Polymer Reaction Engineering
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Lecture – 55
Living and Dormant Polymerization

Welcome to the new chapter of living and dormant polymerization. these two things are uncommon, but play a very vital role in polymer reaction engineering. before we go into detail, let us have a look that what we covered previously.

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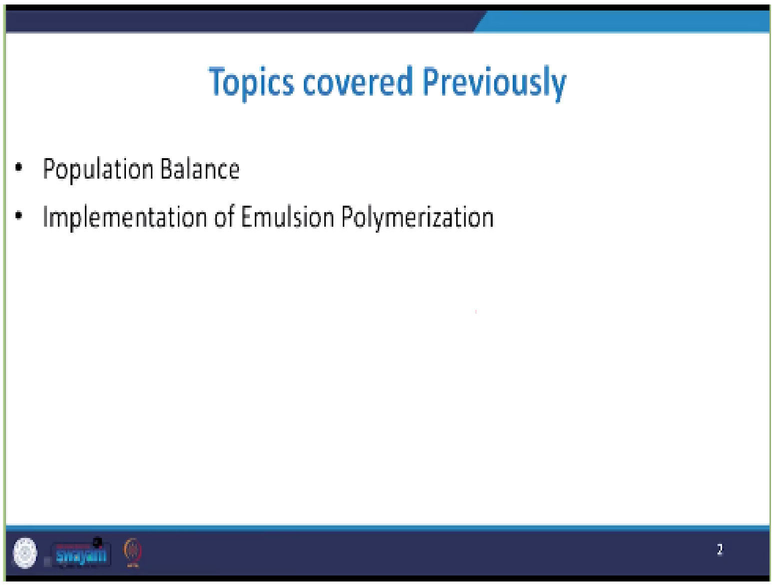

Topics covered Previously

- Population Balance
- Implementation of Emulsion Polymerization

We had a discussion about the population balance concept and its importance in the polymer reaction engineering. We discussed about the implementation of various parameters in the emulsion polymerization.

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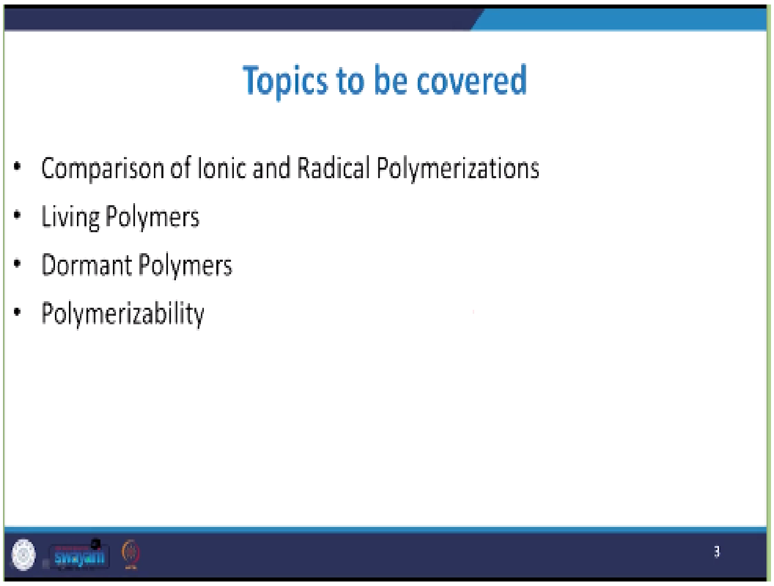

Topics to be covered

- Comparison of Ionic and Radical Polymerizations
- Living Polymers
- Dormant Polymers
- Polymerizability

in this particular lecture, we are going to discuss about the comparison between ionic and radical polymerization. We will have a discussion discussion about the living polymers. Thereafter, we will discuss about the dormant polymers and polymerizability of all these living and dormant polymers. before we go into detail, let us have a comparative note between ionic and radical polymerization.

ionic polymerization, we have already discussed in detail about this ionic polymerization. This polymerization like the well-known radical polymerization is the chain polyaddition. it begins with the reaction of a monomer with a species capable of forming an electrically charged or high polar active group. interaction of these groups with another molecule of the monomer results in the formation of covalent bond between these two groups.

Because ultimately, whenever we talk about the polymer of formation of the polymer chain, then definitely we have to look into some affinity concept between the monomers and the chain and a monomer. So, that is why these charged particles on charged radical ions, they are having the capability of interaction, so that they can form the covalent bond. Simultaneously the active group is continuously being regenerated in the newly inserted molecule.

And ionic polymerization is referred as the classical cationic polymerization when active terminal group is positively charged. ionic polymerization is referred to as the pseudo cationic for or a cationic coordination. When this group forms the positive and often active dipole, it is sometimes referred to as the classical anionic, when the charge of the active group is negative.

Ionic polymerization is sometimes referred as a pseudo anionic or anionic coordination when the active group forms the negative end of an active dipole. So, this is the difference among the pseudo cationic, classic anionic and pseudo anionic one. let us have a small thing about the radical polymerization. It is initiated by adding a small radical derived from an appropriate initiator to the monomer molecule.

the added radical deforms the tail group of the polymer that is ultimately formed. However, its existence does not effect the rate constant of propagation, the selectivity of the or stereochemistry of the subsequent propagation. So, all these characteristics of radical polymerization or radical propagation are defined by the nature of polymerized monomer it is quite obvious.

Number 2 by the condition prevailing in the reaction such as temperature, pressure or lesser degree, the solvent nature etcetera. So, all these things are the contributing factor in this regard. The nature of the solvent or the the ultimate unit that has the marginal impact on the rate of most radical polymerization. So, this type of approach need to be considered the class of monomers polymerized by the radical mechanism is restricted to the vinyl, vinylidene and diene forms.

there are several additional monomers like aldehydes, ketones, various heterocyclic and so on, they are not polymerizable by the radical technique. just for the sake of an example, I would like to give as an example, related to the polymerization of isobutene. isobutene is not polymerized either by a radical or anionic process. So, a cationic polymerization mode is the only one that produces the high molecular weight of poly isobutene.

And it is having the vast industrial application in different cores of chemical aspect. a high molecular weight poly isobutane may be formed by the radical mechanism at a very low temperature, if the activation energy of its propagation is lower, because you know that activation energy during the propagation aspect play a very vital role. let us have an example of the living polymers or the concept of living polymers.

living polymers, and there is stability, these are again a very important segment of polymer reaction engineering. this these living polymerization gives the deepest insight into the processes of ion polymerization. it allows the most thorough control of the size and composition of the resulting macro molecules. So, the polymerization was considered to be the live one as the growing polymers hold their growth tendency indefinitely.

So, in other words, you may say that all the growing polymer chains they are termed as a living polymers, because they are having the capability of joining those monomer molecules or other chains on its own. they are spread continuous with the absence of termination and chain transition; it is quite obvious. Otherwise, the polymer will become the dead chain or polymer chain will become the dead chain.

So, in time every living polymer ultimately decomposes sometimes isomerizes or reacts with its environment and consequently loses its activity. So, you may term that this may be the the concept of termination or a chain transition. we shall refer to the polymers as leaving if their end group maintain the potential for growth for at least as long as it required the completion of the intended synthesis.

So, the polymers of uniform size they are produced when the propagation is initiated by synthetically prepared living monomeric polymers. $C_6H_5.C^-(CH_3)_2,K^+$ (cumyl potassium) is a "living monomeric poly-α-methylstyrene" that initiates anionic growth yielding living poly- α -methylstyrene.

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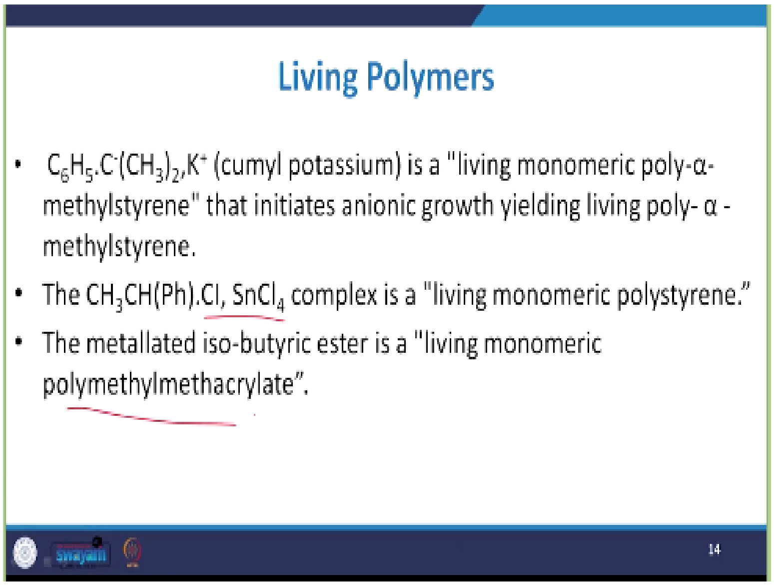

Living Polymers

- $C_6H_5.C^-(CH_3)_2,K^+$ (cumyl potassium) is a "living monomeric poly-α-methylstyrene" that initiates anionic growth yielding living poly- α -methylstyrene.
- The $CH_3CH(Ph).Cl$, $SnCl_4$ complex is a "living monomeric polystyrene."
- The metallated iso-butyric ester is a "living monomeric polymethylmethacrylate".

The $CH_3CH(Ph).CI$, $SnCl_4$ complex is a "living monomeric polystyrene." The metallated iso-butyric ester is a "living monomeric polymethylmethacrylate". Let us do some mathematical calculation that is related to the average degree of polymerization of macromolecules those who are resulted with the help of these living polymers.

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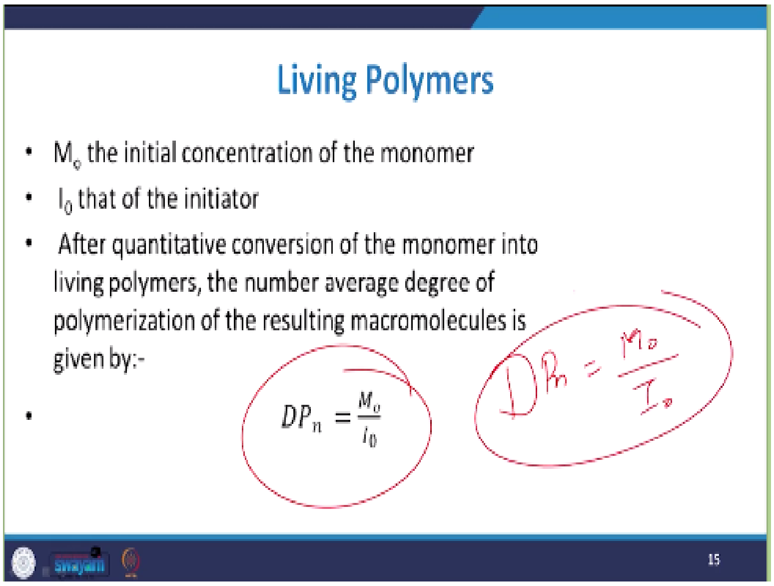

Living Polymers

- M_o the initial concentration of the monomer
- I_0 that of the initiator
- After quantitative conversion of the monomer into living polymers, the number average degree of polymerization of the resulting macromolecules is given by:-
- $DP_n = \frac{M_o}{I_0}$

$DP_n = \frac{M_o}{I_o}$

Denoting by M_o the initial concentration of the monomer, and by I_0 that of the initiator, one finds, after quantitative conversion of the monomer into living polymers, the number average degree of polymerization of the resulting macromolecules is given by

$$DP_n = \frac{M_o}{I_0}$$

provided that all the initiator was utilized effectively.

The resulting polymers should have Poisson molecular mass distribution provided that the propagation is irreversible, the polymerized solution or melt remain homogeneous during the whole course of polymerization, the termination and transfer are rigorously excluded, and the initiation is not slower than propagation.

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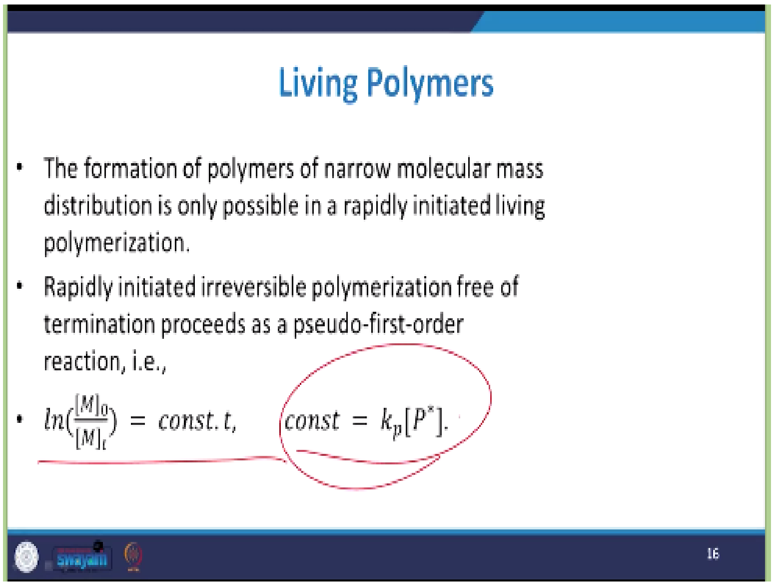

Living Polymers

- The formation of polymers of narrow molecular mass distribution is only possible in a rapidly initiated living polymerization.
- Rapidly initiated irreversible polymerization free of termination proceeds as a pseudo-first-order reaction, i.e.,
- $ln(\frac{[M]_0}{[M]_t}) = const.t, \quad const = k_p[P^*].$

the formation of polymers of narrow molecular mass distribution is only possible in a rapidly initiated living polymerization, a broad distribution does not imply that the polymerization is not living since various incidental factors could lead to its broadening, even when the propagation proceeds with exclusion of termination and chain-transfer.

Rapidly initiated irreversible polymerization free of termination, but not necessarily of chain-transfer, proceeds as a pseudo-first-order reaction, i.e.,

$$ln(\frac{[M]_0}{[M]_t}) = const.t, \qquad const = k_p[P^*].$$

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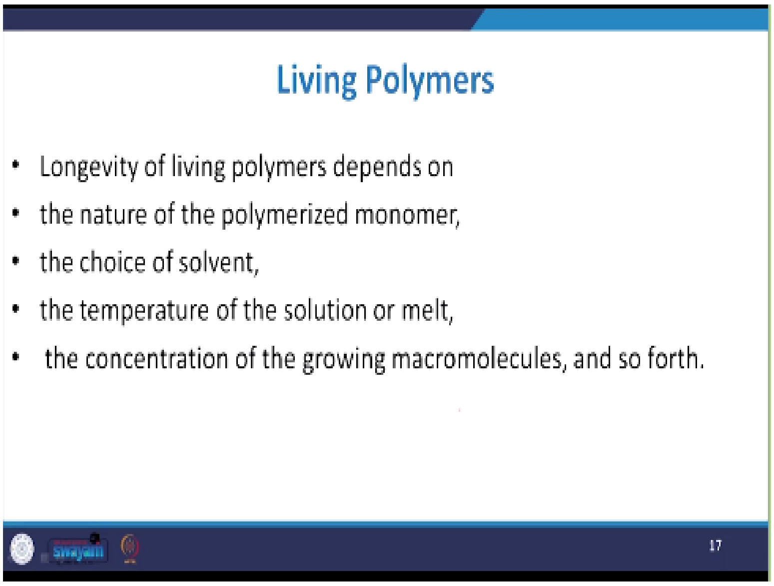

Living Polymers

- Longevity of living polymers depends on
- the nature of the polymerized monomer,
- the choice of solvent,
- the temperature of the solution or melt,
- the concentration of the growing macromolecules, and so forth.

The longevity of living polymers usually depends on the nature of the polymerized monomer. It also depends on the choice of the solvent, what different what different type of solvents you are taking for the for the polymerization process, the temperature of the solution or melt and the concentration of the growing macromolecules. So, these are the various parameters, those affects the longevity of the living Polymer.

There are certain prerequisites before we taking up this particular concept. The living polymers, they must be held at a very low temperature all the time to avoid their decomposition or isomerization during the preparation and storage. The dilution of living polymer is detrimental to their stability. The dilution usually increases the ratio of concentration to harmful impurities found in the solvent to that of the living polymers.

This is a trivial factor shortening their lifetime. sometimes people may ask about the stability of those living polymers. So, the stability of many living polymer is usually increased by their complexation with appropriate agent. the degree of complexation is reduced by the dilution again reduce reducing the stability of the system. So, the lifetime of living polymer growing by a direct monomer addition is given by this particular equation.

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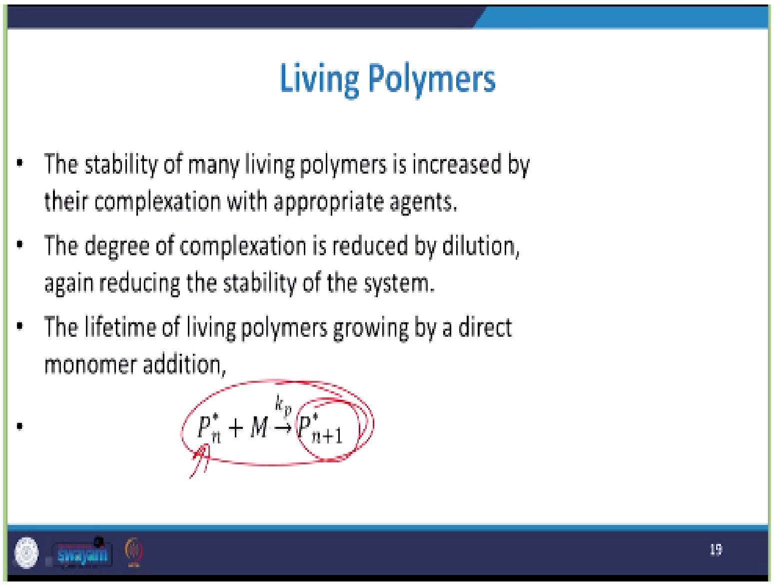

Living Polymers

- The stability of many living polymers is increased by their complexation with appropriate agents.
- The degree of complexation is reduced by dilution, again reducing the stability of the system.
- The lifetime of living polymers growing by a direct monomer addition,
- $P_n^* + M \xrightarrow{k_p} P_{n+1}^*$

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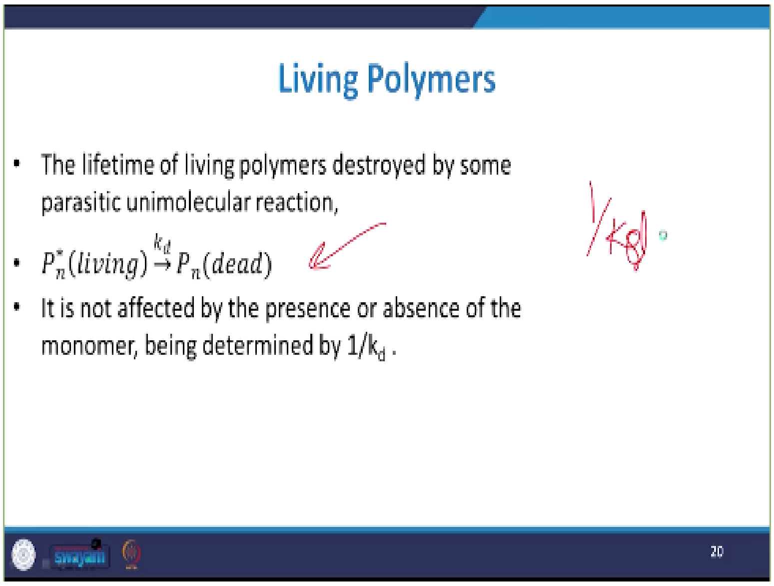

Living Polymers

- The lifetime of living polymers destroyed by some parasitic unimolecular reaction,
- $P_n^*(living) \overset{k_d}{\rightarrow} P_n(dead)$
- It is not affected by the presence or absence of the monomer, being determined by $1/k_d$.

$1/k_d$

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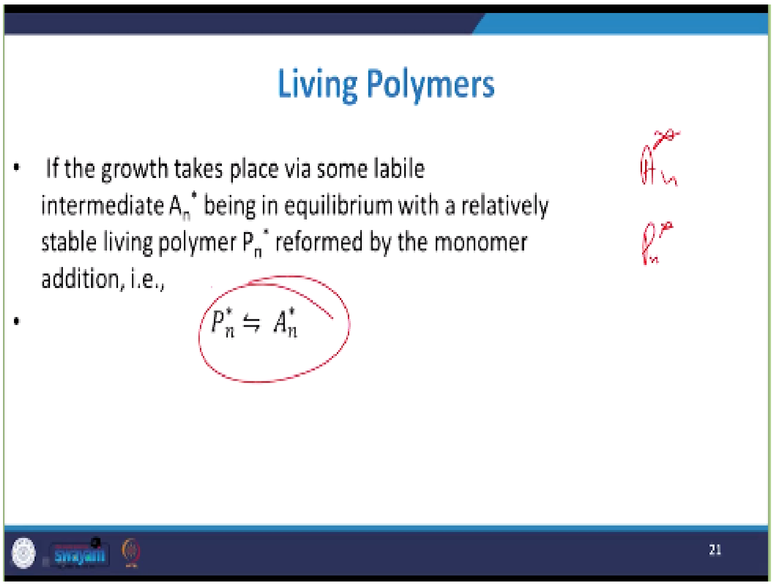

Living Polymers

- If the growth takes place via some labile intermediate A_n^* being in equilibrium with a relatively stable living polymer P_n^* reformed by the monomer addition, i.e.,
- $\boxed{P_n^* \leftrightharpoons A_n^*}$

A_n^*

P_n^*

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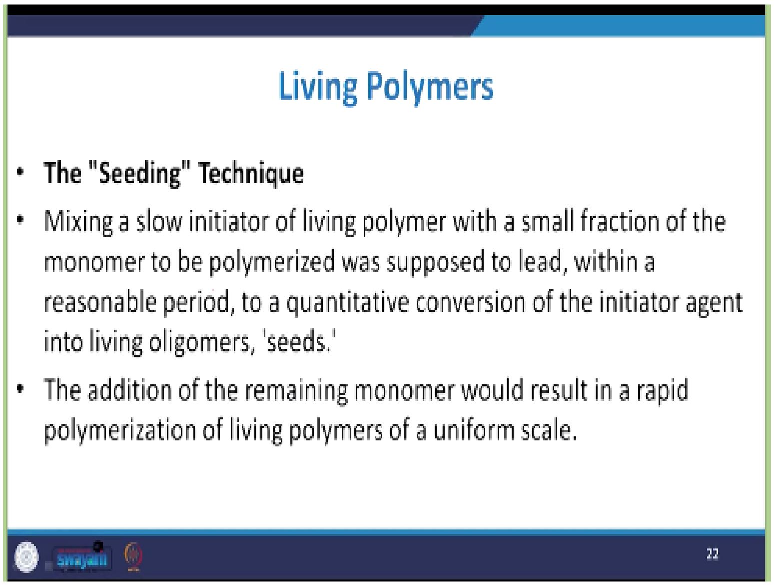

Living Polymers

- **The "Seeding" Technique**
- Mixing a slow initiator of living polymer with a small fraction of the monomer to be polymerized was supposed to lead, within a reasonable period, to a quantitative conversion of the initiator agent into living oligomers, 'seeds.'
- The addition of the remaining monomer would result in a rapid polymerization of living polymers of a uniform scale.

Seeding Technique

When we discuss about the living polymer concept, there is a technique called seeding. the what is seeding technique the mixing a slow initiator of living polymer with a small fraction of monomer to be polymerized it is supposed to lead within a reasonable period to a quantitative conversion of the initiator agent into the living oligomer that is called seed. So, this is again important thing while we discuss about the living polymers.

So, the addition of the remaining monomer sometimes results in a rapid polymerization of living polymers of a uniform skin. The most common polymerizations yielding living polymer are those involved some irreversible initiation and propagation. So, the rate of both being proportional to the monomer concentration that we which we have already discussed in the previous lectures.

The various species involved in the living polymerization sometimes coexist in a rapid equilibrium with each other. Therefore, the rates of initiation and propagation there depends only on the total concentration of all polymeric species the referred as P and all the initiating is species referred as I.

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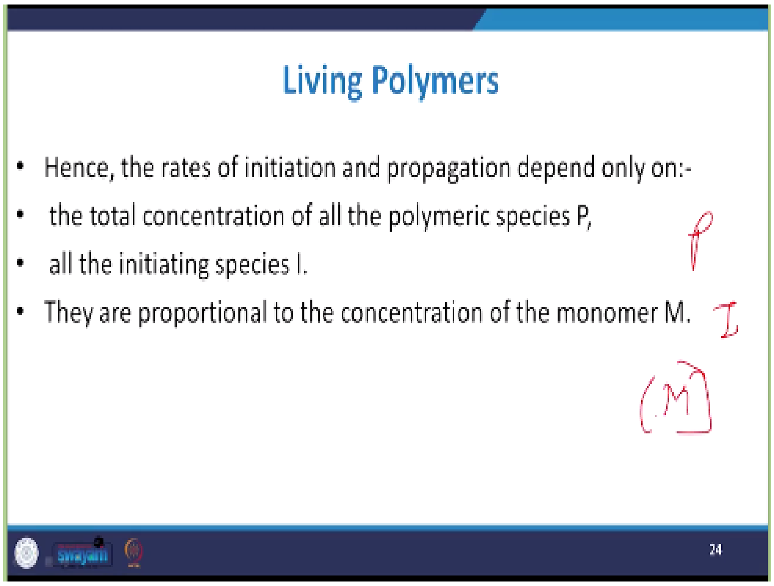

Living Polymers

- Hence, the rates of initiation and propagation depend only on:-
- the total concentration of all the polymeric species P,
- all the initiating species I.
- They are proportional to the concentration of the monomer M.

P

I

(M)

So, they are proportional to the concentration of the monomer which is represented as M.

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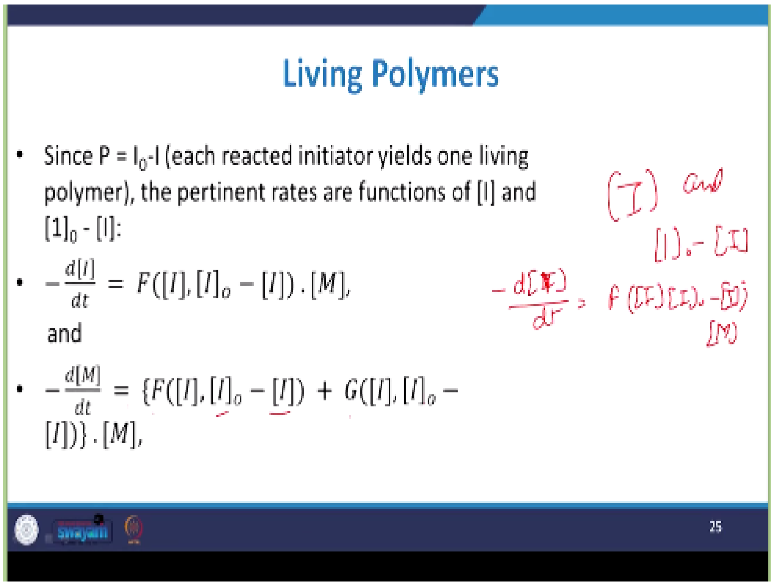

Living Polymers

- Since P = I_0-I (each reacted initiator yields one living polymer), the pertinent rates are functions of [I] and $[1]_0$ - [I]:
- $-\frac{d[I]}{dt} = F([I],[I]_o - [I]) \, . [M],$
  and
- $-\frac{d[M]}{dt} = \{F([I],[I]_o - [I]) + G([I],[I]_o - [I])\} \, . [M],$

(I) and

$[I]_0 - [I]$

$-\frac{d[I]}{dt} = F([I][I]_0 - [I])$
$[M]$

So, when we talk about the mathematical approach of those living polymer.

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$$-\frac{d[M]}{dt} = \{F([I],[I]_o - [I]) + G([I],[I]_o - [I])\} \, . \, [M],$$

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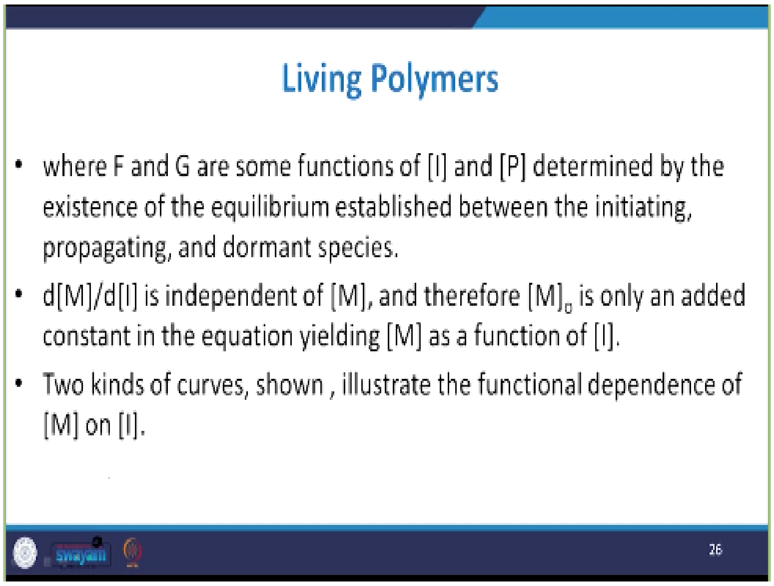

Living Polymers

- where F and G are some functions of [I] and [P] determined by the existence of the equilibrium established between the initiating, propagating, and dormant species.
- d[M]/d[I] is independent of [M], and therefore $[M]_0$ is only an added constant in the equation yielding [M] as a function of [I].
- Two kinds of curves, shown , illustrate the functional dependence of [M] on [I].

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Two kinds of curves, shown , illustrate the functional dependence of [M] on [I].

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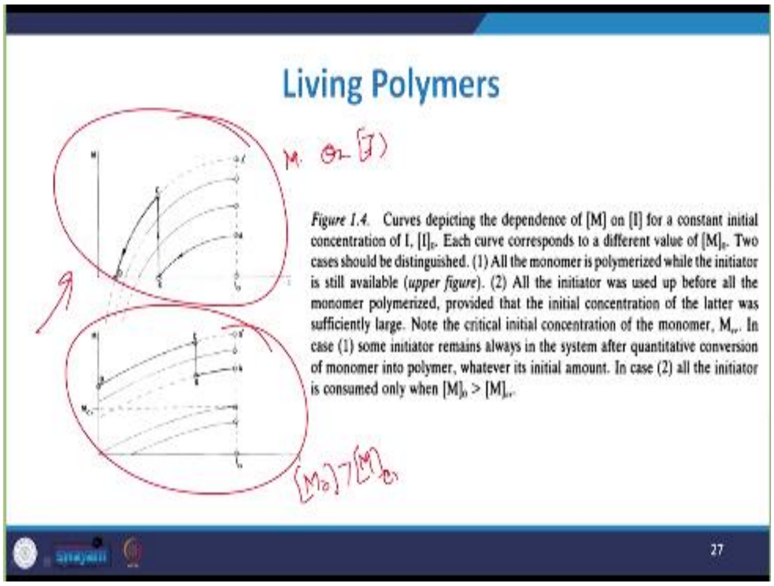

Living Polymers

M. Or [I)

Figure 1.4. Curves depicting the dependence of [M] on [I] for a constant initial concentration of I, $[I]_0$. Each curve corresponds to a different value of $[M]_0$. Two cases should be distinguished. (1) All the monomer is polymerized while the initiator is still available (*upper figure*). (2) All the initiator was used up before all the monomer polymerized, provided that the initial concentration of the latter was sufficiently large. Note the critical initial concentration of the monomer, M_{cr}. In case (1) some initiator remains always in the system after quantitative conversion of monomer into polymer, whatever its initial amount. In case (2) all the initiator is consumed only when $[M]_0 > [M]_{cr}$.

$[M_0] > [M]_{cr}$

You can see here there are 2 things, one is the dependent depicting the dependence of concentration of monomer on I for constant initial concentration of I. So, each curve corresponds to the to a different value of M_0. And these 2 cases should be distinguished that all the monomer is polymerized while initiator is still available that is this one. all the initiator was used up before all the monomer polymerized provided that the initial concentration of the latter was sufficiently large.

the critical initial concentration of the monomer that is MCR. So, in case in this case, some initiated remain always in the system after quantitative conversion of monomer into polymer. Whatever is the initial amount that is immaterial. in in this case, all the initiators initiator is consumed only one when $M_0 > M_{crit}$.

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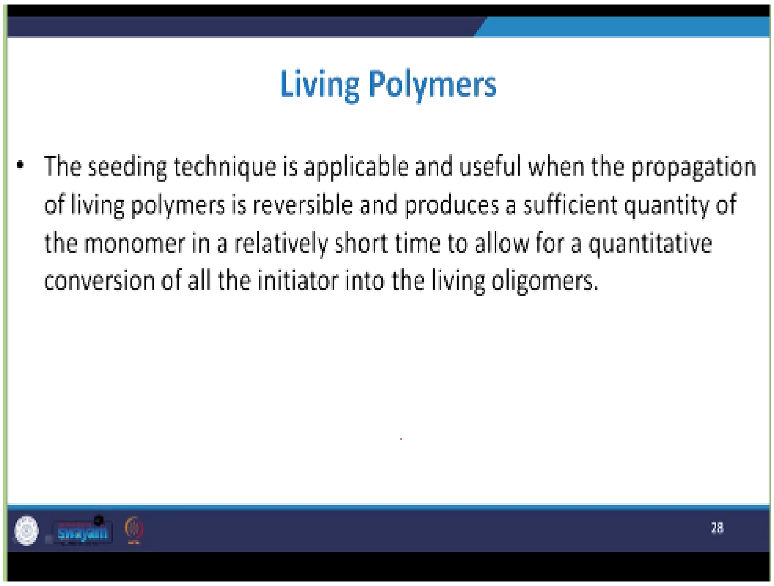

Living Polymers

- The seeding technique is applicable and useful when the propagation of living polymers is reversible and produces a sufficient quantity of the monomer in a relatively short time to allow for a quantitative conversion of all the initiator into the living oligomers.

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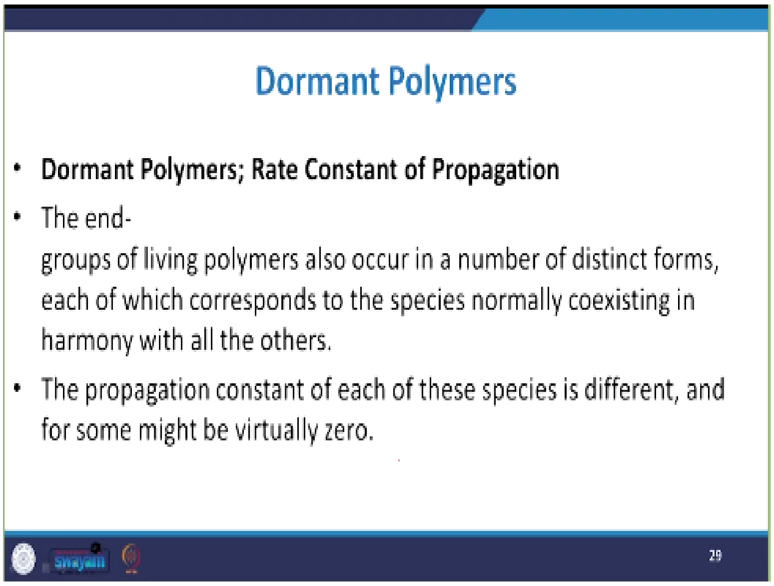

Dormant Polymers

- **Dormant Polymers; Rate Constant of Propagation**
- The end-groups of living polymers also occur in a number of distinct forms, each of which corresponds to the species normally coexisting in harmony with all the others.
- The propagation constant of each of these species is different, and for some might be virtually zero.

let us have a look about the dormant polymers the dormant polymers the rate constant of propagation etcetera. So, in this case, the end group of living polymer also occur in a number of distinct forms, each of which may corresponds to the species normally coexisting in harmony with all the others. So, the propagation constant of each of these species is different and for some might be virtually zero.

So, they are not specifically contributing to the propagation nor the dead because of the spontaneous and reversible interconversion transforms them into the propagating polymers. these temporarily inactive species are called dormant polymers, right. So, these some times if you can actuate all those dormant species or inactive species, then they may or may become the active one.

The dynamic equilibrium usually established between them and the active polymers, they allow all of them to participate in the polymerization process. The presence of dormant polymer is usually revealed by the kinetics of the observed overall propagation and sometimes by molecular mass distribution of resulting polymers. Usually, the dormant polymer they do not participate in the polymerization during the time of their dormancy, but eventually they do react.

So, that is another important aspect you need to understand. Usually they are not the participating one in during the process but still they can continue their reactive attitude. So, the span of their dormancy is determined by the reciprocal of the rate constant of their conversion into the active form. So, the extent of their contribution to the overall reaction usually depends on the relaxation time of the reversible process.

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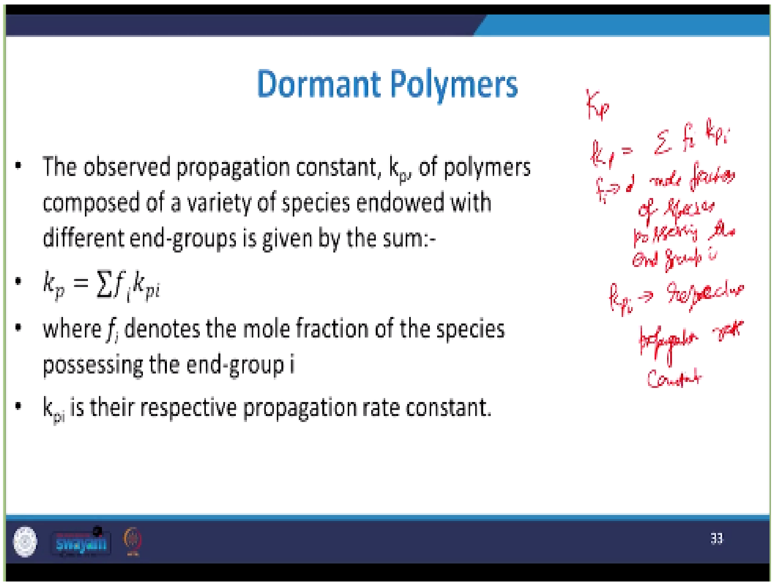

Dormant Polymers

- The observed propagation constant, k_p, of polymers composed of a variety of species endowed with different end-groups is given by the sum:-
- $k_p = \sum f_i k_{pi}$
- where f_i denotes the mole fraction of the species possessing the end-group i
- k_{pi} is their respective propagation rate constant.

K_p

$k_p = \sum f_i k_{pi}$

$f_i \Rightarrow$ d mole fraction of species possessing the end group i

$k_{pi} \Rightarrow$ respective propagation rate constant sometimes when we talk about the kinetics of these dormant polymers.

The observed propagation constant, k_p, of polymers composed of a variety of species endowed with different end-groups is given by the sum:-

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where f_i denotes the mole fraction of the species possessing the end-group i

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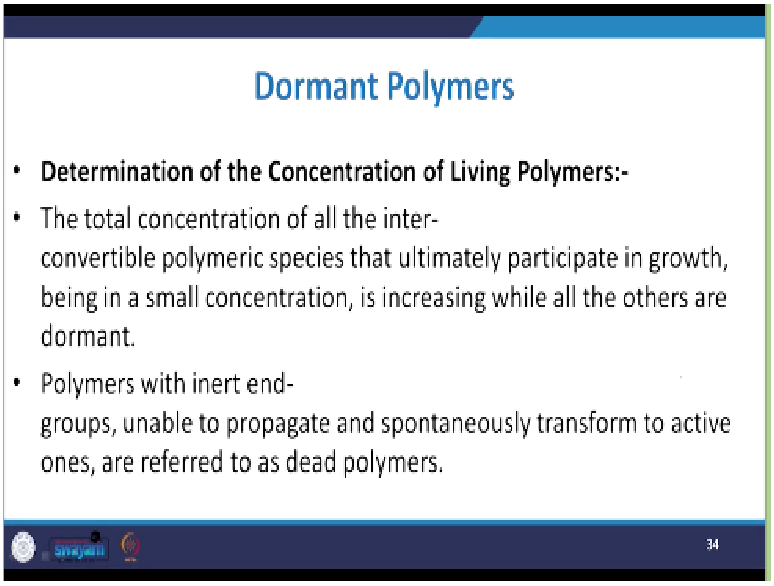

Dormant Polymers

- **Determination of the Concentration of Living Polymers:-**
- The total concentration of all the inter-convertible polymeric species that ultimately participate in growth, being in a small concentration, is increasing while all the others are dormant.
- Polymers with inert end-groups, unable to propagate and spontaneously transform to active ones, are referred to as dead polymers.

let us talk about the determination of the concentration of living polymer. The total concentration of all the interconvertible polymeric species that ultimately participate in growth, being in small concentration usually increasing having the increasing trend while all other are dormant. So, the polymer with inert end group unable to propagate and is spontaneously transformed to active ones.

And they are referred to as the dead polymer which we have already explained in the previous slides that how we can refer all these things as a dead polymer. So, they cannot propagate, they may be termed as sometimes terminated or inactive polymeric chain. sometimes people may talk about the capping technique. So, the capping technique is a convenient and reliable method for determining the concentration of living polymer.

The addition of a carefully chosen reagent to a solution of living polymer transforms their active and sometimes liable end group into new ones. The capping method sometimes determine the the concentration of the active end groups and usually does not provide information about their nature. So, that that is again important point. So, you cannot address the the knowledge about the nature of those polymers through the the capping methodology.

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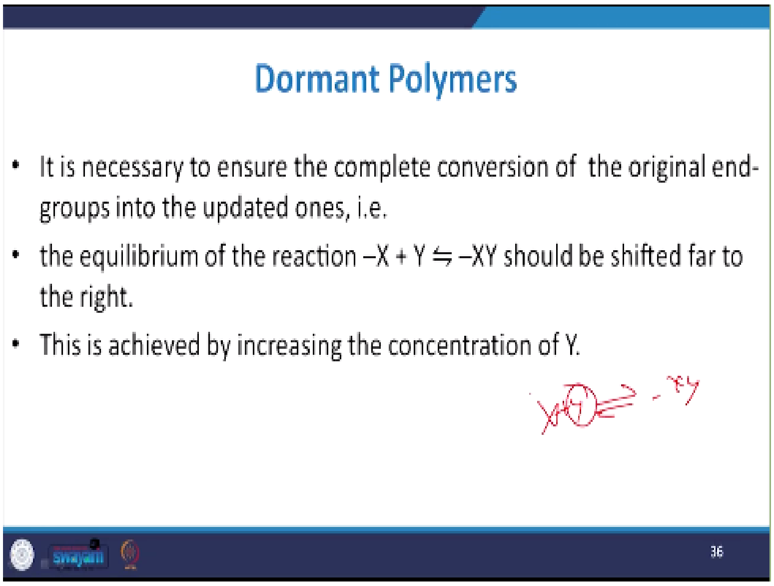

Dormant Polymers

- It is necessary to ensure the complete conversion of the original end-groups into the updated ones, i.e.
- the equilibrium of the reaction $-X + Y \leftrightharpoons -XY$ should be shifted far to the right.
- This is achieved by increasing the concentration of Y.

$X + Y \rightleftharpoons -XY$

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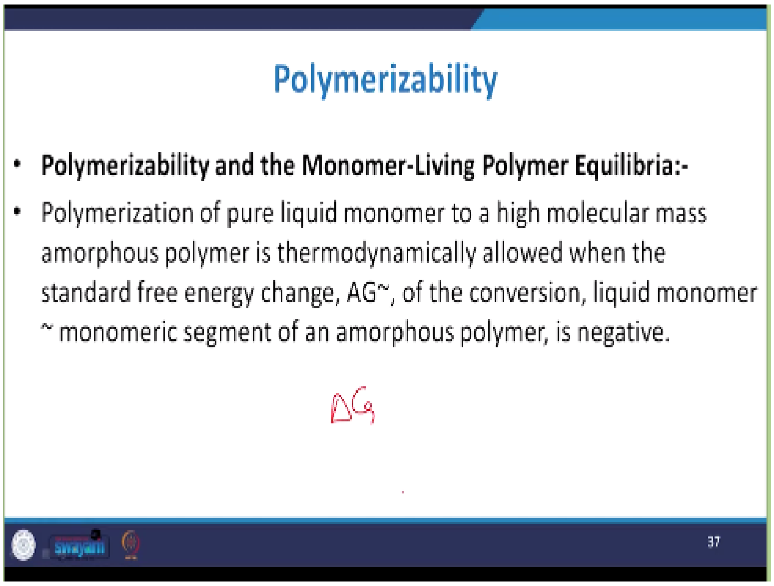

Polymerizability

- **Polymerizability and the Monomer-Living Polymer Equilibria:-**
- Polymerization of pure liquid monomer to a high molecular mass amorphous polymer is thermodynamically allowed when the standard free energy change, AG~, of the conversion, liquid monomer ~ monomeric segment of an amorphous polymer, is negative.

ΔG

at last, we talk about the polymerizability of the things. The polymerizability and the monomer living polymer equilibrium. This is again unique concept. the polymerization of pure liquid monomer to a high molecular mass amorphous polymer is thermodynamically allowed when the standard free energy changes ΔG of the conversion liquid monomer monomeric segment of an amorphous polymer is negative.

remember this ΔG is a very important phenomenon that is the Gibbs free energy and it is it it gives you an information about the feasibility of the reaction and you can assess that whether this reaction is possible or not. So, the knowledge of this change in the Gibbs free energy is extremely important in due course of time.

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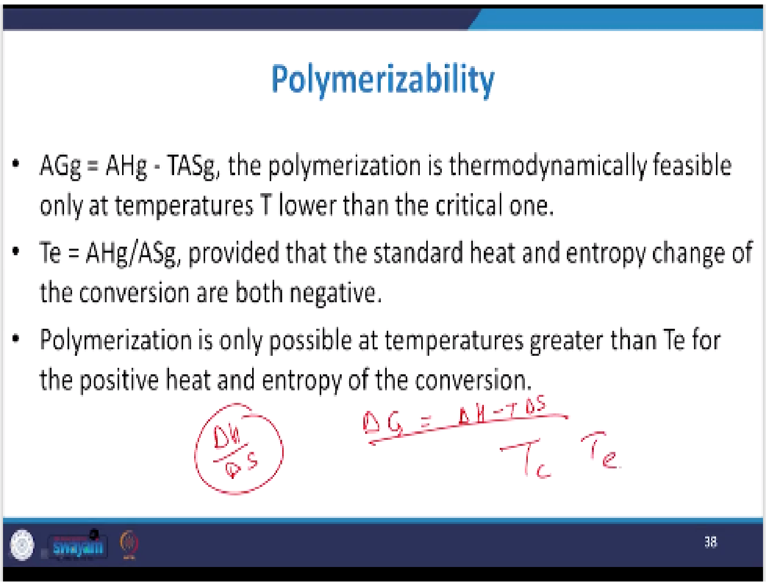

Polymerizability

- AGg = AHg - TASg, the polymerization is thermodynamically feasible only at temperatures T lower than the critical one.
- Te = AHg/ASg, provided that the standard heat and entropy change of the conversion are both negative.
- Polymerization is only possible at temperatures greater than Te for the positive heat and entropy of the conversion.

$\frac{\Delta H}{\Delta S}$

$\Delta G = \Delta H - T\Delta S$

T_c T_e

$\Delta G_g = \Delta H_g - T\Delta S_g$, the polymerization is thermodynamically feasible only at temperatures T lower than the critical one.

$T_e = \Delta H_g/\Delta S_g$, provided that the standard heat and entropy change of the conversion are both negative.

So, the polymerization is the only possible or polymerization is only possible at temperature greater than T extent for the positive heat and the entropy of the conversion so that you make this ΔG negative therefore, you can make that particular reaction feasible in due course of time. The critical temperature Te is referred to as the ceiling temperature in the former case, and as the floor temperature in the latter case.

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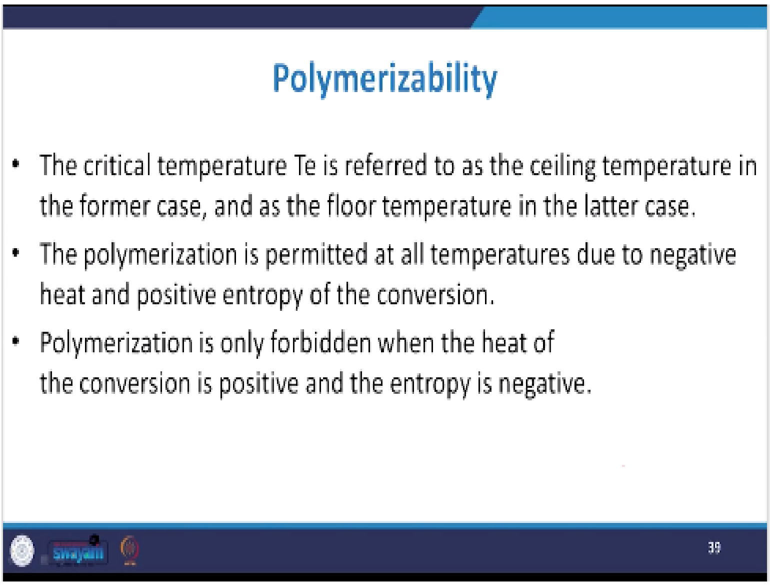

Polymerizability

- The critical temperature Te is referred to as the ceiling temperature in the former case, and as the floor temperature in the latter case.
- The polymerization is permitted at all temperatures due to negative heat and positive entropy of the conversion.
- Polymerization is only forbidden when the heat of the conversion is positive and the entropy is negative.

So, the polymerization is permitted at all temperature due to negative heat and the positive entropy of the conversion so that the delta G may become negative. So, polymerization is only forbidden when the heat of conversion is positive and entropy is negative. So, whenever you wish to seize the polymerization, then you have to look into this delta G concept and in that case, you can see is the polymerization when there is the heat of conversion is positive and by making the entropy negative.

So, in this particular chapter, we discussed about the living polymers, we discussed about the dormant polymers, we discussed about the feasibility of polymerization processes, especially under the head of polymerizability of those monomer and initiators.

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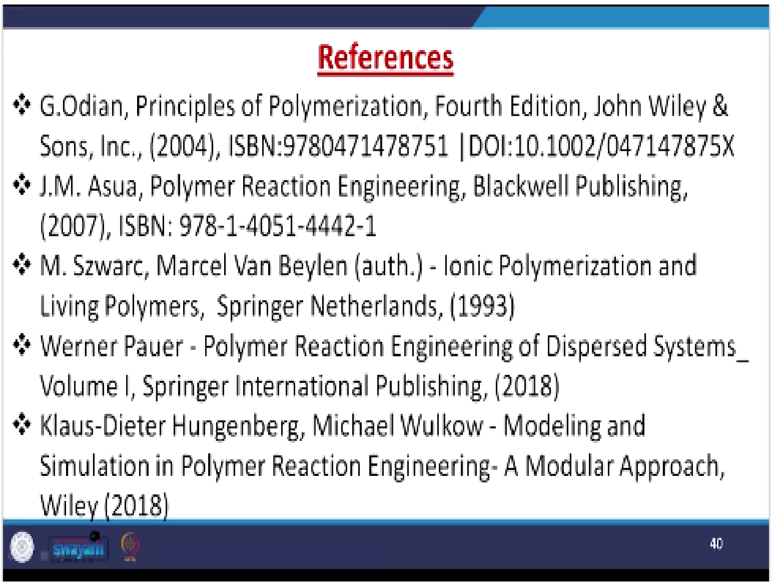

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For your convenience, we have listed several references, which may be used as a further reading and further research if you'd like to have it on. Thank you very much.