

**Introduction to Polymer Science**  
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**Lecture - 19**  
**RAFT Polymerization (Contd.), Ionic Polymerization**

Welcome back, in this lecture I plan to start a new module, which is about other type of chain polymerization methods, but I have to take about first 10 minutes to complete the remainder of last module, which is about radical chain polymerization.

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**Content of Lecture 19**

- ❖ RAFT Polymerization (continuation of Module 3)
- ❖ Common polymers synthesized by radical chain polymerization (continuation of Module 3)
- ❖ General characteristics of ionic chain polymerization and its comparison with radical chain polymerization
- ❖ Practical considerations in ionic chain polymerization
- ❖ Anionic chain polymerization
- ❖ Cationic chain polymerization

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**Radical Addition–Fragmentation Transfer (RAFT)**

Polymerization is carried out with a conventional initiator such as a peroxide or AIBN in the presence of the chain-transfer agent (RAFT agent)

$I \rightarrow 2 R^\bullet$

$\begin{array}{c} Z \\ | \\ S=C-S-A \end{array}$

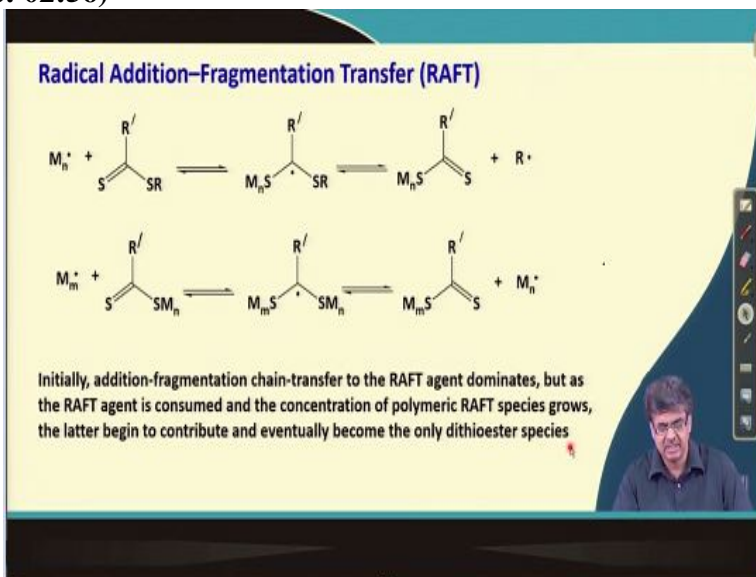
- ❖ Reactivities of the two radicals ( $R^\bullet$  and  $A^\bullet$ ) must be similar
- ❖ The Z group must activate the exchange process
- ❖ RAFT agent must be highly active in chain transfer

❖ Number of RAFT agent  $\gg$  total number of primary radicals generated from the initiator during the course of the whole polymerization

I was talking about RAFT polymerization in last lecture that consists of reversible transfer reactions by which we actually can achieve the radical polymerization in control fashion. In this case the original, the initial radicals are generated in the conventional initiation fashion, like using peroxides and AIBN but in presence of a chain transfer agent. Typically, the concentration or number of these chain transfer agents is much higher compared to the initiator molecule. So, as soon as these initiator radicals are generated, they will react with this chain transfer agents (RAFT agents) and form dormant species which can actually further fragment to produce a new radical  $A'$ , which can further react with the monomers and take part in polymerization reaction. Therefore, the fundamental difference between the RAFT polymerization and NMP and ATRP is that in the RAFT process, the propagating radicals are not the original radicals, but are the radicals generated due to the transfer processes.

In this case, this radical is not a stable radical, not an unreactive radical like the other two examples. It can take part in polymerization, can actually react with monomers and propagate the polymer chain. In addition, it can take part in transfer reaction with the chain transfer agent or RAFT agent in a reversible way. We explained how this name, radical addition fragmentation transfer, originated, because it consists of addition, fragmentation and in this way original radical is gets transferred and produce new radical.

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After the initial time, when all the initial RAFT agents are consumed, the reaction proceed in the following way. A polymeric propagating radical reacts with a RAFT agent and form a dormant intermediate radical, which then is fragmented and produced a new radical. This new radical again can react with monomers to propagate the chain; it can take part in reaction and produce a propagating step. This continues and we generate longer polymer chain. Because the number of RAFT agents originally added was much more than the initiator molecules, even though the original radicals are produced from the initial initiator species, the numbers of polymer chains that are being produced in this case are dominated by the number of RAFT agents present in this medium. So, initially radical addition to RAFT agents dominates, but as the original RAFT agents are consumed, the concentration of polymeric RAFT agents become higher. Later, the polymeric RAFT agent species eventually become the only the dithioesters species present in the medium.

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**Radical Addition-Fragmentation Transfer (RAFT)**

$$X_n = \frac{c[M]_0}{(c'[RAFT]_0 + \frac{2}{2-\alpha} f c''[I]_0)}$$

$c/c'$  : fractional monomer/RAFT agent/initiator conversion

RAFT agents are consumed with first few percent of monomer conversion,  $p' = 1$ , due to large chain-transfer coefficient of RAFT agent

$[RAFT]_0 \gg [I]_0$  and  
 $p'[RAFT]_0 \gg \frac{2}{2-\alpha} f p''[I]_0$

$$X_n = \frac{p[M]_0}{[RAFT]_0}$$

- ❖ Reaction rate expression is similar to conventional radical polymerization
- ❖ Can be used for synthesizing block, graft, star copolymers as shown for ATRP

The degree of polymerization in this case is given by,

$$X_n = \frac{c[M]_0}{\left(c'[RAFT]_0 + \frac{2}{2-\alpha} f c''[I]_0\right)}$$

$c$  is the fractional monomer conversion in this case, and  $c'$  is the fractional RAFT agent conversion and  $c''$  is the fractional initiator conversion. If all the monomers are reacted then  $c$  is equal to 1. If all the RAFT agents are consumed, which is generally the case as most of the RAFT agents are

anyway consumed within first few percentages of monomer conversion,  $c' = 1$  in almost all cases. In this expression, the denominator gives the number of polymer chains that are produced. In this case,  $c'[RAFT]_0$  is the number of polymer chains that have the RAFT agent at one end and these are the living chains. One can use these chains containing the RAFT agent at the end for making further reaction like for making block copolymer and so on. However, there will inherently be some bimolecular reactions between the propagating radicals which will generate dead chains like a conventional radical polymerization and obviously, the chain length will depend on the type of termination reaction - coupling and/or combination or, by disproportionation reaction, and  $a$  is the fraction of dead chains which are produced by coupling or combination reaction.

As I said earlier, the RAFT agents are consumed within the first few percentage of monomer conversion. Therefore,  $c' = 1$ , and because we are using the initial RAFT agent concentration much higher than initiator concentration ( $[RAFT]_0 \gg [I]_0$ ), the first term in the denominator is much higher than the second term. Therefore, we can actually write the following equation by ignoring the second term from the denominator,

$$X_n = \frac{p[M]_0}{[RAFT]_0}$$

If all the monomers are consumed, then it will be just initial monomer concentration by initial RAFT agent concentration. In case of NMP, SFRP and ATRP processes the effective radical concentration during polymerization is much low, hence, the reaction rate is also low. However, in case of RAFT, the effective radical concentration is same throughout the process and is given by the original concentration of radicals that are produced from the initiator molecules. Because the propagating radicals are more reactive towards the chain transfer agents, which are the RAFT agents in this case, the probability of a propagating radical to participate in a bimolecular radical-radical termination reaction is much lower compared to the probability of this propagating radical reacting with the chain transfer region and transferring the chain. As a result, the inherent termination reactions are suppressed in this way. Therefore, the rate of polymerization does not change significantly compared to a conventional radical polymerization process. At the end of RAFT polymerization, we can use the polymer to produce block, graft, and star copolymer like the examples shown in case of ATRP.

Next, I will quickly run through few examples of polymers that are synthesized using radical chain polymerization. It is not necessary for you to remember these examples, but this is for completion of this module.

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**Polyethylene**  $\text{H}_2\text{C}=\text{CH}_2 \longrightarrow *-\text{[H}_2\text{C}-\text{CH}_2\text{]}_n^*$

- ❖ Synthesized at high pressure at a temperature above it's melting temperature
- ❖ Continuous process
- ❖ Mostly LDPE are produced in this process – highly branched
- ❖ Low crystalline (40-60%)
- ❖ Low density ( $0.91 - 0.93 \text{ g cm}^{-3}$ )
- ❖ MW 20,000 – 100,000; PDI 3-10
- ❖  $T_g \sim -120 \text{ }^\circ\text{C}$ ;  $T_m \sim 105 \text{ }^\circ\text{C} - 110 \text{ }^\circ\text{C}$
- ❖ Low density ( $0.91 - 0.93 \text{ g cm}^{-3}$ )

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One of the examples is polyethylene, especially the low molecular. These low density polyethylene are produced by radical chain polymerization process. As these are branched polymers, crystallinity is low and  $T_g$  data is given by the exact process.

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**Polyethylene**

$$\text{H}_2\text{C}=\text{CH}_2 \longrightarrow *-\text{[H}_2\text{C}-\text{CH}_2\text{]}_n^*$$

- ❖ Good combination of strength, flexibility, impact resistance and melt flow behavior
- ❖ Mostly used as films – e.g. packaging and household use (bags, pouches, wraps for foods, clothes, etc); agricultural and constructional applications (green houses, industrial tanks, etc.)

Trade names: *Alathon, Fertene, Marlex, etc*

The slide features a yellow background with a dark blue header and footer. A small video inset of a man is visible in the bottom right corner. A vertical toolbar with various icons is on the right side of the slide.

This polyethylene has good combination of strength, flexibility, impact resistance, melt flow behavior, and are mostly used as films like packaging, household bags, pouches, wraps, food clothes. Alathon, Fertene, Marlex, etc. are some of the trade names by which it is sold in the market.

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**Polystyrene**

- ❖ Generally synthesized by continuous solution process
- ❖ Some cases by suspension polymerization
- ❖ MW 50,000 – 150,000; PDI 2-4
- ❖  $T_g \sim 85^\circ\text{C}$ ;
- ❖ Rigid plastics, completely amorphous
- ❖ Good strength and dimensional stability
- ❖ Good resistance to aq. bases and acids
- ❖ Poor weatherability, resistance to hydrocarbon solvents
- ❖ Often used with additives, and as blends or copolymers

$\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_5 \rightarrow \left[ \text{H}_2\text{C}-\text{CH}(\text{C}_6\text{H}_5) \right]_n$

Another polymer which is synthesized using this radical chain polymerization is polystyrene and generally by a continuous process. Suspension processes produce polystyrene beads, and if the polymerization is carried out in presence of present cross-linker then, we generate crosslinked polystyrene beads. Some useful data regarding this polymer is given in the slide. This is rigid plastic material, completely amorphous, has good strength and dimensional stability, and good resistance to aqueous base and acids. Because of the aromatic groups it has poor weatherability and it is not good resistant to hydrocarbon solvent.

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### Polystyrene


Applications as inj. molded articles:

- ❖ Office fixtures, tumblers, etc
- ❖ In medical – pipettes, petry dishes, containers, etc

$$\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_5 \longrightarrow \left[ \text{H}_2\text{C}-\text{CH}-\text{C}_6\text{H}_5 \right]_n$$

- ❖ Expanded PS is formed by impregnated blowing agents – PS Foams
- ❖ Disposable drinking cups, cushioned packaging, thermal insulations, egg cartoons, fast food trays, etc
- ❖ Cross-linked PS beads – used in chromatographic columns

Trade names: *Carinex, Cellofoam, Dytene, Styrofoam, etc*




Some of the uses for polystyrene are shown in the above slide. As I also told that you do not need to remember all this information, you should be aware of some applications of polystyrene. Carinex, Cellofoam, Dytene, Styrofoam, etc are some of the trade names by which polystyrene is sold in the market.

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### Vinyl family: Poly(vinyl chloride)

$$\text{H}_2\text{C}=\text{CH}-\text{Cl} \longrightarrow \left[ \text{H}_2\text{C}-\text{CH}-\text{Cl} \right]_n$$

- ❖ Generally synthesized by suspension polymerization batch process
- ❖ Low crystalline
- ❖  $T_g \sim 81^\circ\text{C}$ ;
- ❖ HCl formation during processing at high temp.; heat stabilizers like metal oxides, fatty acid salts are always added
- ❖ Tough, rigid plastics, find extensive application
- ❖ Often plasticized by adding additives – flexible PVC



Among other polymers, poly(vinyl chloride) is synthesized by radical polymerization. Some properties of the polymer and few applications are also shown in the above slide.

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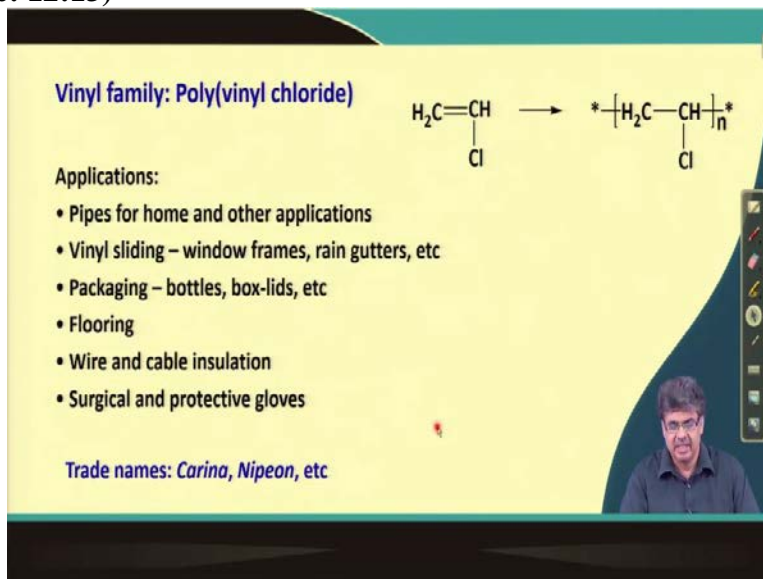
**Vinyl family: Poly(vinyl chloride)**

$$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ | \\ \text{Cl} \end{array} \longrightarrow \text{*} \left[ \text{H}_2\text{C}-\underset{\text{Cl}}{\text{CH}} \right]_n \text{*}$$

Applications:

- Pipes for home and other applications
- Vinyl sliding – window frames, rain gutters, etc
- Packaging – bottles, box-lids, etc
- Flooring
- Wire and cable insulation
- Surgical and protective gloves

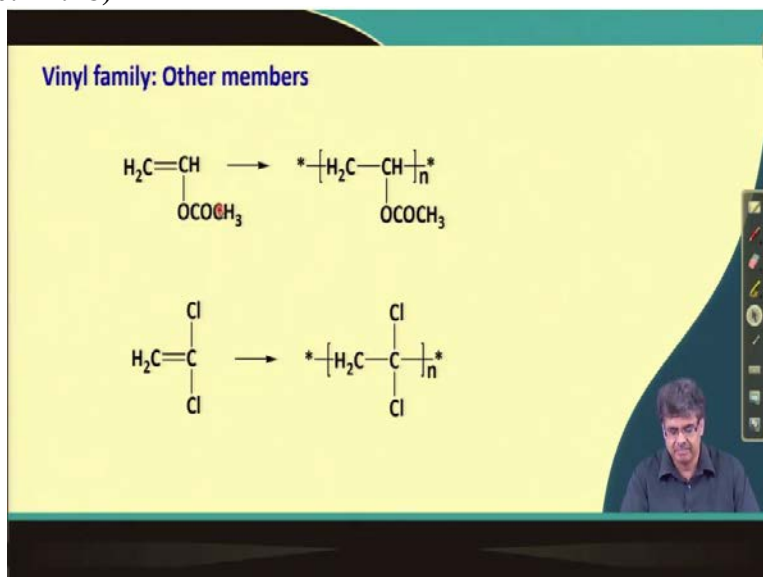
Trade names: *Carina, Nipeon, etc*



Especially, black pipes for home are made of poly(vinyl chloride). It is also used for flooring, packaging and sliding. Carina, Nipeon, etc are some of the trade names by which poly(vinyl chloride) is sold.

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**Vinyl family: Other members**

$$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ | \\ \text{OCOCH}_3 \end{array} \longrightarrow \text{*} \left[ \text{H}_2\text{C}-\underset{\text{OCOCH}_3}{\text{CH}} \right]_n \text{*}$$
$$\begin{array}{c} \text{Cl} \\ | \\ \text{H}_2\text{C}=\text{C} \\ | \\ \text{Cl} \end{array} \longrightarrow \text{*} \left[ \text{H}_2\text{C}-\underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}} \right]_n \text{*}$$


There are other members in the vinyl family like poly(methyl methacrylate) that are synthesized by radical chain polymerization.




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**Acrylic family: Poly(methyl methacrylate)**

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}=\text{C} \\ | \\ \text{COOCH}_3 \end{array} \longrightarrow \left[ \text{H}_2\text{C}-\underset{\text{COOCH}_3}{\overset{\text{CH}_3}{\text{C}}} \right]_n$$

- ❖ Synthesized by solution, suspension, and emulsion polymerization
- ❖ Amorphous
- ❖  $T_g \sim 105^\circ\text{C}$ ;
- ❖ Low RI – exceptional optical clarity, weatherability, strength, etc.
- ❖ Sheets, rods, etc
- ❖ Safety glasses, indoor and outdoor lighting, optical fibres for light transmissions, eye glass lenses, etc.

Trade names: *Plexiglass, Leucite, etc.*




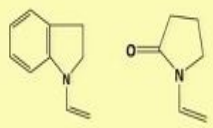
Poly(methyl methacrylate) is one of the important polymers. Some of the properties of this polymer are given in the above slide. Poly(methyl methacrylate) is used for safety glasses, indoor & outdoor lighting because it has a very low RI. As the transparency is much higher, poly(methyl methacrylate) is used for optical application where transparency or clarity it is needed. Some of the common trade names are like plexiglass, Leucite and so on.

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**Acrylic family: Other Members**

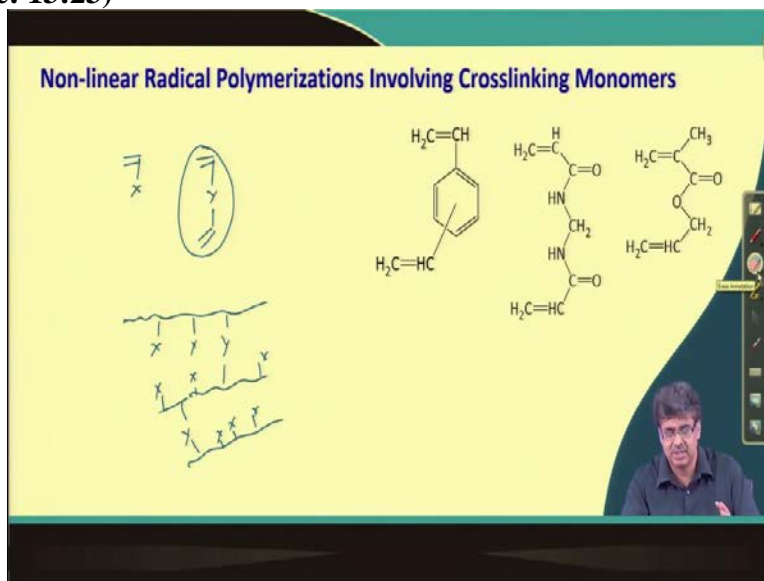
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{C}=\text{C} \\ | \\ \text{COOH} \end{array} \longrightarrow \left[ \text{H}_2\text{C}-\underset{\text{COOH}}{\overset{\text{CH}_3}{\text{C}}} \right]_n$$
$$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ | \\ \text{CONH}_2 \end{array} \longrightarrow \left[ \text{H}_2\text{C}-\underset{\text{CONH}_2}{\text{CH}} \right]_n$$

**Other Monomers**

$$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ | \\ \text{COOH} \end{array} \longrightarrow \left[ \text{H}_2\text{C}-\underset{\text{COOH}}{\text{CH}} \right]_n$$
$$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ | \\ \text{CN} \end{array} \longrightarrow \left[ \text{H}_2\text{C}-\underset{\text{CN}}{\text{CH}} \right]_n$$


The other members are, some of them are given in the slide above, like acrylamide, acrylonitrile are synthesized using radical chain polymerization.

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We can also use this radical polymerization to make crosslinked polymers. If we have a monomer containing one double bond like the one shown in the slide and another monomer with more than one double bond, then if we mix and polymerize then we can make crosslinked or network polymer. So by just adding one multifunctional monomer like in this case, we make network polymer or gel. Some of the examples of this type of crosslinker is given in the slide like the very common divinyl benzene, which is used for crosslinking styrene in a polystyrene molecule. When you crosslink, you should try to use the functionality like divinyl benzene to crosslink polystyrene, or bis-acrylamide can be used to synthesize cross-linked acrylamide polymers, like polyacrylamide.

Bis-acrylate or bis-methacrylate group can be used to crosslink poly(methyl methacrylate) type polymers. We can use multifunctional monomers, as shown in the slide, containing 2 double bonds to crosslink between linear polymer chain and form network polymer.

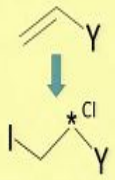
We will move to a new module and discuss about other methods of polymerization. These methods are not that important commercially because they are not used as frequently as step growth polymerization and radical chain polymerization. I will spend less time for these other polymerization techniques. For example, we will talk about ionic chain polymerization.

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**Ionic Polymerization**

❖ Cationic

❖ Anionic



$M + I^+ \rightarrow MI^+$

$M + I^- \rightarrow MI^-$

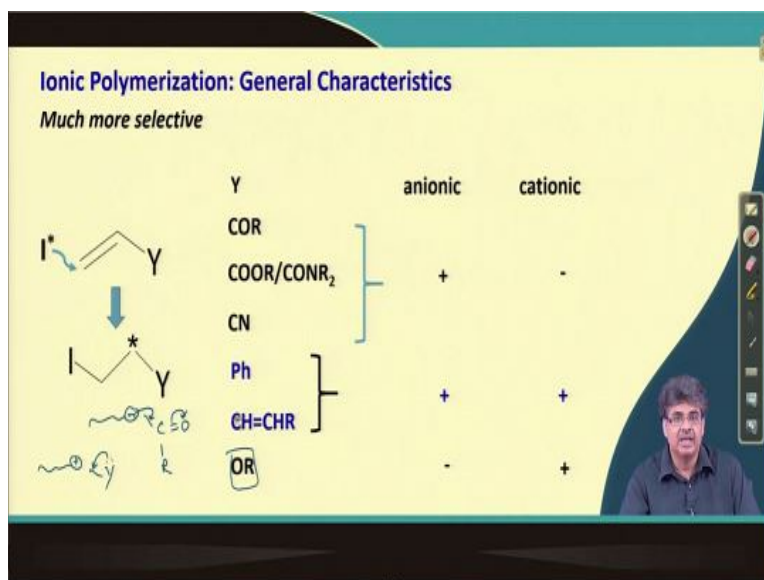
$M + e^+ \rightarrow \bullet M^+ \rightarrow \bullet MM \bullet$

$M + e^- \rightarrow \bullet M^- \rightarrow \bullet MM \bullet$

1. No inherent termination: Living
2. Pre-decide molecular weight
3. Scope of generating functional groups at the ends
4. Fast reaction

As the name suggests, in this case, instead of a radical that was used to initiate the chain polymerization, we have ionic species, which initiate the polymer chain, for example, a cation or an anion as shown in the slide where the CI means counter ion. Unlike in the case of radical, in case of ionic polymerization, we always have a counter ion associated with the active chain end or active part of the polymer. We can use also an electron transfer process to generate a radical ion that may produce a bi-radical. Instead of bi-radical, we may have bi-anion  $^{\ominus}MM^{\ominus}$  or bi-cation  $^{\oplus}MM^{\oplus}$ . The fundamental difference of these types of ionic polymerizations with radical polymerization that, in case of radical, we have seen that there are inherent bimolecular termination reactions between two propagating radicals, but in case of ionic polymerization, these inherent terminations are not possible because two cations or two anions cannot interact with themselves. Like a living or RDRP polymerization, we can actually pre-decide the molecular weight in ionic polymerization and again because the chain end will be anion or cation, we can actually functionalize the end of the polymer chains. Therefore, in this polymerization, there are scopes of generating functional groups at the end of polymerizations. These ionic reactions are fast.

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Some general characteristics of an ionic polymerization: these are much more selective unlike radical polymerization, the number of monomers which we be polymerized using ionic polymerization is less because, as we discussed earlier that, to propagate a chain we need to stabilize the resulting active site. So, if you have a cation the Y, as shown in the slide, must be electron donating group to stabilize this cation or if we have anion, then this Y should be electron withdrawing group either by inductive effect or by resonance effect, so that we can stabilize this active ion so that the polymerization can proceed. As we discussed earlier also, the monomers that especially have electron-withdrawing group either by inductive effect or by resonance effect, we can have anionic polymerization. For example, if Y is this -COR, then the anion can be stabilized by resonance. For a cation then Y must be electron donating to stabilize the resulting cation that will happen, for example, with -OR type substitution, if Y is -OR then it can donate the lone pair on oxygen to the cation and stabilize it. As we discussed earlier also, if the Y is COR, COOR/COONR<sub>2</sub> or CN substitution, anionic polymerization is possible, and if Y is OR type of substitution then cationic type polymerization is possible, and if you have substitution like phenyl or another conjugation, then because of resonance, both anionic polymerization and cationic polymerization are feasible. Therefore, we realize that ionic polymerizations are much more selective. So, the number of monomers that can participate in ionic polymerization is less compared to the number of monomers which can participate in radical polymerization.

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**Ionic Polymerization: General Characteristics**  
**Effect of Polarity of the Solvent**

$$M_n^{+/-} X^{-/+} + M \rightarrow M_{n+1}^{+/-} X^{-/+}$$

$$M_n X \leftrightarrow \boxed{M_n^{+/-} X^{-/+} \leftrightarrow M_n^{+/-} \parallel X^{-/+}} \leftrightarrow M_n^{+/-} X^{-/+}$$

I                      II                      III                      IV  
 covalent      tight ion-pair      solvated ion-pair      free ion-pair  
 bonded      contact ion-pair      loose ion-pair

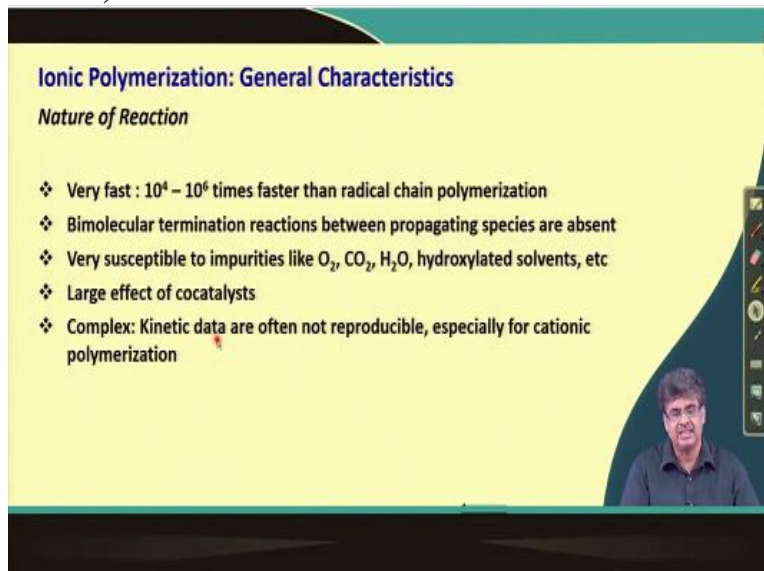
→ Polarity of solvent increases

Low to moderate polarity solvents like THF, ether, mixed solvents of THF-toluene, etc

Another very important feature is the effect of polarity of the solvent. In case of ionic polymerization, we have a polymer chain having either an anion or a cation at the end along with a counter ion associated with that. Hence, the polarity of the medium effect the reactivity of this chain end which is an ionic species. The ionic chain ends and their combination ions could be present in four ways. First, in a non-polar solvent, they can actually combine with each other forming covalent bonds, in that case, obviously, there is no ionic species present and the species is not reactive at all for carrying out further the polymerization. On the other extreme, if we have a highly polar solvent, then the ions and their CIs will be separated and they will form free ion-pairs and in this case, the reactivity of the chain ends will be much higher because the electrophilicity or nucleophilicity depend on the available charges that are much higher in this case. Therefore, the rate for polymerization will be much higher in case of highly polar solvent. In the two intermediate states, as shown in the slide, we can have tight ion-pair and we can have solvated ion-pair or solvent separated ion-pair depending on the polarity of the medium. So, as we understand, the covalent bonded ion pairs cannot carry out any initiation reaction or they cannot carry out any polymerization further, whereas the reactivity of the free ion-pairs are too fast that cause lot of complications like side reactions because of the highly reactive ion species. So, these two extremes are not recommended. Generally, ionic polymerizations are not done on highly polar solvents or in solvents of very low polarity. These are done either in a low to moderate polarity solvent so that the ionic chain ends are present either as a tight ion pair or as solvated ion-pair. These two intermediate states of the ion pairs are the preferred for carrying out ionic

polymerization in low to moderate polarity solvent. Low to moderate polarity solvent like THF, or mix solvents like toluene - THF are used for ionic polymerization.

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**Ionic Polymerization: General Characteristics**  
*Nature of Reaction*

- ❖ Very fast :  $10^4 - 10^6$  times faster than radical chain polymerization
- ❖ Bimolecular termination reactions between propagating species are absent
- ❖ Very susceptible to impurities like  $O_2$ ,  $CO_2$ ,  $H_2O$ , hydroxylated solvents, etc
- ❖ Large effect of cocatalysts
- ❖ Complex: Kinetic data are often not reproducible, especially for cationic polymerization

The ionic reactions, as we discussed, are very fast because of the ionic nature of the reactions. They are actually  $10^4$  to  $10^6$  times faster than radical chain polymerization, because ionic species are much more reactive than radicals are. And as we discussed, the bimolecular termination reaction between the propagating species, as in the case of radical chain polymerization, are absent in this case, because two anions or two cations cannot interact with each other and do further reaction. Because the ionic species are very reactive, they are very much susceptible to impurities like oxygen, carbon dioxide, water or any hydroxylated compounds that are present in the medium. Additionally, there is a large effect of catalysts that we will discuss briefly in this case and the polymerization is quite complex. Therefore, kinetic data are often not reproducible; it is very difficult to generate reproducible kinetic data for these ionic polymerizations especially for cationic polymerization.

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**Comparison Between Radical-Cationic-Anionic Chain Polymerization**

- ❖ Ionic polymerizations are very susceptible to  $O_2$ ,  $CO_2$ ,  $H_2O$ , etc
- ❖ Ionic polymerizations are very sensitive to solvent polarity, especially anionic polymerization; radical polymerizations are not that sensitive
- ❖ Ionic polymerization are generally carried out at ambient or lower temperatures; radical polymerization  $> 50\text{ }^\circ\text{C}$ 
  - $E_{\text{radical}} > E_{\text{ionic}}$  (low, sometimes negative)
- ❖ Radical scavengers stops/inhibits radical polymerization; no effect on ionic polymerization
- ❖ Ionic polymerizations can be easily employed to make copolymers

If you compare between radical, cationic and anionic polymerizations, ionic polymerizations are very susceptible to the impurities than radical polymerization because of higher reactivity of the ionic groups. For example, for an anionic polymerization, small amount of water present in medium can actually quench the anion and generate a hydroxide anion that is not reactive enough to proceed make a polymer, the reaction is stopped. Small amount of water present in the medium can kill the propagating anion. Ionic polymerizations are very sensitive to solvent polarity as we discussed and it is preferable to do a polymerization in low to moderate polarity. Ionic polymerization can be carried out or may be carried out in ambient to lower temperature to avoid the side reactions. Presence of radical scavengers do not inhibit ionic polymerization, they actually inhibit radical polymerization. An ionic polymerization can be easily employed to make copolymer as we can have a living chain ends that are ionic.

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**Ionic Polymerization: Practical considerations**

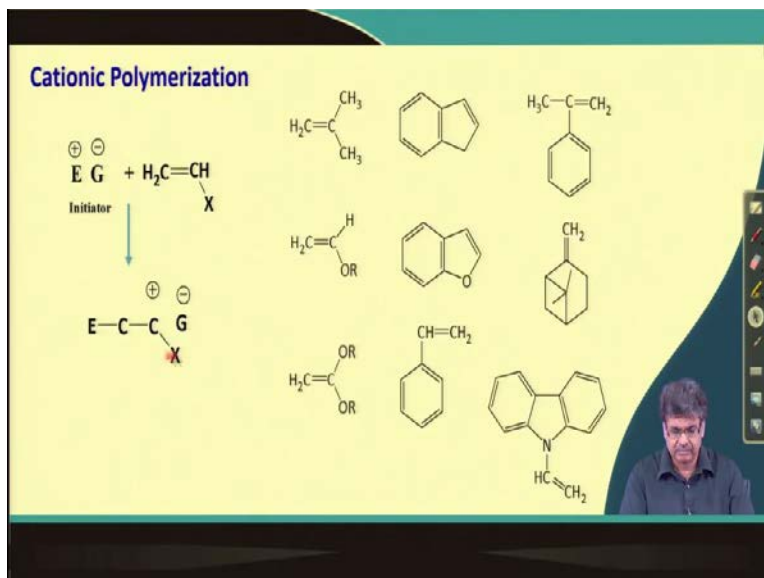
- ❖ Very susceptible to  $O_2$ ,  $CO_2$ ,  $H_2O$ , etc
- ❖ All reagents must be extremely pure
- ❖ Glasswares should be cleaned rigorously – generally high vacuum techniques are used
- ❖  $N_2$  / Ar (used for creating inert atmosphere) must be extremely dry and pure

Commercial applications of anionic chain polymerizations are limited to making specialty copolymers and MW standards

From practical aspect, it is very difficult to carry out ionic polymerization, because this is very, very susceptible to the impurities present. We have to have all the reagents extremely pure; otherwise, there will be impurities that will kill the resulting ionic species. The glassware should be cleaned rigorously and generally, high vacuum techniques are used for the ionic polymerization to remove oxygen and carbon dioxide or water from the medium to create inert atmosphere. We use generally use nitrogen and argon during reaction. Therefore, in this case, the nitrogen or argon that is used to generate the inert atmosphere must be very pure enough, so that there is no impurity is present. As a result, commercial applications of these, especially anionic chain polymerization, is limited to making specially copolymers and molecular weight standards that are the polymer molecules having very narrow dispersity.

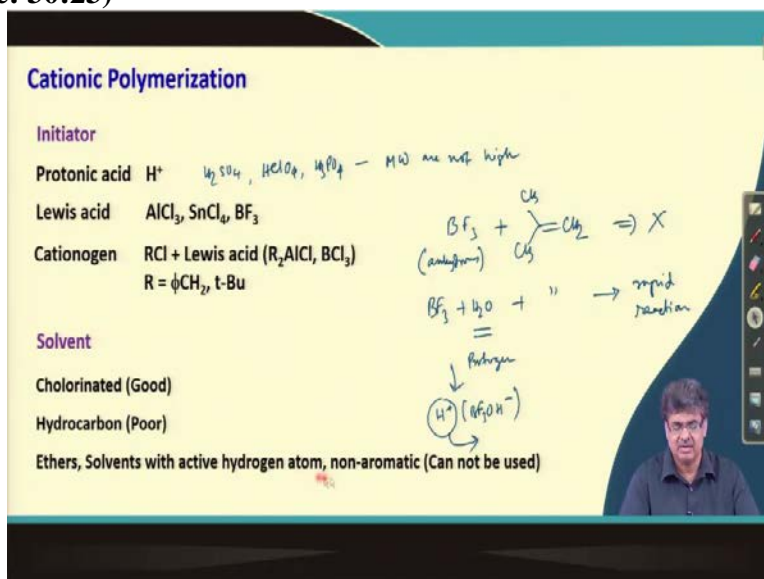
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We will quickly go through the two polymerization mechanisms. In cationic polymerization where we have an electrophile that attacks the double bond and it can form an initiator molecule like shown in the slide. Some of the monomers that can be polymerized using cationic polymerization are also presented in the slide.

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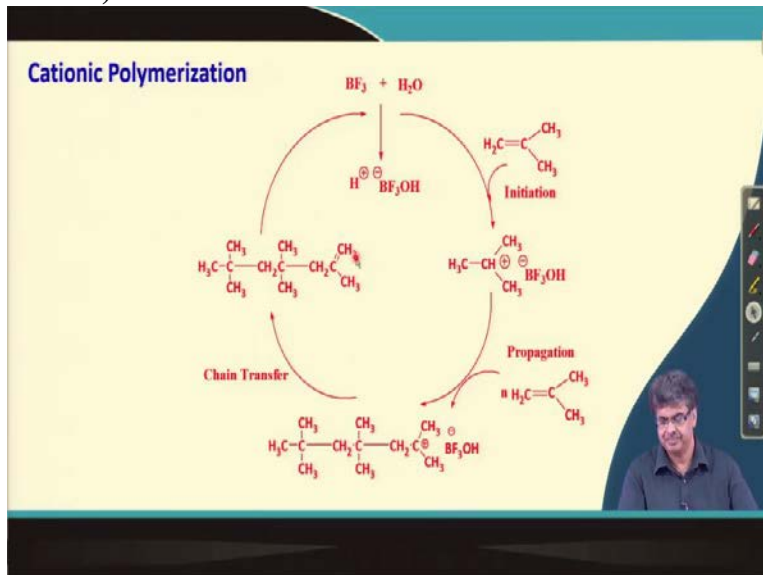


Typical initiators that are used for cationic polymerization are protonic acids like HCl, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> etc. In these cases the molecular weight generated are not very high, these are not very effective initiators. Other type of initiators is Lewis acids, some examples of typical Lewis

acids are shown in the slide. In fact, if we use just pure Lewis acids then also the reaction is very low. For example, if we use  $\text{BF}_3$  as initiator, then the reaction does not happen, but if we add a co-catalyst,  $\text{BF}_3$  plus water and the monomer then we have a very rapid reaction. So, in this case, just Lewis acid is not enough to carry out the reaction, we need a co-catalyst like  $\text{H}_2\text{O}$  that acts as a protogen, supplier of proton, producing a complex type as shown in the slide, which initiates the cationic reaction.

Chlorinated solvents are good for cationic polymerization, hydrocarbons are not good, as I explained earlier that, the polarity is so low that the ionic species form very tight ion-pair nearly like covalent bond. So, the reactivity is very low. In addition, solvents like ethers, with active hydrogen, can give hydrogen to the ionic species, are also not used in this cationic polymerization process.

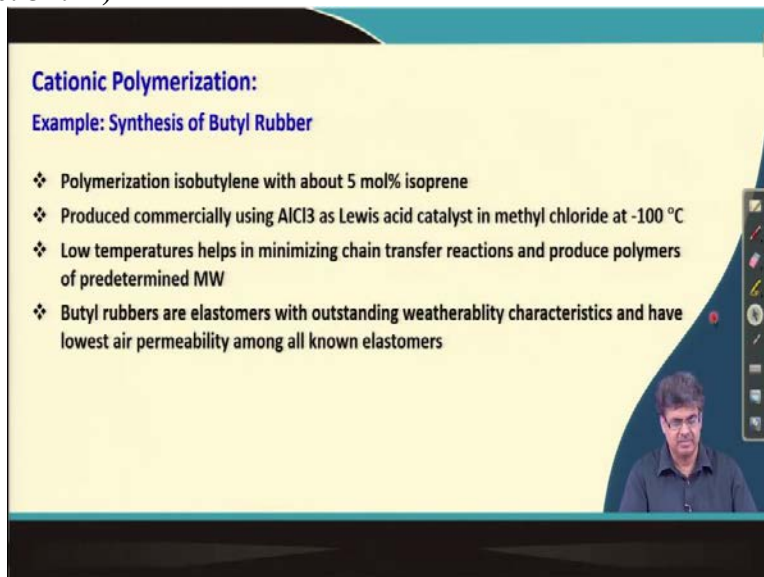
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The slide presents example of one cationic polymerization. The initiation step is like the radical chain polymerization, which is followed by propagation step. Now, in this case, inherently, two propagating cations cannot react with themselves and terminate the reactions, but there are some chain transfer reactions may happen like, chain transfer to the monomer, chain transfer to the counter ion, or to solvent or to some other chain transfer agents. They can actually participate in chain transfer process and can quench this cation and by doing this it can be terminated. Therefore,

cations inherently cannot react with themselves to terminate chains, but because of the possibility of some other chain transfer reactions like to monomer or to counterion, the reaction can actually be terminated, one of the example as shown in the slide.

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**Cationic Polymerization:**  
**Example: Synthesis of Butyl Rubber**

- ❖ Polymerization isobutylene with about 5 mol% isoprene
- ❖ Produced commercially using  $\text{AlCl}_3$  as Lewis acid catalyst in methyl chloride at  $-100\text{ }^\circ\text{C}$
- ❖ Low temperatures helps in minimizing chain transfer reactions and produce polymers of predetermined MW
- ❖ Butyl rubbers are elastomers with outstanding weatherability characteristics and have lowest air permeability among all known elastomers

One example of a cationic polymerization which is used for synthesize an important polymer is butyl rubber. In this case, isobutylene is copolymerized with 5% isoprene, and in that case,  $\text{AlCl}_3$  is used as a catalyst at  $-100\text{ }^\circ\text{C}$ . Low temperature actually minimizes the chain transfer reactions and produce polymers of predetermined molecular weight. Butyl rubbers are elastomers with outstanding weatherability characteristics and have lowest air permeability among all known elastomers.

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**Anionic Polymerization**

- ❖ Initiation
- ❖ Propagation
- ❖ Termination

**Initiation**

$$\text{Nu}^- \text{M}^+ + \text{C}=\text{C} \begin{matrix} \text{X} \\ \text{Y} \end{matrix} \longrightarrow \text{Nu}-\text{C}-\text{C} \begin{matrix} \text{X} \\ \text{Y} \end{matrix} \text{M}^+$$

In anionic polymerization also, we have these three steps, initiation, propagation, and termination. Initiation reaction involves a nucleophile that initiates the polymer chain.

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**Anionic Polymerization**

**Initiation**

Organometallic compounds -  
electron transfer process

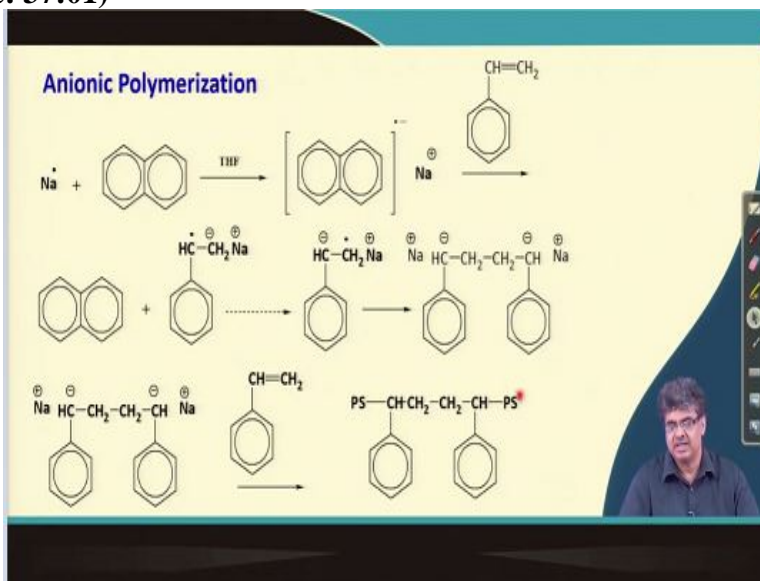
$\text{Bu}^\ominus \text{Li}^\oplus \rightarrow \text{Styrene, isoprene}$

$\text{C}_6\text{H}_5^\ominus \text{Mg}^\oplus \rightarrow \text{MMA}$

$\text{CH}_3^\ominus \text{K}^\oplus \rightarrow \text{cyanoacrylate}$

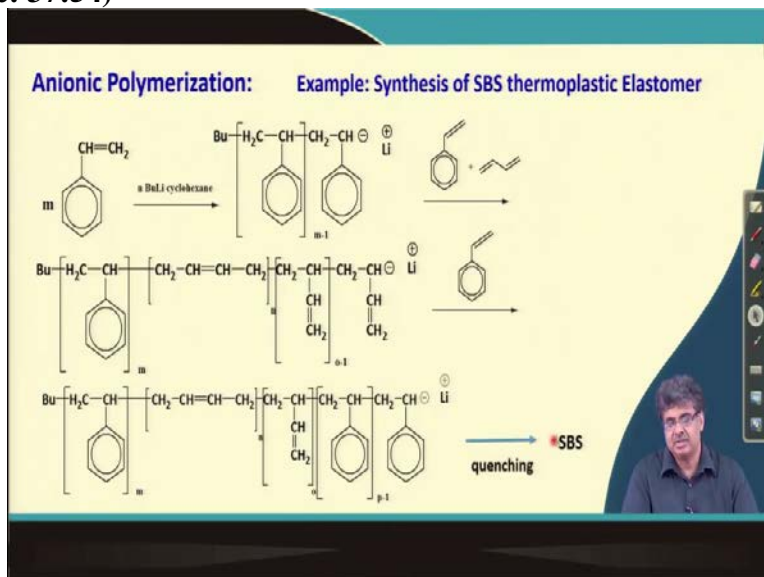
Examples of the initiator molecules like are mentioned in the slide. We can have organometallic compounds or we can have electron transfer process for generating initiating a radical anion. One very common initiator is butyl lithium, which is used to polymerize styrene, isoprene. The initiators that are used for polymerizing methyl methacrylate and cyanoacrylate are shown in the slide.

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In the example presented in the slide, because of electron transfer process we get radical anion which on reaction with a styrene molecule generate a bi-anion, so, we have a species with two anionic ends which propagate anionic chains from both sides. So, we can use this for polymerizing and making polymer chains from both the sides.

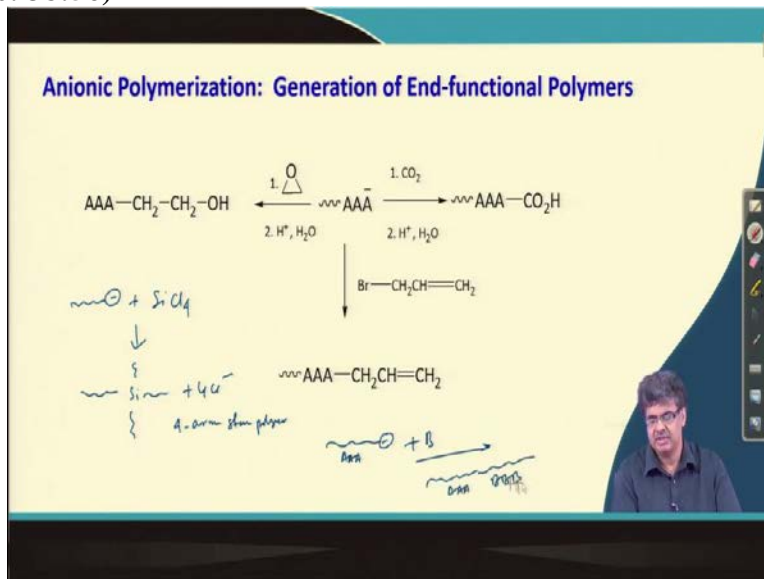
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Anionic polymerization is employed in the synthesis of SBS, styrene butylene styrene thermoplastic elastomer. In this case, we use butyl lithium in cyclohexane to generate the first

block of polystyrene, then a mixture of styrene and butadiene is used to make the second block. In the third step, again a polystyrene block is synthesized. Therefore, we now have a first block of polystyrene, then we have a copolymer of styrene and butadiene as a middle block, and we have polystyrene as a third block. Therefore, we have a tri block copolymer.

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One very important use of anionic polymerization is to make functional polymers. For example, if the anion shown in the slide is reacted with carbon dioxide followed by acidification then we generate acid functionalized polymer chain, we can react with epoxy followed by hydrolysis in presence of acid to produce OH functional polymer. We can react with monomers to make macro-monomers, and we can use the anion to make four-arm star polymer as described in the slide. And we can easily synthesize block copolymers using anionic polymerization, as was described in case of SBS.

With this, I end the lecture on anionic polymerization and next I will move to another type of polymerization reaction in the next lecture.