

Polymer Reaction Engineering
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Lecture - 28
Step-Growth Polymerization-I

Welcome to the next lecture of polymer reaction engineering. Now, this particular reaction is attributed to the step growth polymerization. Here we will discuss about the step growth polymerization. We will discuss couple of examples with the help of some basic knowledge. We will discuss about the properties attributed to this step growth polymerization.

Then, we will have a discussion about the reactivity of various functional groups those who are involved in this step growth polymerization. So, which let us have a look about that what kind of the topic we have covered previously?

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Topics covered previously

- Problem solving on types of reactors used (batch, plug flow, mixed flow reactor), different order of reactions & types of reaction (series/parallel)



We covered the problem-solving aspects of various types of a reactor, batch reactor, plug flow reactor, mixed flow reactor and discussed about the different order of a reaction and type of a reaction mechanism maybe the series and parallel. In this particular lecture, we will discuss about the step growth polymerization with the help of certain examples related to the commercially important polymers.

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Topics to be covered in this lecture

- Step-growth polymerization
 - ✓ Examples of commercially important polymers
 - ✓ Basic properties of step-growth polymerization process
 - Melt polymerization
 - Solution polymerization
 - Interfacial polymerization
 - Emulsion polymerization
 - Solid-state polymerization
- Reactivity of functional groups



We will have a discussion about the basic properties of a step growth polymerization process under the head of melt polymerization, solution polymerization, interfacial polymerization, emulsion polymerization, solid state polymerization. And lastly, we will discuss about the reactivity approach of those functional groups. Now, let us talk about the step growth polymerization.

Now, step growth polymerization usually is a stepwise reaction between the bifunctional or a multifunctional monomer. Usually, this results in the formation of high molecular weight polymers after extensive number of steps. So, it is just a sequential thing step by step things progresses and it goes into the polymerization process. So, in this case, all molecules are reactive.

Therefore, most monomers they form the short chains of polymers like oligomers. Usually, this starts early in the reaction step, which forms a long chain polymer later in case of if reaction proceeds further. So, the type of polymer they formed depends on the number of functional groups in the monomeric unit. Now, step polymerization or step growth polymerization that involves small by-product molecule formation.

And they are sometimes called as the condensation polymerization. So, unlike addition polymerization, the step growth polymerization involves the elimination of simple molecules such as water, ammonia etcetera. So, once you remove those condensed polymeric products, then it favours this particular act favours the forward direction reaction so that you can improvise the efficiency or a yield of your polymerization reaction.

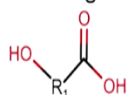
Now, this step growth polymerization is essential for the product production of several important polymers like polyester, polyether, polyamide, polyurethane, etcetera. And there are certain sulphur containing polymers they are also being produced with this step growth polymerization. Now, linear step growth polymerization they fall into various categories and especially we will be talking about the 2 categories. Now, here you see that the AB type of polymerization.

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Step-growth polymerization

➤ Linear step-growth polymerizations falls into two categories.

- AB-type polymerization: Each monomeric unit has two types of functional groups.



- ✓ Each consumed monomer unit corresponds to a repeat unit along the polymer chain, for example, $\text{HO}-(\text{R}-\text{C}-\text{OO}-)_n$



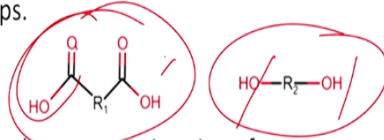
Now, each monomer unit has 2 type of a functional group. Like, if you see in this particular example, we have 2 different functional groups. Now, each consumed monomer unit correspond to a repeat unit along the polymer chain. That is for example, like we are having a HO, RCO and etcetera.

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Step-growth polymerization

- AA and BB-type polymerization: Each bi-functional monomer has similar functional groups.

AA
BB



- ✓ Each repeat unit arises from two monomer molecules. For example, let us consider the esterification of ethylene glycol and terephthalic acid to produce poly(ethylene terephthalate).

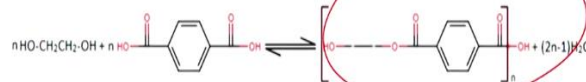


Now, another thing is that AA or BB type of polymerization, each bifunctional monomer they has the similar functional groups. So, you see that here we have similar type of functional groups, whether this one or this one or this one or this one. Now, each repeat unit this arises from the 2-monomer molecule. So, if we take the example, so, we may consider the esterification of ethylene glycol and terephthalic acid to produce the polyethylene terephthalate, PET.

PET is more common it is being all the water bottles they are being produced by either PET or a glass. Now, here you see that each repeat unit in this polymer.

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Step-growth polymerization



✓

- ✓ Each repeat unit of this polymer arises from an ethylene glycol unit and a terephthalic acid unit joined by an ester linkage.
- ✓ Commercially important polymers produced using AA and AB-type polymerization include aliphatic polyamides such as nylon 6,6, which is extremely valuable for producing carpeting and textiles.



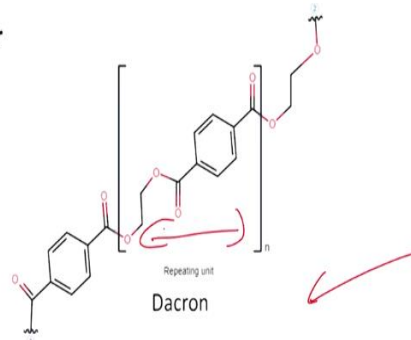
This arises from an ethylene glycol unit and you may see that the terephthalic acid unit they joined by the ester linkage. So, here you see this particular figure. Now, the commercially

important polymers they produced using AA or AB type of a polymerization. They include aliphatic polyamides such as nylon 6, 6, extremely valuable for producing carpeting, textile etcetera.

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commercially important polymers

1. Polyester



- ✓ Dacron is a material used to wrap cushions to create a sharper and fulfilled appearance.

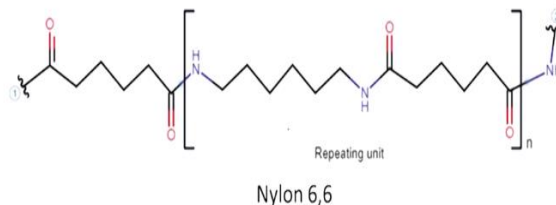


Now, let us have a brief look about the various commercially important or commercially available polymers. One important polymer is the polyester which is being produced to the step growth polymerization and that is one is the Dacron. Now, you here you can see that this is the repeating unit of this Dacron. This is the material used to wrap the cushion or to create a sharper or fulfilled appearance etcetera.

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Examples of commercially important polymers

2. Polyamide



- ✓ Polyamides such as Nylon 6, Kevlar and Nomex are also commercially very important.



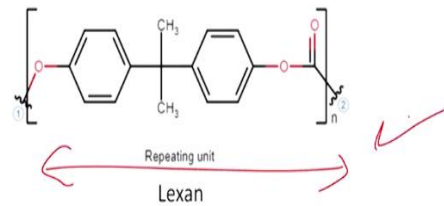
Then, you may see that other examples like polyamide. Now, polyamide is again a very important spun specially it is being used to produce the nylon 6, 6, And nylon 6 is extremely

important. It has a variety of uses right from the tyre to their fabrics, etcetera. Then, Kevlar: Kevlar is again used as a bullet-proofing material for various detonating type of thing. Now, these are commercially available and their importance with respect to the commercialization you cannot overlook.

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Examples of commercially important polymers

3. Polycarbonate



- ✓ Lexan is a trademarked term for polycarbonate sheeting, one of the most widely used plastics in the world.



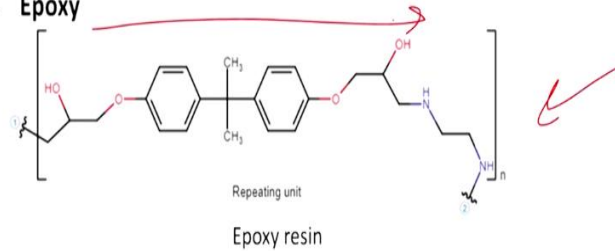
Another is the polycarbonate. Now, here the polycarbonate the important one is the Lexan. Now, you see here the repeating unit it is quite evident. Now, this is the trademark term that is Lexan is a trademark term for the poly or carbonate sheet. And one of the most widely used plastic in the world. You may see the presence of these polycarbonate either with respect to the various indicating lights on automotive sectors.

Day to day affairs like various mechanical utensils etcetera, where we find the use of polycarbonate. Another one is the epoxy. Now this you can see with in this figure.

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Examples of commercially important polymers

4. Epoxy



- ✓ Step-growth polymerization is also used for synthesizing a class of adhesives and amorphous solids called epoxy resins.



The repeating unit is with respect to this one. Now, step growth polymerization usually it is also used for the synthesis of the various class of adhesive and amorphous solid. They are called the epoxy resin. They are find very wide application in the composites as well as the sealing agent too.

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Step-growth vs chain-growth polymerization

Table 1

Step-growth	Chain-growth
All molecules present can react with any other molecule	Monomers react to active site at the end of growing chain
There is no termination step. Oligomers and polymers are reactive throughout the process	Initiation and propagation being two distinctive steps involve termination in most cases
Reactions begins rapidly but high MW's are attained slowly at the end of the process	Reaction speed depends on the concentration of initiator and high MW polymers are formed throughout the reaction



Now, here in this particular table we discussed about the comparative note with respect to the step growth polymerization and a chain growth polymerization. Now, in a step growth polymerization, all molecules they present can react with any other molecule, whereas, in the chain growth polymerization, the monomers they can react to active sites at the end of the growing chain.

So, you can say the step growth deals with the macroscopic approach and the chain growth deals with the microscopic approach. Now in the step growth polymerization there is no termination step. Oligomer and polymers are reactive throughout the process. So, they can achieve to the desired product after some time if they are allowed to proceed further.

Here in the chain growth, initiation propagation being the 2 distinctive steps involved and the termination is again one of the important steps in the chain growth polymerization. Otherwise, the agglomeration and the viscosity of the polymeric product may go on the higher side. And you may face the difficulty in the processability of this polymer being developed in due course of time.

Now, in their step growth polymerization reaction begins rapidly, but, high molecular weight or high molecular weight distribution are attained slowly at the end of the process, because of the consumption of all reactive or molecules or monomers or oligomers. They are on the depletion side. Whereas in the chain growth polymerization the reaction is speed this depends on the concentration of initiator and high molecular weight polymers are thus formed throughout the reaction process.

Now, let us have a brief look about the step growth polymerizations basic property. Now, in the early stage of step growth polymerization process, the polymerization rate increases significantly with the partial modification of the functional group. It is quite evident, because the concentration of the monomer those who are having the reactive sites are available in the (()) (10:30) in abundance. Now, in most of the cases, the groups have been used to produce the high molecular weight polymer chains.

Now, small changes in the conversion or yield thus lead to the high molecular weight distribution at the end stages of polymerization. Because of large number of polymers molecules, they club together and deform the larger chains. So, the higher molecular weight because of the abundance availability of those reactive oligomers they can form the larger chains. So, average molecular weight distribution in the step growth polymerization process is usually limited by the reaction equilibrium.

Sometimes, we may ask the equilibrium functional groups. So, the equilibrium functional group concentration usually they are affected by the concentration of eliminated compound.

As we discussed that there are so many compounds being formed in due course of time. And you need to remove all those things to make the reaction favourable or equilibrium shifting towards the right-hand side direction. So, removing the any kind of a by-product sometimes may be water, sometimes it may be ammonia etcetera.

So, you have to intend to remove all those by-products from the reaction medium, this reduces its concentration. Thereby reducing the rate of the reverse reaction and promoting the use of the functional groups. And thereby you can increase the rate of the polymerization drastically. Now, since the product removal this can limit the growth of polymer chain, the mass transfer is often a key factor in controlling the rate of a step growth polymerization.

So, apart from, because sometimes when you are removing the condensed product in due course of time it poses certain limitation. So, whenever you face such kind of a limitation, then other aspect is to deal such kind of scenario is to you to seek the help of mass transfer. Now, there are several reactors for polycondensation that cater the large surface area to promote the condensation by-product from polymer phase.

In some process very high vacuum sometimes may also be applied to remove all those by-products being generated in due course of time. So, polycondensation sometimes can be carried out with the help of various polymerization techniques like melt polymerization, solution polymerization, interfacial polymerization, emulsion polymerization, solid state polymerization. So, let us have a look about the step things related to the melt polycondensation.

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Melt polycondensation

- ✓ In melt polycondensation, a step-growth reaction occurs in the homogeneous molten polymer at a temperature above the melting point of the polymer.
- ✓ To promote the removal of by-products from polymer melt, vacuum conditions may be applied to remove the volatile by-products, or an inert purge gas can be supplied to the reactor to reduce the partial pressure of side product contacting the polymer phase.



Now, in melt polycondensation, the step growth reaction usually occurs in the homogeneous molten polymer at a temperature above the melting point of the polymer. Now, to promote the removal of by-product from polymer melt, vacuum conditions sometimes may be applied to remove the volatile by-product or an inert purge gas it can be supplied to the reactor.

And sometimes to reduce the partial pressure of site product contacting the polymer phase. Now, the polymer product that is obtained by the melt polymerization, they are generally pure. And sometimes, if you are using any kind of additive or pigments, then they may impart certain changes in the appearance or sometimes they may extend or sometimes they may impart some effect over the life of the polymer.

Now, as sometimes the viscosity play a very vital role. So, as the viscosity of the reaction solution increases, because it is quite evident that whenever the monomer or oligomer, they react together the size of the chain becomes more and more on the higher side. Then subsequently the viscosity of the reaction mass or a reaction solution increases significantly.

So, if we say that this increases with the increase in the conversation, the removal of small by-product molecules from the viscous mass become a process of the rate control. And that is why you may experience the shifting of those equilibrium signals towards the product side. Now high temperatures usually are favoured so as to keep the polymer in a molten state. Because when it becomes more and more viscous in nature, then temperature usually favours this real logical behaviour.

And that is why and it is essential because the polymer mass may have oligomers may have the final chains etcetera. So, to make the polymer mass more reactive, you may you have to incorporate some tools to improvise the temperature and adopt that high temperature zone. Now, let us have a look about the solution polycondensation. The solution polycondensation is employed in various industries to synthesise the polyurethane, polycarbonates and certain sort of polyamides and polyesters.

So, this process mostly used when keeping the reactants within the same phase is usually difficult while using the bulk polymerization or sometimes the melting point of the resulting polymer is just too high. Now, the lower the viscosity enables the efficient heat transfer although sometimes it is not advisable to have this particular approach because of the processability aspect. But, when it enables efficient heat transfer in solution polycondensation, if we compare with the melt polymerization.

So, if you are adopting for the case sensitive or speciality polymer, then you are having another option that the solution polycondensation offers the lower viscosity concept. Now, when the polymer separation from the solution is intended the recovery of solvent and a polymer washing and drying they are sometimes most evident to in the solution polycondensation. Now, let us discuss about the interfacial polycondensation.

Now, in interfacial polycondensation the formation of polymer takes place at the interface of 2 immiscible liquid. Therefore, the starting reactants are usually dissolved separately. So, you may have 2 phases and the reactant may dissolve in any of the phases. Now, the interfacial reaction, they are diffusion limited. And sometimes the system is typically stirred to ensure better contact of 2 liquids.

Whenever we talk about this processability of these polymers, there are slight difficulty because you need to handle these 2 immiscible liquids. So, the polymer whatever they formed in the interface, they are usually filtered, washed and dried. So, they are very useful this particular process is extremely useful for the speciality polymers like polyamides, polyurethane, polyesters, polysulfonamides, polyformaldehyde.

They are can be prepared using this interfacial polymer condensation. Now, since these polymers they are having very wide spectrum. So, in case if any special uses of these polymers

are attributed then we can use these interfacial polycondensation phenomena. So, usually in this case the material applied need not to be the utmost purity. And the polycondensation takes place rapidly at a low temperature and atmospheric pressure.

Now, interfacial polycondensation is usually utilised for making reverse osmosis membrane because here you are having very limited thickness. And you require very limited thickness and some sort of the semi permeability aspect or porosity is the prerequisite for these kinds of uses. And for this the encapsulation of inks and insecticides and medicines etcetera, they are the foremost user of these kind of membranes.

Now, let us have a look about the emulsion polymerization. Now, this polymer formation reaction occurs in the bulk of one of the liquid phases, reversible, exothermic polycondensation. These are the involved steps in the formation of site product. And whatever being site product being generated utilise this polycondensation technique. They are highly reactive monomers.

They are the most suitable for the emulsion polycondensation. Number of ester growth polymers prepared using the emulsion polymerization method is small and this technique require further developments. Now, let us have a look about the solid state polycondensation. This also known as the solid phase polycondensation. This is used as a final stage of industrial processes.

This produces high molecular weight distributive polymers. Molecular weight distribution plays a very vital role in deciding the properties of the polymer. And the pallets in the solid-state reactors, they are usually held at a temperature above the glass transition temperature. And, but below the melting point of the polymer that makes the functional group mobile to react because initially they may have an entangled position.

And when you supply the little quantum of heat, all the polymer chains they are trying they used to try to unentangle themselves to align in a regular array. And that is why this is the beauty of this particular solid state polycondensation process. Now, here the by-products are removed from the pallet through the high vacuum or with an inert gas system. Now, this process involves the low temperature that is an advantageous for the production of polymers that are prone to undesired thermal degradation reaction.

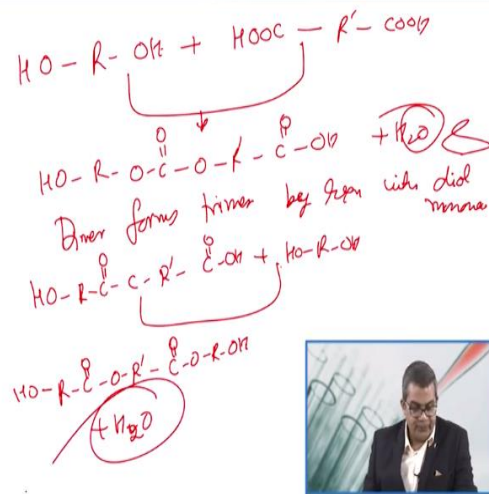
Now, because let us have a small thought over this particular concept. Because this low temperature phenomena also offers the economic feasibility of the polymerization process as well as when we go for the higher temperature zone then there may be a chance that whatever polymer or other products or side products being formed in due course of time, they may get dissociated over the period of time and may impart the several impurities in the final outcome of the product stream.

So, the lower rate of polymerization in terms increases the residence time of reactant in solid state polymerization system. Now, let us have a brief look about the reactivity of the functional group. Now, there are several aspects which we need to look into in this particular approach. One is that basis of analysis of a polymerization kinetics. The kinetics of reaction are of interest from practical and a theoretical viewpoint.

Now, practical synthesis of high molecular weight polymers sometimes requires the understanding of kinetics of polymerization reaction. The difference between a step and a chain polymerization resides in their respective kinetic features if we look at the form of the theoretical perspective. Now, there is relatively slow increase in molecular weight of the polymer in this step growth polymerization.

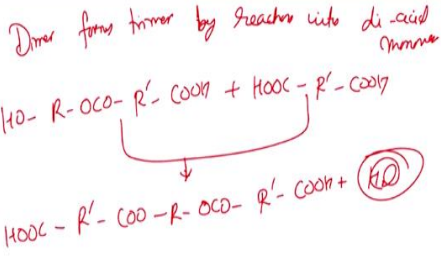
That is quite evident, because the number of reactive sites tend to align in a different fashion. Now, let us consider the synthesis of a polyester from a diol or diacid. The reaction of a diol and a diacid monomer they form a dimer.

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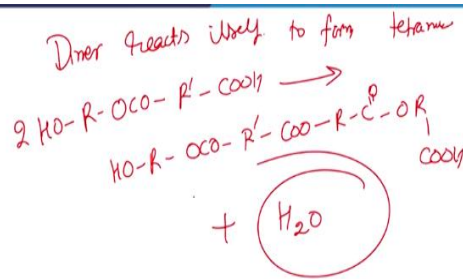
Now, here you see that this is my diol and this is reacted with the diacid. Now, you may have this HO R O C double bond O + HO. This is H₂O. This is the condensation product. Now, dimer forms trimer by reaction with diol all monomer. So, in that case this double bond O this may give you OH plus H₂O. This is again the condensation product.

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Now, dimer this dimer forms trimer by reaction with diacid monomer that is HO R OCO R dash COOH plus HOOC. HOOC R dash COO R dash COOH plus H₂O. Now, this is again my condensation product. And sometimes this dimer reacts itself to form tetramer.

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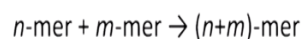


Now, this is HO R OCO R dash COOH. This can react and this gives you HO R OCO R dash plus H₂O. This is the condensation product.

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Reactivity of functional groups

- The tetramer and trimer then react with themselves, each other and other molecules.
- Hence, polymerization proceeds in a step-wise fashion with MW of polymer increasing with time.
- Monomers in the reaction disappear far before the formation of any significant high MW polymer.
- The rate of a step polymerization process is therefore the sum of all the rate of reactions of molecules of various sizes. General reaction equation being:



Now, the tetramer and trimer when they react themselves, they form other molecules. So, therefore, we can say the polymerization proceeds in stepwise fashion with molecular weight of polymer increasing with the time. Now, monomers in the reaction sometimes they disappear far below the formation of any significant higher molecular weight polymer. So, the rate of step polymerization process is therefore, the sum of all the rate of a reaction of molecule in different stages. So, you can say the general equation can be given like this n 'mer' plus m 'mer' that is n plus m monomer.

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Reactivity of functional groups

- At any time during the reaction any HO- containing molecule may react with any COOH- containing molecule. This is general characteristic of step polymerization.
- It is difficult to analyze kinetics of such innumerable no. of reactions. However, it can be simplified using certain assumptions.
 1. Reactivities of both functional groups of a bi-functional monomer (e.g., both hydroxyls of a diol) are the same.



So, at any time during the reaction at any HO containing molecule may react with any COH containing molecule. Now, this is the general characteristics of step polymerization. Now, it is usually sometimes people will find it difficult to analyse the kinetics of such things, number of reactions. Now, it can be simplified using various assumptions. However, when we take these assumptions, one prerequisite at that, that when we design those reactors for different aspect, then we try to nullify those assumptions.

So, the assumptions are the reactivities of both functional group of bifunctional monomers that is the both hydroxyl of a diol. They are the same. Second is that the reactivity of one functional group of bifunctional molecules is same irrespective of whether the other functional group reacts or not. And the third is that the reactivity of functional group is independent of the size of a molecule to which it is attached. That is sometimes independent of the values of n or m.

Now, this particular assumption concept is termed as equal reactivity concept of functional groups. Now, when we talk about the experimental evidence sometimes whatever you generated theoretically sometimes you need to validate the things with respect to the experiment so that you can simplify the things with respect to the reactor design. Now, the reaction rate constant of several polymerizations are seen to be independent of a reaction time or polymer molecular weight distribution.

Therefore, you may justify the things with the assumptions whatever your assumptions you have taken in due course of time. Now, studies of a reaction of a certain non-polymeric molecule they come in handy, sometimes you may take the reference of all those things, all

those data whatever being presented with respect to the non-polymeric material, they are quite useful for the discussion of polymerization kinetics.

Now, for example, we can take the help of esterification of a series of homologous carboxylic acid. Now, here you see that various reactivities we have presented.

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Reactivity of functional groups

Table 2

Molecular size (x)	$K \times 10^4$ for $H(CH_2)_xCO_2H$	$K \times 10^4$ for $(CH_2)_x(CO_2H)_2$
1	22.1	-
2	15.3	06.0
3	07.5	08.7
15	07.7	-
17	07.7	-

- Rate constants are in units of $L \text{ mol}^{-1} \text{ s}^{-1}$
- Data from Bhide and Sudborough [1925]

✓ We can see that, although there is a decrease in reactivity with increase in molecular size, the effect is significant only at a very small size.



Like molecular size with respect to x 1, 2, 3, 4, 5 up to 17 and respective rate constant for carboxylic group. Now, here you see that there is a decrease in the reactivity. If you see if you go downside of this table, we see that there is a decrease in the reactivity with increase in the molecular size, this effect the significant only at a very small size. So, you see that what we are discussing previously it is in the closed agreement of these experimental data.

Now, the reaction rate constants they can they are very quick and they can quickly reach its limiting value and remain constant and sometimes independent of molecular size. Now, this particular approach can be vetted through the polyesterification of sebacoyl chloride with alkyne diols with this reference. Now, the thought of that the reactivity decreases with increase in the molecular weight is just a misconception.

Because people thought that okay in one fine morning, you find this particular result. But sometimes it is not at all feasible for the design of any reactor. That is why they thought it and the difficult solubility of high molecular weight polymer molecules in homogeneous series is a pitfall. That needs to be avoided. So, based on this particular approach you people give the various theoretical considerations.

And these theoretical considerations suggest that observed reactivity of a functional group. This it usually depends on the collision frequency of the group and not the diffusion rate of the entire molecule. However, this particular approach is partially correct for the interfacial phenomena. Now, number of collision one functional group makes with other per unit in time its collision frequency.

Terminal functional group may be attached to a growing polymer are which is having the appreciable mobility. Now, sometimes this is attributed to the conformational rearrangement nearby segments of the polymer chain. The collision rate of such functional group with neighbouring group will be similar to a small molecule. And lower diffusion rate arises when any 2 functional group undergo more total collision before they are diffusing apart.

Therefore, for a given time interval, larger molecule sometimes undergo less collision with the different partners and compared to the functional group attached to the small molecules. So, overall collision frequencies are same for all both the cases. And if you take the reaction between the 2 functional group in a step polymerization, it can occur only about, once in every 10 to the power 13 collisions.

And this was determined by P J Flory in way back 1953. And he is termed to the father of chemical reaction engineering. Now, during the time interval required for this many collisions, sufficient diffusion of the molecules may take place and a functional group occurs that maintains the equilibrium concentration of collision pair of the functional group.

So, the net result when we talk about the net result. The net result of this consideration is the reactivity of a functional group will be independent of the size of the molecule to which it is attached. Now, at last, when we talk about this, we can say that an exception to this may arise when reactivity of the group they are very high or the molecular weight of polymer are very high, because that is make them polymer chain very bulky in nature.

So, the polymerization then become the diffusion controlled, because mobility is too low to allow the maintenance of the equilibrium concentration of reactive pairs and their collision frequency. Now, at last, we can discuss about the equivalency aspect of the groups in

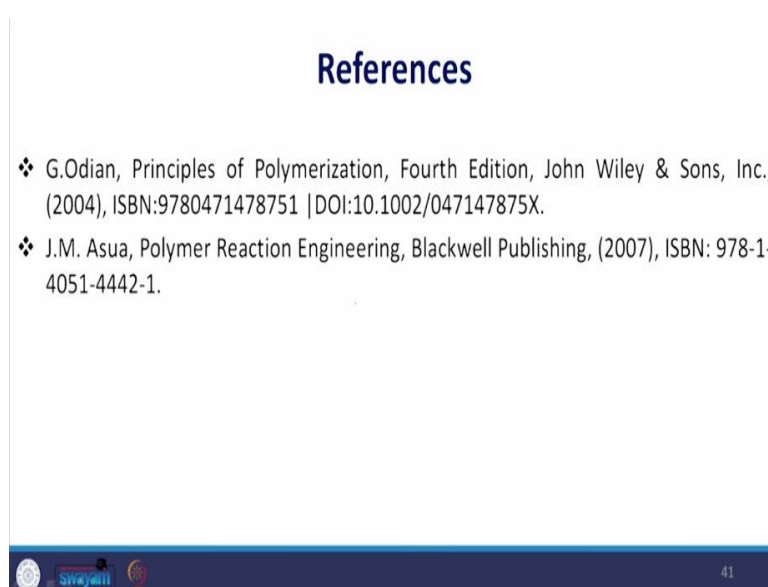
bifunctional reactants. Now, equivalency aspect of the group is again equal importance, when we talk about the reactivity of functional groups.

So, the rate constant for the 2 carboxylic group, they were the same and the reactivity of a one functional group usually is not dependent on whether the other has reacted or not. So, still to consider the reactivity of a functional group is not affected by the presence of a second group that would be false. So, according to the data that is usually affect the presence of second group maybe up to say x is equal to 4 or 5.

So, the difference in the reactivities of the functional group of a bifunctional reagent that may compare to the functional group in mono functional reagent is not an important consideration in handling any kind of kinetics of step growth polymerization. The only significant consideration they are that the reactivity of a functional group of a bifunctional monomer remains unaltered, unchanged by the reaction to another group.

And the reactivities of the 2 functional group they are the same throughout the polymerization process.

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So, in this particular chapter or lecture, we discussed the different aspect of this step growth polymerization. We presented the comparative note of this step growth polymerization with respect to the chain growth polymerization, discussed the efficacy of this step growth polymerization with respect to the certain parameters. In case if you wish to have further

studies, then we have listed couple of references for your convenience and for your further research if you wish. Thank you very much.