Polymeric Materials of Different Kind
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Lecture - 27
Copolymers 2

So, in this week we continue looking again polymer systems of different kinds. And we started looking at copolymers first, we saw in the last lecture, how different copolymers can be used in various applications. And in this case, we will look at some of the properties of these copolymers.

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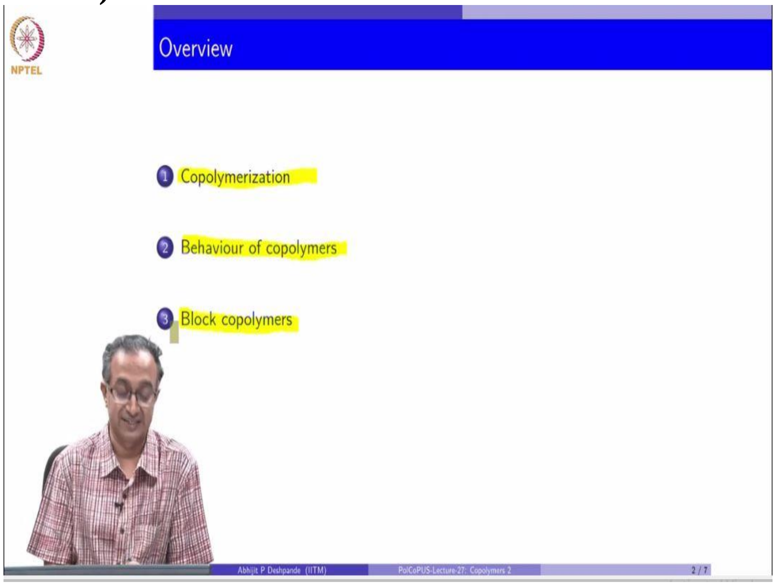

Overview

1. Copolymerization
2. Behaviour of copolymers
3. Block copolymers

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And we will do this by first looking at quickly, how do we exploit and understand the reactions of 2 monomers and achieve a type of copolymer that we want, whether it is a block copolymer, or a random copolymer, and so on. And then we will look at the behavior of copolymers. And more specifically, we will look at 1 example of a block copolymer, which has very interesting behavior, like we saw in case of silicon polyether in the last lecture on 26th lecture.

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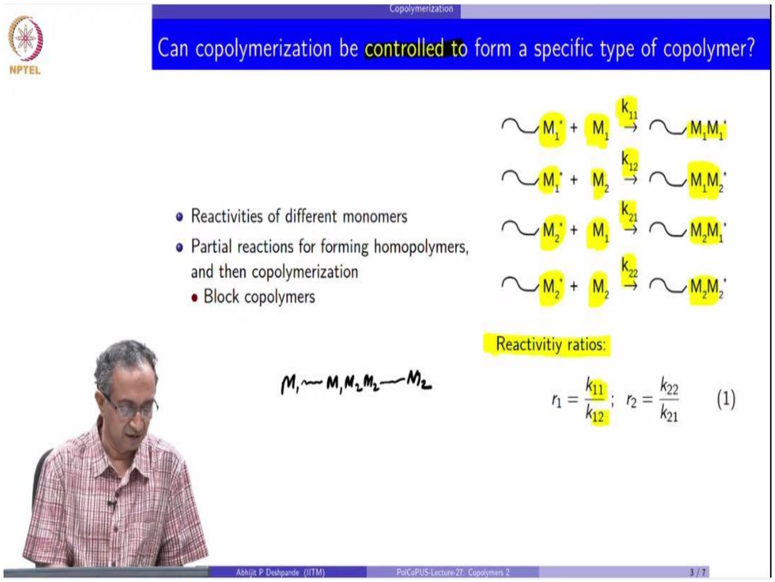

Copolymerization

Can copolymerization be controlled to form a specific type of copolymer?

- Reactivities of different monomers
- Partial reactions for forming homopolymers, and then copolymerization
  - Block copolymers

$M_1 \sim M_1 M_2 M_2 \sim M_2$

$\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1 M_1^*$

$\sim M_1^* + M_2 \xrightarrow{k_{12}} \sim M_1 M_2^*$

$\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_2 M_1^*$

$\sim M_2^* + M_2 \xrightarrow{k_{22}} \sim M_2 M_2^*$

Reactivitiy ratios:

$$r_1 = \frac{k_{11}}{k_{12}}; \quad r_2 = \frac{k_{22}}{k_{21}} \qquad (1)$$

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So, copolymerization is a technique to make sure that we achieve a target sequence that is desired for a given application. So, the question of course, is how well can we control it, and what I have shown here is, let us say reaction between 2 different monomers M_1 and M_2. So, the active species of a chain which has M_1 as the active species can react with M_1 itself to give you M_1 M_1. So, this is one possibility of course, M_1 can also react with M_2 and get you an M_1 M_2 bond.

Similarly, M_2 itself can also react either with M_1 or M_2 to give us M_2 M_2 or M_2 M_1. So, these are the 4 possibilities, when we think of reaction between M_1 and M_2 M_1 can react with M_1 itself or M_1 reacts with M_2 and similarly for M_2. Now, the question is, can we control this polymerization, so, that we obtain, let us say a random copolymer, in which case M_1 M_2 are randomly distributed, or we obtain a block copolymer, in which case M_1 should react with M_1.

So, that we get M_1 M_1 M_1 M_1 and then eventually because of statistical distribution, 1 M_2 will react, but as soon as M_2 M_1 M_2 bond is form. Now, we would like M_2 react with itself, so that, if we do a reaction like this, then in that case, we will get M_1 M_1 M_1. And then after that M_2 reacts, and then M_2 reacts with M_2 again and then we get a block of M_2. So, this is the way we can look at control of polymerization. And the way we think about it quantitatively is look at these rate constants, which are present for each of these reactions.

And we look at their ratios. So, for example, reaction rate for M_1 to M_1 reaction to reaction rate to M_1 to M_2 reaction. And by looking at these reactivity ratios, we can find out whether 1 would like to react with 1 or 1 would like to react with 2 what are the different rates of reactions.

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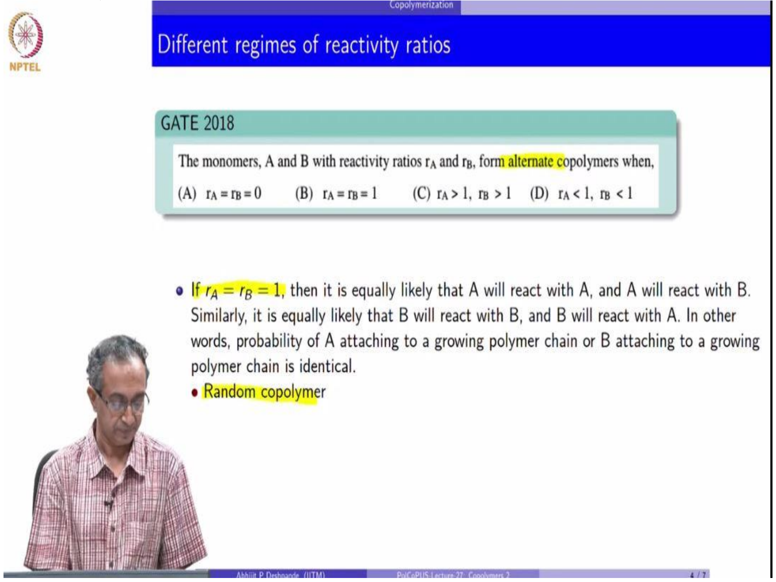

Copolymerization

Different regimes of reactivity ratios

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The monomers, A and B with reactivity ratios r_A and r_B, form alternate copolymers when,

(A) $r_A = r_B = 0$ (B) $r_A = r_B = 1$ (C) $r_A > 1$, $r_B > 1$ (D) $r_A < 1$, $r_B < 1$

- If $r_A = r_B = 1$, then it is equally likely that A will react with A, and A will react with B. Similarly, it is equally likely that B will react with B, and B will react with A. In other words, probability of A attaching to a growing polymer chain or B attaching to a growing polymer chain is identical.
  - Random copolymer

And this is one common way of quantifying the copolymerization tendencies. And so, in this exam question, for example, 2 monomers which have reactivity ratios of r A and r B, as we just defined, when do they form alternate copolymer, which means it is A B, A, B, A, B, kind of a polymer. And so, there are various options depending on the k A A or k A B rate reactions that we talked about all these. So basically, it is an issue related to how are these rate constant?

And their ratios are, of course r A and r B. So you can think about answer to this. I will just give you a hint related to the answer, which is not there, which is let us say r A = r B = 1 in which case all the rate constants are equivalent. So, the rate for A reacting to A is equivalent to A reacting to B and B reacting to A and B reacting to B. So, therefore, if such a possibility is there, then basically any species can react with any other species and in the end, we will get a random copolymer, but in this question, the target is alternate copolymer. So, what should the reactive ratios be?

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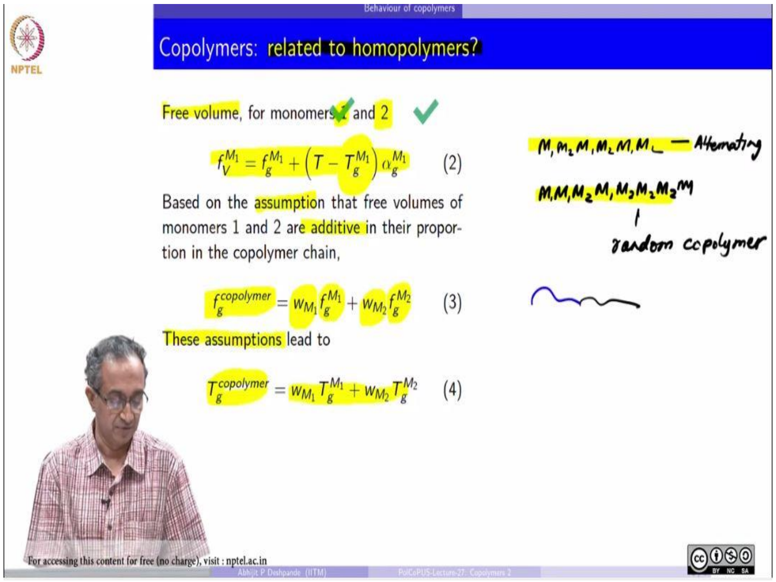

Behaviour of copolymers

Copolymers: related to homopolymers?

Free volume, for monomers 1 and 2 ✓

$$f_V^{M_1} = f_g^{M_1} + \left(T - T_g^{M_1}\right) \alpha_g^{M_1} \quad (2)$$

Based on the assumption that free volumes of monomers 1 and 2 are additive in their proportion in the copolymer chain,

$$f_g^{copolymer} = w_{M_1} f_g^{M_1} + w_{M_2} f_g^{M_2} \quad (3)$$

These assumptions lead to

$$T_g^{copolymer} = w_{M_1} T_g^{M_1} + w_{M_2} T_g^{M_2} \quad (4)$$

$M_1 M_2 M_1 M_2 M_1 M_2$ — Alternating

$M_1 M_1 M_2 M_1 M_2 M_2 M_2 M_1$

random copolymer

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So, in terms of properties, when we look at copolymers, r properties related to the homopolymers that are found and in lot of cases, there are thumb rules and rules based on theories which we have arrived at. And so therefore, we can understand the copolymer properties based on what are the homopolymer properties. And the key determinant of course, is also the type of sequence which is there. And so far, alternating copolymers and random copolymers these mixing rules work very well.

Because you will have basically a distribution where you have M_1 and M_2 are systematically this is a case of alternating copolymer or even if we have random copolymer, since, we have them randomly distributed, we can again have, so, this is a random copolymer. So, properties of these kinds of copolymers are easy to determine based on our knowledge of the homopolymers and here one example is given for a glass transition temperature.

Because if the question is; if we know the copolymer glass transition temperature, can I find out the copolymer glass transition temperature? Now, before I give you this example, you can think of why is it that I have not included block systems in this. So, if I have let us say a block of M_1, connected to block of M_2, why is it more difficult to predict the property of copolymer based on the knowledge of homopolymers. And next slide when we discuss an example of block copolymer, hopefully, the answer will be a little more evident.

So, let us continue looking at glass transition temperature of a copolymer. We have already seen in the lectures related to glass transition the 22nd 23rd lecture that we have free volume theory which can be used to describe class transition, and we know that this free volume is known for let us say the homopolymer 1 and 2 and here what is shown is free volume for homopolymer 1 and so, it depends of course, on the glass transition of polymer 1 and so, similarly, there can be an expression for the free volume of homopolymer 2.

So, now, we have these 2 monomers combined together either in a random or alternating fashion. And so, if we make an assumption that whatever is the free volume of 1 and whatever is the free volume of 2, they combine each other in an additive fashion. So, that in the final copolymer, the free volume of 1 weighted by whatever is the weight fraction of that homopolymer and similarly, free volume of homopolymer 2 weighted with whatever is its weight fraction.

So, if we do this and if you go back and look at the free volume and how we derive the WlF equation and overall dependency of properties around glass transition, these assumptions can immediately lead to the copolymer being a simple mixing rule. So, it is the copolymer will be closer to the polymer which is in larger amount and this is just a linear relationship between the homopolymer glass transition temperature and the copolymer glass transition temperature.

So, using mixing rule like this, we can actually estimate the properties of copolymers and also understand the properties and this is also useful in terms of targeting. So, if I have let us say 2 homopolymers with glass transition temperature of - 80 and - 10 and it is my target to achieve a glass transition temperature of - 40 degrees using such thumb rules, I know what kind of relative ratios to suite for in terms of synthesis.

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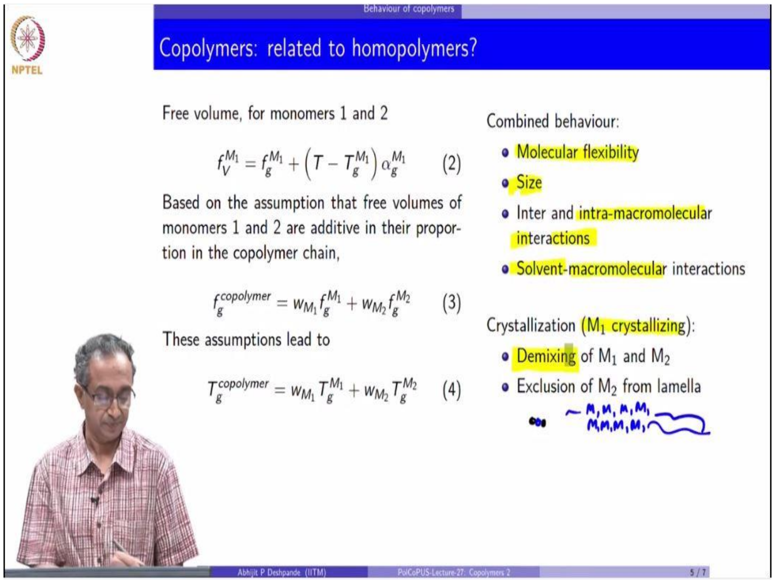

Copolymers: related to homopolymers?

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These assumptions lead to

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Combined behaviour:

- Molecular flexibility
- Size
- Inter and intra-macromolecular interactions
- Solvent-macromolecular interactions

Crystallization (M_1 crystallizing):

- Demixing of M_1 and M_2
- Exclusion of M_2 from lamella

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So, generally this combined behavior for such polymers can be obtained by knowledge of homopolymers. So, if molecular flexibility also can basically be a combination of the flexibility of the 2 repeating units. Similarly, the size in terms of the radius of gyration or end to end distance key of course, is also the inter molecular or intramolecular interactions. So, depending on the hydrophobicity hydrophilicity or hydrogen bonding potential or electrostatic interactions or any of the interactions that we discussed in the 20th lecture.

If we have differences in the 2 monomer units are the 2 repeating units, those can also get basically combined effectively to get us an effective property for the copolymer. Same is the case also how solvent interact with the macromolecule. In case of crystallization, there is interesting possibilities and let us say that we have M1 and M 2 the 2 homopolymers and we are combining them and let us say M1 is crystallizing. If we have a random copolymer then of course, clearly we will not be able to crystallize.

Because it is essentially if I just draw it using if we have some polymer like this, then there is no way we can have M_1 organizing with respect to each other because M_2 will always come in between, but if we have certain it is a random copolymer and there are a few places where there is M_1 combining with M_1 and there is another macromolecule or another part of macromolecule and again M_1 is combining with M_1, then there is a possibility that there can be organization of these M_1 chains.

So, effectively if we have a copolymer of M_1 and M_2, while it is being cooled from the melt state, what needs to happen is the mixing first part of M_1 and M_2 need to separate out from each other and then M_1 can have a chance of the formation of lamella and crystallization. So, the impact of copolymerization non crystal N T is quite complex and it depends on specific systems.

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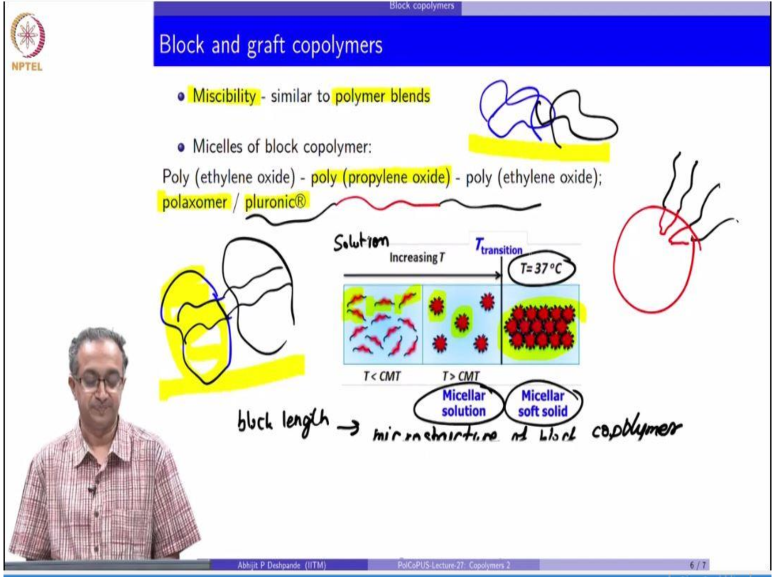

Block copolymers

Block and graft copolymers

- Miscibility - similar to polymer blends
- Micelles of block copolymer:

Poly (ethylene oxide) - poly (propylene oxide) - poly (ethylene oxide);
polaxomer / pluronic®

So, let us finish this lecture by looking at an example of block copolymer block and graft copolymers are quite commonly used in several biomedical applications. And the idea here is again exploiting the properties of block themselves and these 2 blocks have a contrasting set of properties. So, in this case, we will also see when we discuss polymer blends, the miscibility is similar the way we think of whether 1 block is mixing with other blocks or do the 2 blocks face separate out will depend on when we mix the 2 polymers in the form of polymer blend.

So, let us say if we have 1 polymer and another polymer mixing with each other, there is a possibility that all the blue macromolecules would like to be together and all the black molecule macromolecules would like to be together then we call it an immiscible blend. So, similarly, in case of block copolymers also, if we have a block of these homopolymers attached to each other, then what we can have is all the similar interaction blocks will come together.

And in the end what we get is a domain of one type of blocks in combination with another type of block the only difference between the blend situation and the copolymer situation is the fact that the blocks are combined using a covalent bond with respect to each other. So, clearly the domains that are formed in this case depend on these block length. So, therefore, block length is a very key determinant of the microstructure of block copolymers and this is the tunability that is being exploited.

When I said that block and graft copolymers are very commonly being researched as well as used for variety of these applications. By changing the block length, you can change that properties very suitably and therefore, obtain different types of performance. I will just leave you with 1 example of biomedical applications of a set of polymers which are called polaxomer or they also are available as a registered trade name with pluronic and they are blocks of polypropylene oxide in the center.

So, we have polypropylene oxide block in the center and then the blocks of polyethylene oxide on the 2 end and which is what is depicted here where there are basically blocks of red blocks surrounded by 2 black blocks. And this kind of a material system has very interesting properties, because at lower temperatures, basically all these blocks are randomly oriented and therefore, the system is molecularly mixed and it is a solution.

Once we increase the temperature, what happens is all the red blocks get together. So, polypropylene oxide blocks get together. So, what we have is basically the blocks arranged themselves so, that polyethylene which is more hydrophilic starts interacting with water more strongly and polypropylene which does not like water as much would want to cluster together with each other. So, therefore, we get what is called a micell very similar to surface active agents surfactants giving us micell and more interestingly, if we increase the temperature further.

Then many of these micellar systems form assembly where you get a gel like response. So, because of this interaction between the blocks and the surrounding solvent water in this case, we can have a solution or we can have a micellar solution, or we can have a gel, micellar soft solid. So you can see how copolymers in this case, can give you very different properties. If we just change the temperature and look at the temperature here 37 degrees Celsius.

I do not know if anything strikes you in terms of temperature of 37 degrees and biomedical applications. So if you just remember, our body temperature is just above this kind of temperature. So if we tune this transition point very well, what we can do is one state when it is stored under refrigerated condition, because then the temperature will be much less and as soon as it reaches our body it reaches another condition.

So, therefore, these kinds of block copolymer systems can become gel when they are injected in the body at 38 degrees Celsius, but they will remain in perfect liquid like so, therefore, you can inject them easily. So, you can see these are examples of smart polymeric systems. And in this case, the smartness is achieved because of interactions of 2 different blocks. And clearly if we vary the lengths of these blocks, we can vary the micell size we can vary how the gel is obtained, what is the temperature at which the gel is obtained.

And so, this is the strength of polymeric materials of different kind, where by tuning, physico chemical details at the macro molecular level, we can achieve performance at the bulk scale.

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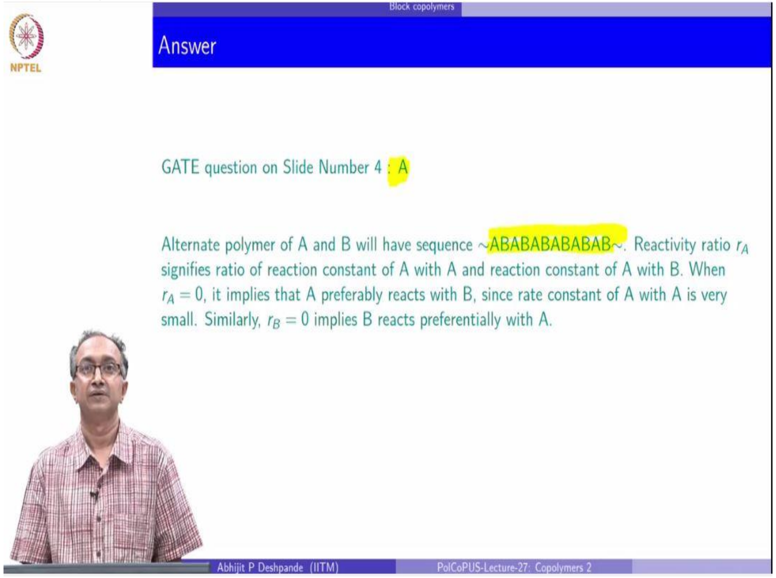

Answer

GATE question on Slide Number 4 : A

Alternate polymer of A and B will have sequence ~ABABABABABAB~. Reactivity ratio r_A signifies ratio of reaction constant of A with A and reaction constant of A with B. When $r_A = 0$, it implies that A preferably reacts with B, since rate constant of A with A is very small. Similarly, $r_B = 0$ implies B reacts preferentially with A.

So with this, we will close this lecture looking at the answer related to copolymerization. I am sure you have been able to see that if we really have to get an E B A B, which is the alternating copolymer, then the rate of reaction of A to A needs to be much less compared to the rate of reaction of A to B similarly, the rate of reaction of B to A needs to be much more than reaction of B to B. So therefore, then B A bond will preferentially form and A B bond will preferentially form and then of course, that will imply that we will get there and the alternating copolymer. Thank you.