

Polymer Reaction Engineering
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Lecture - 02
Introduction to Polymerization Process-II

Welcome to this introduction to polymerization process part two. So, in the previous lecture, we studied about different type of a polymeric system classification and there subsequently we were discussing about the different type of their applications and efficacy through which we can improvise those polymeric products.


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Classification of Polymers

- **Thermoplastic polymers**

Applications of thermoplastic polymers

- ✓ The main thermoplastics include high-density polyethylene (HDPE) have applications in Industrial wrappings and films, pipes, Containers, toys and housewares.
- ✓ Low-density polyethylene (LDPE) used in toys, coatings, containers, pipes, Pallet and agricultural film and bags etc.
- ✓ Poly(vinyl chloride) (PVC) used in pipes, toys, flooring, wallpaper, cable insulation, credit cards, bottles, Window frames, cling film, guttering, and medical products etc.



So, we truncated at the application of thermoplastic polymers. Now the main thermoplastic polymers which we were discussing that they are using, we may use as the industrial wrapping, film, pipe, containers, toys, house wares etc. And LDPE that is referred as low-density polyethylene, they are used in the toy, coating, containers, pipe, different type of a pallets.

These pallets are sometimes used as a supporting material for various kind of applications, sometimes agricultural films, bags etc. PVC it is a very common thing and all of you are aware about their various application. They are mostly used in the pipe, toys, floorings etc. So, these types of the applications are very common with respect to the thermoplastic polymers.

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Classification of Polymers

▪ Thermoplastic polymers

Applications of thermoplastic polymers

- ✓ Polypropylene (PP) used in Automotive parts, electrical components, battery cases, crates, Film and microwave-proof containers etc.
- ✓ Polyethylene terephthalate (PET) used in Fibers, Bottles, food packaging, textile and films etc.



Other are like polypropylene. They are very commonly used in the automotive part, electrical component, various kind of a battery cases etc. Then PET, they are used in the fibers, bottle every I mean if you go for packaged drinking water if you see the different type of other like juices, etc, you will find the application of the polyethylene terephthalate bottles. Food packaging, textile, film etc.

So, these are the various spectrum of thermoplastic polymers. Now why I am telling all of this application because you can imagine, that the wide variety of application of all those polymeric products.

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Classification of Polymers

▪ Thermosetting polymers


The thermoset polymers melt only the first time when they are heated, and during the first heating, the polymer is cured, and after that, it does not melt on reheating and degrade after that. e.g. polyurethanes, Epoxy and Phenolic resins.

Applications of thermosetting polymers

- ✓ Epoxy resins is another example which have applications in Sports equipment, boats, adhesives, automotive components.



Thermosetting polymers



Now the second part of this heat sensitive polymer is to the thermosetting polymers. Now these thermoset polymers melt only the first time when they are heated and

during the first heating of the polymer, they are usually cured. After this they are not having the tendency to melt. Therefore, the reheating or degradation of these particular polymers are often is very difficult or practically impossible.

The some of the examples of these thermoset polymers, you can see the polyurethanes, epoxy, phenolic resins and if you see that, these are the some of the applications or products attributed to the thermoset polymers. Let us have a look about the various application of a thermoset polymers like epoxy resins, they are the example of applications in the sports equipments, boats adhesive, automotive components, etc.

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Classification of Polymers

Applications of thermosetting polymers

- ✓ Polyurethane is the best example of thermoset polymer which have wide applications in Coatings, film, packaging, adhesive, automotive parts, home appliances, sealants, paint, composite sheets, and cushions many more.
- ✓ Phenolic resins also known as Bakelite which is invented by Dr. Leo Baekeland in 1907, have wide applications in adhesives, home appliances, general appliance moldings, electrical components and automotive parts etc.



Now the polyurethane is again the best example of thermoset polymers, which is having the wide application in coating, film, packaging, adhesive, automotive parts, home appliances, sealant, paint, composite sheets etc. Now sometimes you may encounter the joining of various adhesive epoxies. Now if you see that there are two types of things, one is the epoxy, another one is hardener.

And if you combine them, then you can seal anything that is the best example of a thermosetting polymers, because once you join and after a certain period of time they get cured and then they form a hard surface. This is the best example of thermoset polymer. The phenolic resin they are also known as bakelite. Bakelite is again very common that is being used in various household appliances, molding, electrical components, automotive parts etc.

So, this bakelite was first invented by Dr. Leo in 1907. And based on the various applications still this bakelite is being used in various day-to-day affairs.


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Classification of Polymers

3. Based on structure of polymers

On this basis of types of monomers (bi-functional, tri-functional and unsaturation present in the molecules such as double and triple bonds) used in polymers structure, it is divided into three types such as: linear, branched and cross-linked polymers.

- **Linear polymers**
Polymers in which the monomer molecules (having functionality-2) were linked together to form the polymer molecules in one continuous length, the polymer obtained are linear polymers.



Now third which we were discussing about the classification scheme when we were discussing that is based on the structure of polymers. Now as an engineering perspective, as a science perspective, this is the most scientific approach of classification of these polymers. So, on this particular basis, the different type of a monomers, bi-functional, tri-functional, unsaturation present in the various kinds of molecules like double and triple bond, they are used in the polymeric structure.

So usually based on this particular approach, they are divided into three different types; linear, branched, and the cross-linked. Now the before we go into the detail of this kind of sub classification, the purpose of classification is that you are having the different basket and if you require any kind of different product or any kind of a different property, you can pick that particular thing from that particular basket.

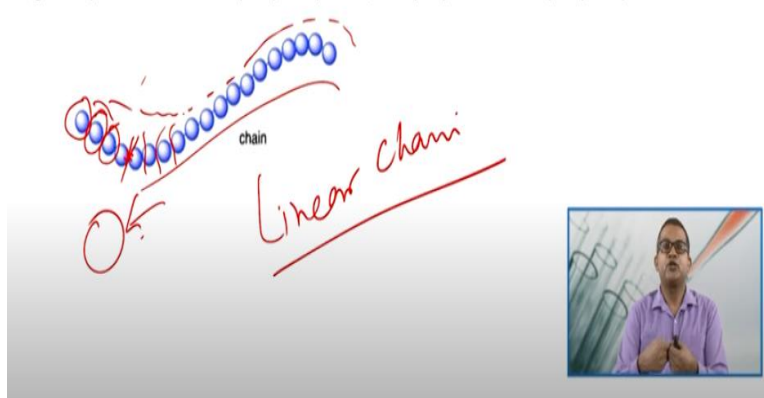
So, you are having the third basket that is the based on the structure of polymer and you are having sub containers in it like linear polymer, branched polymer, and a cross-link polymer. So, we will discuss this thing into the broad spectrum. Now linear polymers in which the monomer molecules having the functionality greater than 2, they were linked together to form a polymeric molecule either in a one continuous length.

These polymers which after the process, they are obtained, thus obtained, they are termed as the linear polymer.

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Classification of Polymers

- **Linear polymers**
e.g. Polymerisation of polyethylene, Polystyrene and polyvinyl Chloride etc.



Now here you see that we discussed about the polymerization of a polyethylene. Now these are the building blocks, which we were discussing in the first lecture. These are the building blocks or you can say that these are the ethylene blocks and they are joined together to form this particular chain. Now this is the linear chain.

Now see, since we are at the beginning you see that when we try to develop this particular linear polymer chain, now here you can see that there must be certain things which need to be apply over here between these two molecules so that they can join together. We will discuss this particular process because this is the ultimate theme of this particular course, that is the polymerization process.

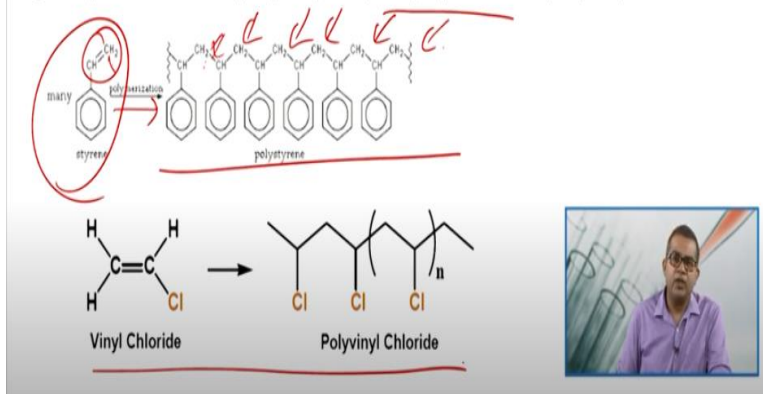
Because ultimately what you require that you are forming a chain. It should not break until it achieves to the desired application. So that is you can say the heart of this particular polymerization process.

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Classification of Polymers

▪ Linear polymers

e.g. Polymerisation of polyethylene, Polystyrene and polyvinyl Chloride etc.



Now to be more practical, you see that the example of a formation of a polystyrene, we discussed that it offers a wide spectrum of properties. Now this is a styrene monomer or a styrene molecule. Through polymerization, it forms a polystyrene. Now you see that these are the building blocks or sometimes referred as a repeating unit.

And here you see that this is the double bond which I discussed in the previous lecture, they must have at least either functionality or a double, triple bond so that they can because, see saturation is the most stable structure. It is difficult to create these kinds of things with a saturated one. So, this type of unsaturation offers a very good route for the development of such kind of a polymeric product.

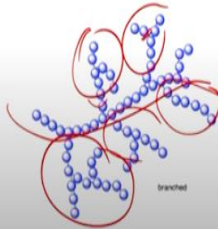
Now here, which I already discussed in the previous lecture, this is the formation of a polyvinyl chloride.

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Classification of Polymers

▪ Branched polymers

- The branched polymer molecules are the ones in which side branches of connected monomer molecules protruding along the main polymer chain from different central points on the main branches i.e. in branched polymers the secondary polymer chains attached to a primary backbone.



Now another sub basket of this basket is the branched polymer. The branched polymer molecules, they are ones in which the side branches, if you see that these are the side branches. The side branches of are connected with the help of various monomeric molecules and protruding along with the main polymer chain. Now this is you can say the main polymeric chain.

And here you see that there are various branched molecules are attached, right. Now here again in engineering perspective, one thing is important that the affinity between these two similar types of molecules and affinity of this one in the similar type of molecule, this thing these things are the extremely important. Important in the perspective that once you apply to a various industrial application, then they do not offer the detachment.

That is why this particular polymer reaction engineering came into existence.

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Classification of Polymers

▪ Branched polymers

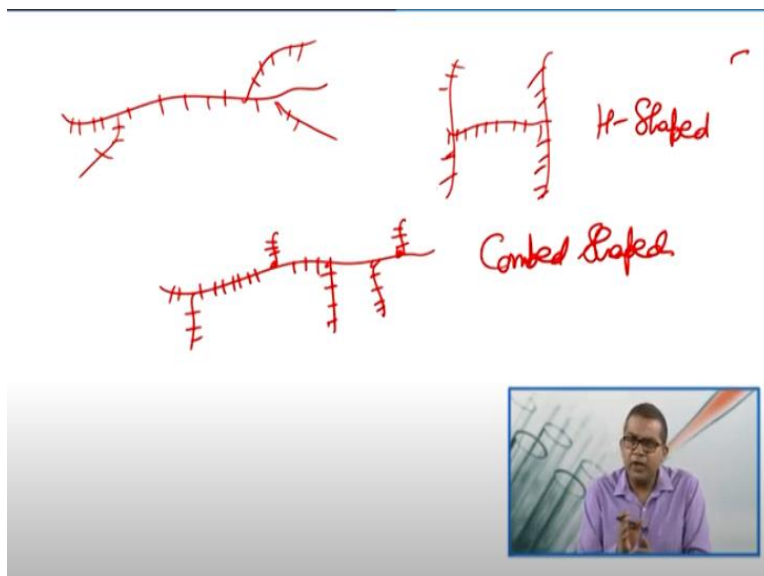
- To form such kind of polymer, the monomer must have capability to grow in more than two directions hence the monomers used must have functionality of two. Which results in H-shaped and comb-shaped polymers.



Now to form such kind of a polymer, the monomer must have a capability to grow in more than two directions like see here one, two. Now it must have an ability to grow in more than two direction. Hence the monomer used must have a functionality of either two, which we discussed in the very first slide of this branched polymer. So sometimes it results in the H-shaped or comb-shaped of polymers.

So, once we intend to develop this branched polymer and sometimes for a very specific application and sometimes for other kind of property-oriented things, we may require H-shaped or a comb-shaped polymer during this polymerization process. So, because this particular approach will be useful in the subsequent studies of this particular course. So, let me introduce that what are those H-shaped and a comb-shaped polymer.

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So sometimes the branched polymers, they are just like they are some branches, I will give you some photographs too of this particular branched type. And here you see that there are various repeating units like this. And when we talk about the H-shaped because for specific reason, sometimes you may require or you may need to alter those polymerization process with the help of certain catalysts, certain pressure, temperature conditions.

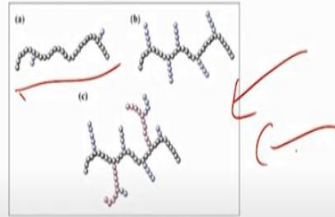
So, these H-shaped polymers are just like this. And here you are, you may have a different repeating unit like this. This is your H-shaped branched polymers. This is the simple branched polymer. Sometimes in various applications, you may require the comb-shaped one. So, these are the some you can say the comb-shaped polymers. These are not straight one, but like this.

And again, you may have a different repeating units or monomeric units in a more scientific term. So, these are the comb-shaped. So, you can see that by a simple alteration or sometimes you may say that they offer various kind of shapes in this particular branch shapes. Or you can say sometimes that you are creating the n number of different sub baskets within this branched polymer.

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Classification of Polymers

- **Branched polymers** Low-density polyethylene(LDPE), High density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) (The Difference)



- (a) HDPE (b) LLDPE (c) LDPE

Now one of the best examples which we discussed about the LDPE or high-density polyethylene or a linear low-density polyethylene. Now this we are discussing that there are three different type of polyethylene, low density polyethylene, high density polyethylene and a linear low-density polyethylene. So, the monomer for each kind of polymer is ethylene.

Now we can form different type of polymeric product by the application of various polymerization protocol, maybe like this that HDPE, then LDPE or LLDPE. Now you see that there is comb like structure, there are H type of structure and there is linear type of structure. So, if you see that based on the requirement, based on the properties you are looking for, you can develop different kind of polymers with the same type of monomer.


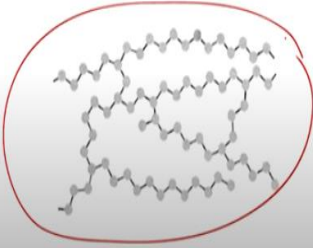
Here the monomer is same that is ethylene. But you are having low density polyethylene, high density polyethylene, linear low-density polyethylene. So, based on the requirement you can develop the protocol. Again, when you are developing the different type of a system for the development of different type of the polymer, you require special attention of reaction engineering.

Because a slight change in the temperature, slight change in the concentration, slight change in the pressure thing may change the ultimate product drastically. So that is why the major impetus towards we focus towards the basic theory towards the engineering perspective.

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Classification of Polymers

- **Cross-linked polymers**
 - The polymer molecules linked together with each other molecules irrespective of the end functional groups in the structure of polymer are termed as cross-linked polymers. Generally, trifunctional monomers are used synthesis of cross-linked polymers.



Now come to the last basket or last sub basket of the third basket that is the cross-linked polymer. Now this cross-linked polymer if you see in this particular figure, the things are linked together in a compact form. The polymer molecule is linked together with each other or other molecules irrespective of to the end functional group in the structure of polymer, they are termed as a cross-linked polymer.

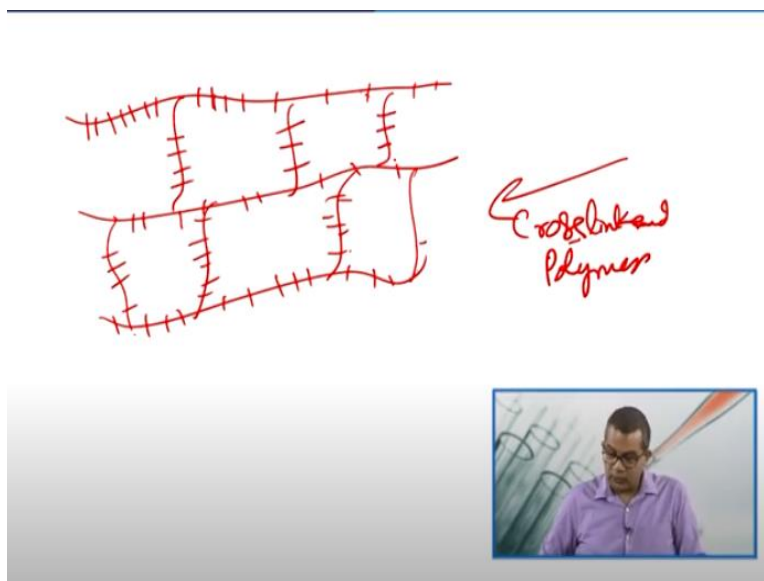
And generally, the trifunctional molecules or monomers are used in the synthesis of a cross-linked polymer. One best part of these cross-linked polymer is that they offer good mechanical strength, because these the polymeric chains are intermingled like this, and they are not only linked with the monomers in a one side, they may link with the couple of other sites too.

So, if you are looking for more and more mechanical strength and more and more you can say the thermal strength, then this particular sub basket offers a wide spectrum, wide opportunity. One best example is that, if you see the polymeric beads, which are used for ion exchange resins in your different type of wastewater applications, you see that these beads are the best example of a class cross-linking polymers.

Now as we go into the detail of this cross-linked polymer, and as I told you that they are linked together with each other to form the different type of things, and as per this particular photograph, you see that they are linked together. To more simplify the

things now to give a brief input or give you a skeleton type of approach for this cross-linked polymer.

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Now you can see that there are different approaches like this. Here you can have this type of thing. Now here this is the different repeating units. I will give you an example of bakelite, so the different monomeric units and they are combined together with the form of this cross-linked polymer. So, these are the small monomeric units or repeating units. So, this is the example of cross-linked polymer.

Now see, when we have this type of structure, it is quite implicated that this particular structure offers more and more mechanical strength, more and more mechanical strength. But simultaneously, when we are knitting together or when we are forming this type of a cross-linking with the help of a different covalent bond, different bonding structure, etc., then they offer some sort of a minimum flexibility.

And that is why if you go to the first slide of this cross-linking approach, then at the time of formation of this cross-linked polymer only then you can form the structure or the application-oriented objects. After curing it is extremely difficult to reorient the object or reorient the product by a simple application of heat or any other process conditions.


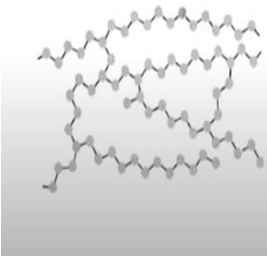
So that is why because of this type of a thing, because of this type of a close bondness, it is extremely difficult to change the structure, change the product

morphology after the curing. And that is why they offer very good approach, but sometimes their recycling is extremely difficult. You just see when you used to discard your used switches then you are not having any option to either recycle or remelt into the different products.

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Classification of Polymers

- **Cross-linked polymers**
 - The crosslinking may vary in the structure to obtain the light crosslinking (such as in rubber light crosslinking provides elastic properties) or highly cross-linked polymers (to provide the high rigidity and structural stability such as in phenol and urea-formaldehyde).



Now they may vary in the structure to obtain the light cross-linking like rubber like cross-linking provides the elastic properties. Best example is your automotive tire or highly cross-linked polymer to provide the high rigidity. Because I told you that sometimes they are just like attached to each other just like this particular approach. So, they offer the high rigidity.

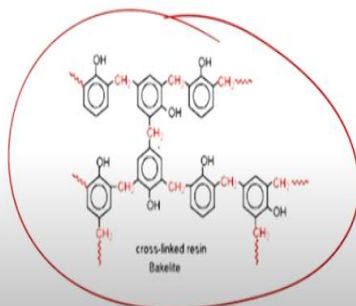
They offer the high structural stability like in phenol or a urea formaldehyde and sometimes you may see that your domestic switches, electrical switches, they are also the best example of your cross-linked polymer. So based on the variety, based on the requirement, you can develop these kinds of cross-linked polymers.

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Classification of Polymers

▪ Cross-linked polymers

e.g. Phenol formaldehyde is a types of thermosetting polymer (or Bakelite used in electric switch board) and urea-formaldehyde etc.



Another example is that your bakelite, which we were discussing about that you see that they are the heavy molecules and they are linked together with the help of this linking. So sometimes phenol formaldehyde, this is again the best type of a thermoset polymer; bakelite, which is sometimes referred as bakelite.

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References

- Joel R. Fried. Polymer Science and Technology,; Prentice-Hall, Inc., (1995), ISBN-81-203-1458-1.
- G. Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 | DOI:10.1002/047147875X.
- J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1.
- Stephen L. Rosen. Fundamental principles of polymeric materials, An SPE textbook, John Wiley & Sons (1937), ISBN:0-471-08704-1.
- V. R. Gowariker, N. V. Viswanathan, J. Sreedhar. Polymer Science, New age international (P) limited, publishers (1986), ISBN-08-522-6307-4.

So based on this particular requirement, either the flexibility or we can say the stiffness or you can see the environmental resistance approach, you can develop these kinds of various polymers and this particular approach that is the classification approach with respect to the linear, branched, and cross-link, they offer a wide spectrum of choices available to you.

Now one major emphasis which I would like to give at the end of this particular chapter is that, that everywhere when we talk about the polymer, nowadays two things should come into our mind. One is that what is the requirement that is based on the couple of things like energy efficient process, eco friendly and above all, it needs to fulfill the requirement of either mankind or industrial application.

Now based on this particular requirement, you can choose the appropriate classification term. And once you choose this appropriate classification stream, then you can choose the appropriate monomer, you can adopt the different polymerization processes etc. Now when we conclude this particular lecture because, if you see that in last two lectures, we discussed the wide spectrum on wide variety of a product profile of these polymeric products.

So, based on the requirement and if you see that they offer the flexibility to the stiffness, they are present in the form of a naturally occurring polymer to the synthetic one based on the other applications, every time people try to develop a new and new polymerization processes and different theories, different modeling streams, etc.

So, in the next lecture, we will discuss a brief history about these polymerization processes so that you can acquainted with that what kind of the things people were looking for in the past. And it gives you an out of a box thinking that how they approached to the desired product. Thank you very much.