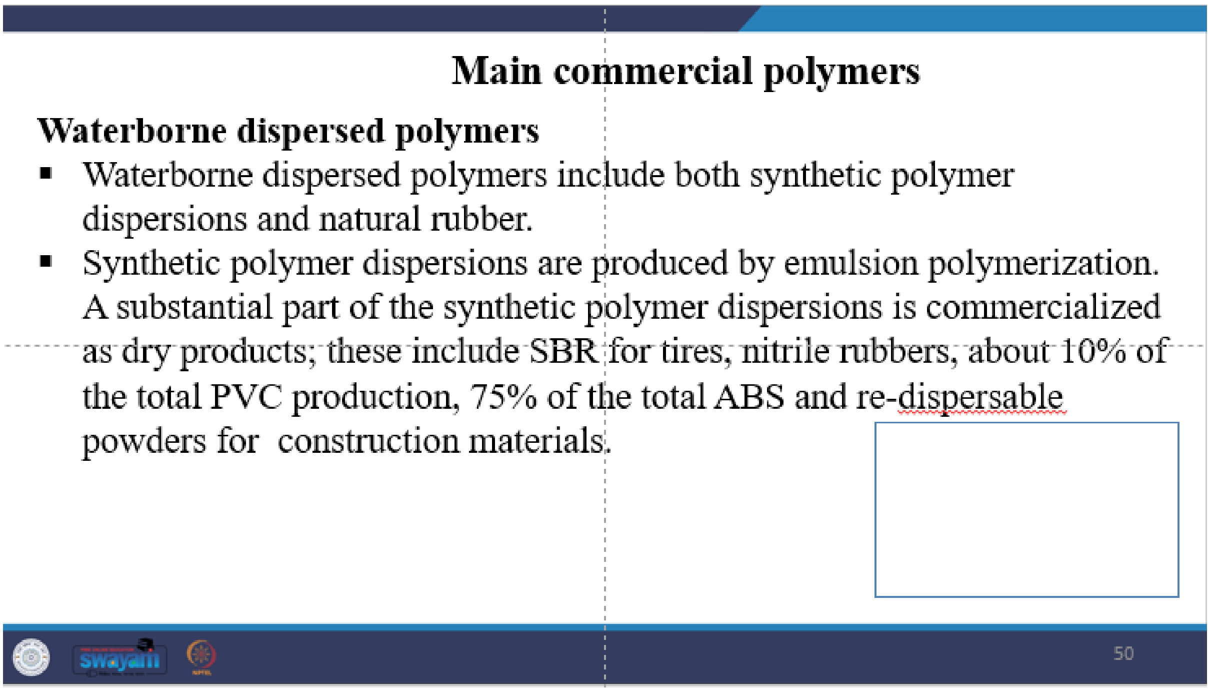
PVC the polyvinyl chloride, is produced mainly by suspension polymerization, and the lower amount of they are produced by emulsion and bulk polymerization. The properties of the PVC are largely due to the bulky chloride atom that leads to an almost syndiotactic configuration. Neat PVC is intrinsically unstable because when subjected to heat, molecular defects in some of the polymer chains initiate a self-accelerating dehydrochlorination reaction. In addition, PVC is a rigid material. So, the PVC is heavily compounded with heat stabilizer, lubricant, different types of processing add, plasticizers, impact modifiers, and fillers.



Main commercial polymers

- Therefore, PVC is heavily compounded with heat stabilizers, lubricants, processing aids, plasticizers, impact modifiers and fillers.
- Immediately after polymerization, PVC is a particulate polymer. Particle morphology, in particular porosity, is a key characteristic because it determines the easiness of incorporation of the additives.
- PVC is used in construction (window frames, pipes, roofing, cable insulation), domestic goods (flooring, wallcoverings, shower curtains, leather cloth), packaging and clothing (waterproofs for fishermen and emergency services, life-jackets).

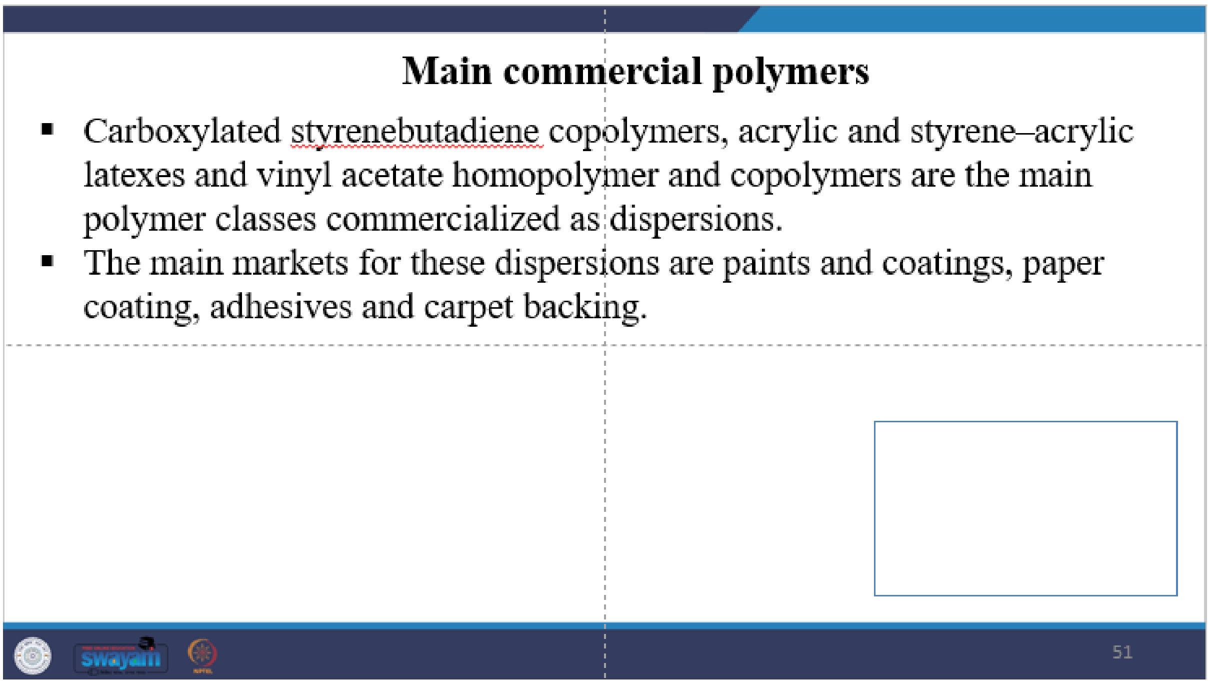
After polymerization, the PVC is a particulate polymer, and particle morphology in a particular porosity is a key characteristic because it determines the easiness of incorporation of different additives. This is used for construction, window frames, pipes, roofing, cable, domestic goods like flooring, wall covering, shower curtains, leather cloths, etc, and packaging, etc all these things but it has some environmental issues. Waterborne dispersed polymers, waterborne dispersed polymer include both synthetic polymers dispersion and natural rubber. Now synthetic polymer dispersions are produced by emulsion polymerization. A substantial part of synthetic polymer dispersion is commercialized as a dry product.



Main commercial polymers

Waterborne dispersed polymers

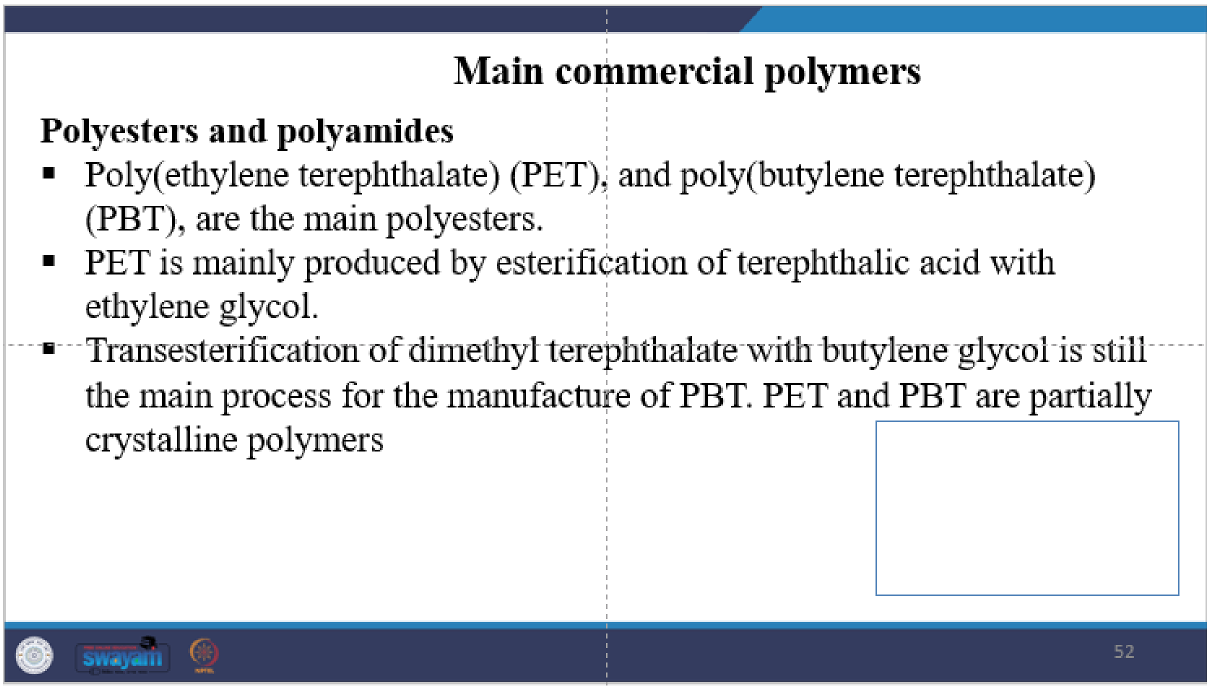
- Waterborne dispersed polymers include both synthetic polymer dispersions and natural rubber.
- Synthetic polymer dispersions are produced by emulsion polymerization. A substantial part of the synthetic polymer dispersions is commercialized as dry products; these include SBR for tires, nitrile rubbers, about 10% of the total PVC production, 75% of the total ABS and re-dispersable powders for construction materials.



Main commercial polymers

- Carboxylated styrenebutadiene copolymers, acrylic and styrene–acrylic latexes and vinyl acetate homopolymer and copolymers are the main polymer classes commercialized as dispersions.
- The main markets for these dispersions are paints and coatings, paper coating, adhesives and carpet backing.

This includes styrene-butadiene rubber for tires; nitrile rubbers, about 10 percent of the total PVC production, 75 percent of total ABS or re-dispersible powder for construction materials. Now carboxylated styrene-butadiene copolymer, acrylic and styrene acrylic latexes, and vinyl acid homopolymer, the copolymers are main polymer classes commercialized as dispersion. The main markets for this dispersion are paint, coating, paper, coating adhesive, and carpet blanketing. Polyesters and polyamides, polyethylene terephthalate PET, and poly butyl terephthalate PBT are the main polyesters. PET is mainly produced by the esterification of the terephthalate with ethylene glycol and transesterification of the dimethyl terephthalate with the butyl glycol butylene glycol is still the main process of manufacturing of PET, PBT, and PBT.

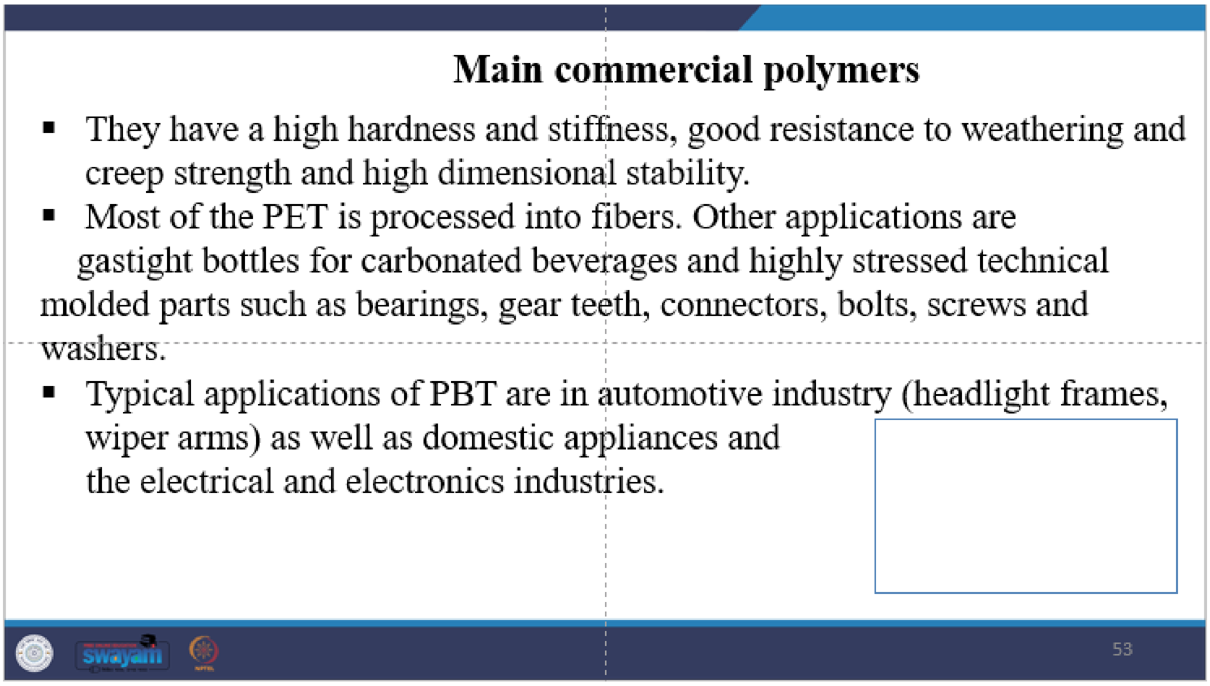


Main commercial polymers

Polyesters and polyamides

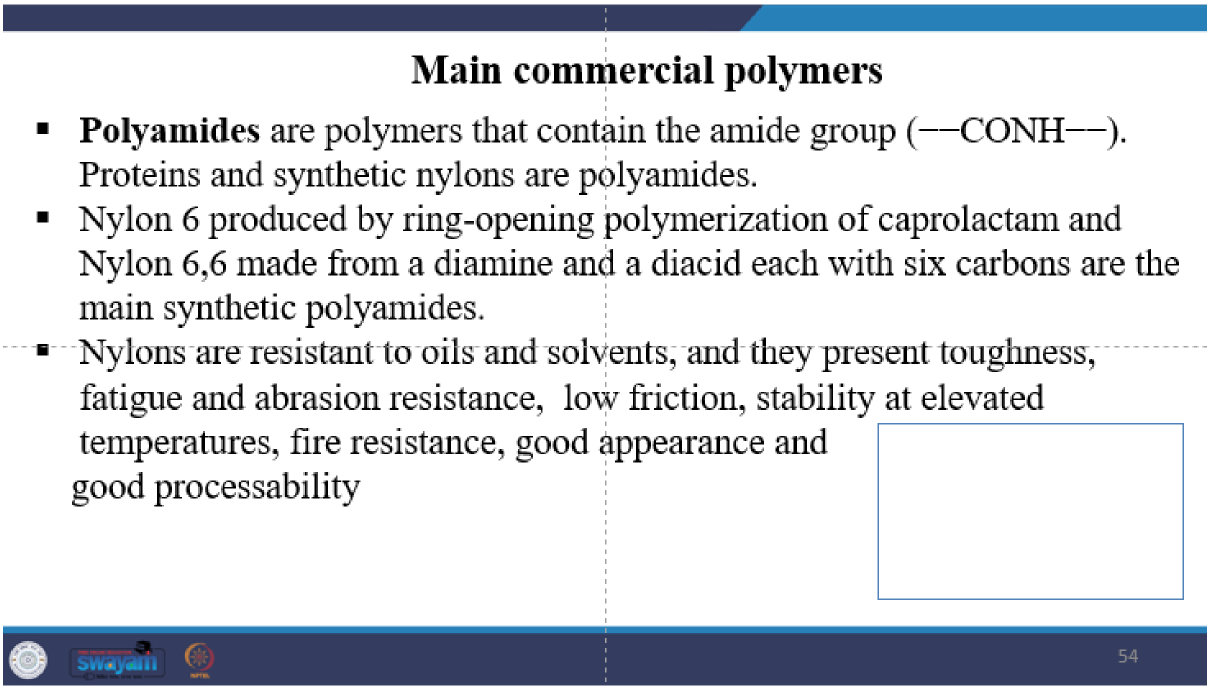
- Poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT), are the main polyesters.
- PET is mainly produced by esterification of terephthalic acid with ethylene glycol.
- Transesterification of dimethyl terephthalate with butylene glycol is still the main process for the manufacture of PBT. PET and PBT are partially crystalline polymers

These PBTs are partially crystalline polymers. They have high hardness and stiffness, good resistance to weathering and creep resistance, and high dimensional stability. Most of the PET is processed into fibers. Other applications are gas-tight bottles for carbonated beverages and highly stressed technical molded parts such as bearings, gear teeth, connectors, bolts, screws, and washers. Typical applications of the PBT are in the automotive industry, headlight frames, and wiper arms, as well as the domestic appliances and the electrical and electronic industries. Polyamides are polymers that contain amide-grouped CONH, protein synthetic nylons, or polyamides.



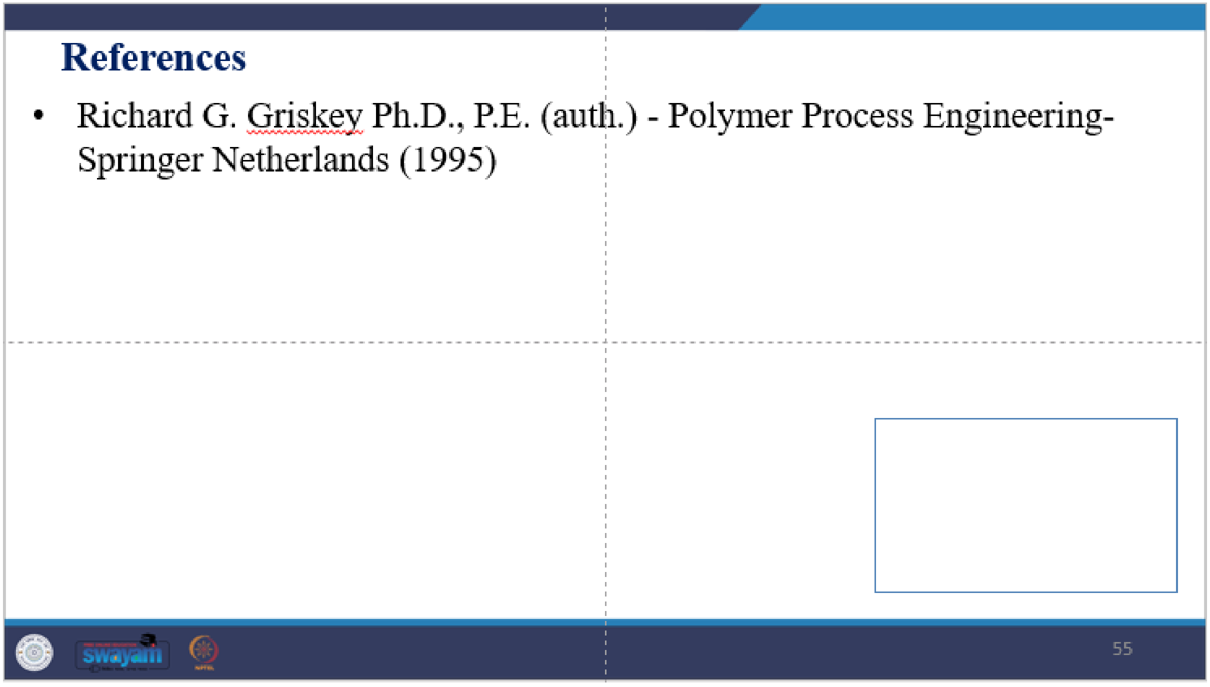
Main commercial polymers

- They have a high hardness and stiffness, good resistance to weathering and creep strength and high dimensional stability.
- Most of the PET is processed into fibers. Other applications are gastight bottles for carbonated beverages and highly stressed technical molded parts such as bearings, gear teeth, connectors, bolts, screws and washers.
- Typical applications of PBT are in automotive industry (headlight frames, wiper arms) as well as domestic appliances and the electrical and electronics industries.



Main commercial polymers

- **Polyamides** are polymers that contain the amide group (—CONH—). Proteins and synthetic nylons are polyamides.
- Nylon 6 produced by ring-opening polymerization of caprolactam and Nylon 6,6 made from a diamine and a diacid each with six carbons are the main synthetic polyamides.
- Nylons are resistant to oils and solvents, and they present toughness, fatigue and abrasion resistance, low friction, stability at elevated temperatures, fire resistance, good appearance and good processability



References

- Richard G. Griskey Ph.D., P.E. (auth.) - Polymer Process Engineering-Springer Netherlands (1995)

So, nylon 6 is produced by the ring opening polymerization of caprolactam, and nylon 6 6 is made from diamine and di-adipic acid to each with the six carbons being the main synthetic polymers. Nylons are resistant to oil, and solvent, and they present toughness, fatigue, abrasion resistance, low friction stability at elevated temperatures, fire resistance, good appearance, and good processability. So, in this particular chapter, we discussed different types of commercial polymers along with different type of polymerization techniques. For your convenience, we include the references which can be utilized in due course of time. Thank you very much. 2