Principles of Polymer Synthesis

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Lecture – 20
Principles of Living Chain Polymerization

Welcome back, to this course on principles of polymer synthesis, until last class we have been discussing about chain growth polymerizations and then afterwards we talked about chain growth polymerization in presence of another monomer. So; that means, copolymerization and we discussed in some detail about different aspects of these copolymerization processes.

And the last class exclusively dealt with the microstructure of copolymerization, where in we found out the details about, how we can determine the number fraction distribution of different lengths of the sequences of different monomers and then that gives us a complete picture of, how the copolymers can be produced at least the copolymers, where we have 2 monomers present.

So, the topic of today is living chain polymerization. So, basically although I am talking about living same polymerization, the chain polymerization could be radical polymerization, it could be anionic polymerization, it could be a cationic polymerization, you might have noticed that we have not talked about anionic or cationic polymerization at all, until now and it will remain. So, until probably we come to certain industrial polymers, where in we might feel important that some of these things need to be discussed.

So, until then that discussion will remain suspended. So, we are talking about living chain polymerization, but in general, but more specifically, we will talk about living radical polymerization that would mean, what about these term living means, it could be applied to say anionic polymerization also so living means something is not dead.

So, if you look at the situation of say a radical polymerization, you have all these radical species which are intermediates, which are actually attaching. So, let us say you have a M1 dot it your starting radical it is attaching with your monomer. So, it is becoming M2 dot 2 units together, then it is attaching with another monomer it is becoming M3 dot so on and so forth.

So, all these radical species that are present of course, they are presenting very low concentration. I have told you, if you remember at the start of this radical polymerization introduction weeks back, that this particular point that our radicals a transient species the lifetime is very, very small in order of seconds or sometimes maybe lower and the concentration is also very small, and why they are transient because, they are not very you know stable and they will react in whichever way they can I mean, they can react with the monomer to grow the polymer chain to higher length or they could react with another radical and then annihilate themselves.

Take the situation of say biomolecular termination sort of chain breaking reaction 2 radicals come together, and then they could terminate the radical species by disproportionation or by coupling, or what you can have is a species that is there in the system which could be your monomer, which could be your solvent, which could be well a compound that you have added from outside, or which could be your initiator itself, to which a growing radical could transfer it is radical and become it chain, they had chain no reactive ends that is, where the polymerization stops for that particular chain and then another chain could be initiated because, the radical has been transferred to the species which is your chain transfer reaction.

So, all these reactions your biomolecular termination like, your coupling termination through coupling, or termination through disproportionation, or termination through chain transfer reactions all of these are chain breaking reactions; that means, that breaks this growth of the chain that is the terminology used here. So, if all of these reactions are occurring, then that limits technologically the application of our polymers in which way, if you could so suppose you have a long chain that has been produced.

Now, at the end of this long chain you have a radical center, if you could somehow stabilize this radical center now you can add another monomer, and then you could have another block of polymer. So, the initial block was for monomer 1. Now monomer 1 is consumed at the end that species is, now somehow stabilized could be radical, could be anion and now, we are putting another monomer then again the polymerization could grow; that means, you have a block of monomer 1, then you have a block of monomer 2, let us say you are getting a block copolymer. If you notice we did not talk about block copolymerization, in your copolymerization principles because, there is a special case where r1 and r2 both are greater than 1, we would not talk about that in terms of that analysis that we had done in the previous class, but we will talk about it in some aspect.

So, if you can create this kind of situation, when you stabilize this reactive center at the end of a growing chain, then you could have specific compositions of the polymer. For example, a length say 1000 units of monomer a and then you want to put say 5100 units of monomer 2 now these say the monomer 2 that you are putting. So, this creates a monomer 2 say a polymer2 block, and then you have a polymer1 block so you have 2 blocks that are stitched together. So, this is a block copolymer.

What is the importance of block copolymer, takes the example of say polystyrene, we had discussed this example a little bit in some other context, but we bring back this example again. Let us take the example of polystyrene, the production is quite high and this property of the polystyrene if you are looking at polystyrene the homopolymer overall the styrene contribution to the industry is quite high, but the homopolymer contribution is respect to that lower, I think one third or something like that, what is the rest you have copolymers block copolymers say.

So, you can have styrene, butadiene, acrylonitrile copolymer. So, you have all the 3 things together styrene, butadiene, acrylonitrile. So, styrene by itself, when you polymerize it is a brittle material, it is it does not have that much of solvent resistance and it does not have impact resistance, which associates itself with toughness.

Now, if you are adding the other block which has a desirable property, that property that does polystyrene lacks. So, you put another block here say you put acrylonitrile unit also together, then what happens this acrylonitrile unit that you have is making this particular copolymer having better property; that means, it is solvent resistance increases it is impact resistance also increases, and then if you are putting say butadiene unit also, it could have elastromanic property stretch ability.

So, all these things can come together we will go to specific examples. So, we need then to go into controlled way up synthesis of these polymers. So, that you can have a composition that you want, and not only that we want to have also a very narrow molecular we distribution. So, that all the chains are almost similar length, it cannot be exactly 1 as far as the pdi is concerned polydispercity index is concerned, but it could be close to one.

Now, if you are looking at say anionic polymerization although, we would not go into details some of them are generally living in nature, when you say living basically you are trying to increase the lifetime of that reactive center. So, that it does not get destroyed that quickly so that you can use it for a subsequent purpose. So, some of these say anionic polymerizations and other polymerization, this could be also converted to say living polymerization, but if you are looking at say radical polymerization, if you can convert it to living polymerization that is very important for you.

Why? Because, as I had told at the start of radical polymerization introduction, that the selectivity is different certain monomers will not undergo anionic polymerization, certain monomers will not undergo cationic polymerization, depending on the group that you have that will stabilized cationic, stabilize anionic it will either undergo cationic polymerization or undergo anionic polymerization, but most of these monomers will undergo radical polymerization anyway because, radicals do not have the kind of selectivity they can be stabilized by both electron donating as well as electron withdrawing group.

So, if you can introduce this kind of living nature to radical polymerization that becomes, technologically much more important. So, after all these lengthy discussion let us now go and start talking about certain substance.

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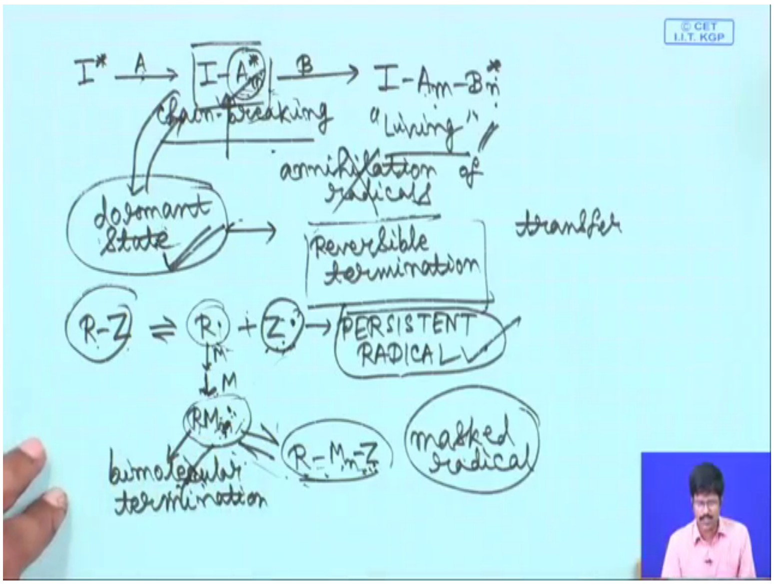

Now, so you have say I star which is your initiator and A is your monomer, and then let us say m number of a units have come. Now somehow, if you can stop all the chain breaking reactions, that could eat away this reactive center we are going to talk about say radical so you have a radical say you want to stabilize this.

So, you stop all the chain breaking you reactions say biomolecular terminations, chain transfer reactions and other things for example, the coupling disproportionation, annihilation of radicals those things you stop. So, you can stabilize this, suppose you stabilize this and now, you can add another block and you can create something like this, at the end of it again you have the radical you stabilize this.

So, you can doubt keep creating different blocks, that will impart different properties to the system and you can actually specifically control the compositions how many number of units here more or less and the molecular w8 distribution also can be quite narrow. If all of these chains say for example, from this stage all the chains here so several of these chains will be growing. So, all the chains are starting to grow at the same time and all the chains, grow for the same length of time and then if you stabilize. So, all the chains will have the same similar length.

So, your molecular distribution also will be quite narrow. So, these are some of the conditions for you know desired conditions for living polymerization because, you want it to living not dead, not being annihilated so or annihilated whatever way. Annihilation or annihilation of radicals you prevent that. So, what you can do to do to achieve that you introduce some dormant state, dormant means sleeping, dormant state for this propagating species.

So, dormant state means once it goes into dormant state there will be some equilibrium between the dormant state and these propagating species once it goes into the dormant state it can be stable it can be even we isolated and again be can B added or you could add B in the reaction mixture itself we will come to that after. So, dormant state you introduce a dormant state. So, that way you can prolong the lifetime of this reactive species, sometimes it can be prolonged from starting from seconds it can be prolonged up to hours.

So, once you have prolonged the life time and if you can stabilize this then you can add another monomer after and then this process becomes technologically important. So, there are 2 ways in which this can be achieved for living radical polymerization you can do. So, one of the ways is reversible termination, and the other is reversible chain transfer.

So, let us talk about reversible termination the general thing here, is you take a initiator R-Z, R-Z you have an initiator now this initiator will decompose to give you R dot and Z dot, these R dot here. So, this homolytic cleavage gives you R dot and Z dot R dot is a highly reactive radical, it immediately initiates the polymerization of your monomer immediately initiates, let us say n number of units are added RMn dot, this Z dot is basically called a persistent radical which means, this is stable and this cannot initiate polymerization.

However, this Z dot can actually react with a propagating species, in an equilibrium reaction to create something like this R-Mn-Z, this does not have any radical here, but this is a masked radical, if you so please you can say this is a must radical now; that means, the radical is actually masked here, it will be released when you go back to in this equilibrium.

So, this is the situation so this persistent radical is stable and it cannot initiate polymerization R dot is reactive it can initiate polymerization. In fact, it initiates polymerization very quickly and this R-Z this initiator here, it decomposes very fast and all at once. So, that all the growing chains will start to grow almost at the same time, because these R-Z decomposes all at once and not only that depending on this equilibrium, all these chains will also grow for the same time they not only start to grow at the same time, but they also will grow for the same time.

Now, why this equilibrium is important is because, of this can also go to biomolecular termination, you want to stop that. So, your Z has to be so chosen that this breaks down very quickly, into these 2 radicals not only that the Z is stable enough not to initiate the polymerization, but still it can effectively in a fast equilibrium process capture these propagating species and from this kind of dormant or sleeping or masked species, masked radical dormant species and this particular equilibrium the equilibrium constant is very, very important here.

Because that equilibrium constant has to be so fine tuned that this concentration of RMn dot these propagating species has to be low ,because if it is very high then what will happen is that is bi molecular termination, which actually depends on the proximity of the 2 radicals and the concentration of also concentration to the power 2. So, that will be prevalent and this can be destroyed you do not want to destroy this.

So, in stop this bi molecular termination in order to stop that in equilibrium constant has to be in such a range, that this concentration is not too high again these concentration cannot be too low also, because if this concentration is very low, then this propagation cannot occur effectively.

So, there has to be some kind of balance in this concentration not too high not too low. So, correspondingly this equilibrium constant has to be also managed accordingly, and that is determined by this Z, and Z is very important because it has to be stable enough. Again, I repeat not to initiate the propagation here. So, this is the overall thing here. So, all the propagating radicals up to will grow for the same time and this way you can increase the radical stability sometimes up to hours.

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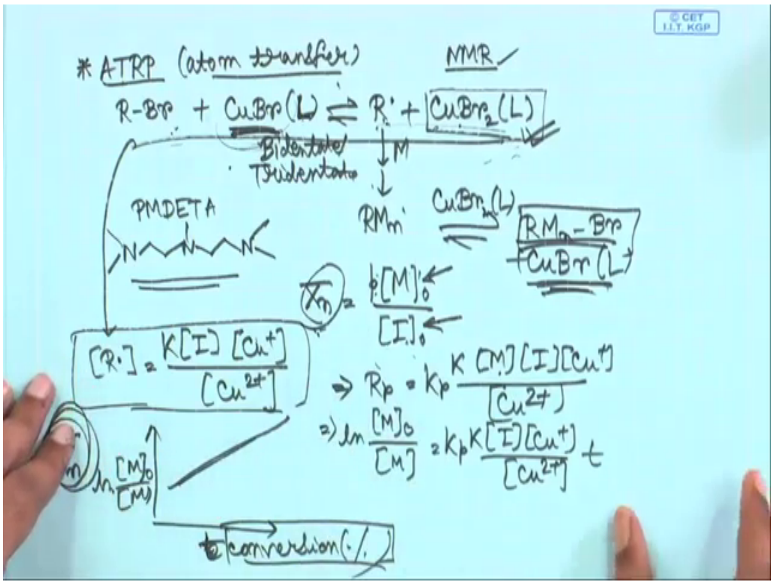

So, we are going to talk about. So, this is reversible termination, because this is termination, but this is reversible. So, this reversible termination can be used this concept can be used for two kinds of important reactions, that I am going to tell you about ATRP atom transfer radical polymerization and another is NMP, we are going to talk about it after which is nitroxide mediated living radical polymerization.

So, ATRP you are using an alkyl halide as the initiator and you are using a cuprous bromide with some ligand, as the you know as the catalyst so your R-Br is basically your R-Z, that we talked about here and you have to use a catalyst here cuprous bromide. So, this will undergo a redox reaction; so, this is copper one. So, it will undergo an electron transfer an atom transfer reaction also and it will create this R dot plus CuBr2 L. So, this goes to plus 2 state and in the process through, electron transfer this creates R dot which is the reactive radical.

So, this is basically a persistent radical, actually it is not a radical. So, it is a persistent species you should say; so, that was a very general terms Z dot I had written here. So, you do not have a radical here, but this is similar. So, you say persistent species. So, this cuprous as bromide you use as a catalyst now what is L, L is say bidentate or tridentate amine-based ligand so it could be say for example, PMDETA which is pentamethyl, diethylene, triamine it could be like this.

So, some of these ligands are used here, amine based for example to solubilize your catalyst in your organic medium and to adjust it is redox potential so that it can effectively do this particular reaction. So, and then this R can react with Ms and it can create RMn dot I have already explained this and it can react now with your persistent species in this case not persistent radical. So, you have RMnBr and then you have CuBr(L) So, this is your catalyst this is created back here.

So, then this is your TRP reaction atom transfer radical polymerization, because atom is being transferred. So, if you are looking into this particular reaction your Xn bar, which is your number of what is degree of polymerization, this will be equal to p into M0 divided by I0, where M0 is the initial concentration of monomer and I0 is the initial concentration of the initiator. So, you can actually predict the degree of polymerization p is the conversion.

So, this ratio will be equal to the degree of polymerization when the conversion is 100 percent, and not only that if you do the kinds simple kinetic analysis, here you can I mean from this particular expression, you can have an expression of R dot; I will not work it out completely you can work it out yourself equals to equilibrium constant for this reaction into I into Cu plus divided by Cu 2 plus, because equilibrium constant is K1 divided by K2 and then your R dot will come and correspondingly you will get this particular value in that expression. So, this is K1 this is K2 forward backward.

So, if you put all these values here, then your rate of polymerization will be equal to Kp into K into M into I into Cu plus divided by Cu2 plus, because rate of polymerization is nothing but Kp propagation constant into your monomer concentration into your R dot which is your radical concentration, that R dot is this so you put it there. So, and then if you understand that this rate of polymerization nothing but, dm dt minus dm dt and then you take a ln after integration ln M0 by M, becomes equal to Kp K I Cu plus divided by Cu2 plus into t.

So, your if you are plotting say, your ln M 0 by M versus t you be a straight line, but the same token if you are plotting your Mn bar; number average molecular w8 also, if your plotting with as a function of conversion, if you are plotting that will also be a straight line. So, number average molecular w8 develops linearly with conversion, this is quite different from what happens in a simple nonliving radical polymerization.

So, they are the number average molecular develops quiet rd or whatever average molecular develops quiet rd. So, this is different from that; so, that is what I wanted to tell you about ATRP, now I will just try to explain to you one of the examples from a recent paper that tells you that this is being used in a very active way. So, I will go to the particular paper here.

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Multivalent hydrogen bonding block copolymers self-assemble into strong and tough self-healing materials†

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Triblock copolymers having glassy PMMA blocks and dynamic hydrogen bonding blocks were synthesized by sequential atom transfer radical polymerization (ATRP). The dynamic triblock copolymers self-assemble into nanocomposite materials exhibiting a combination of mechanical strength, toughness, and self-healing capability.

Self-healing materials have attracted much attention recently because they can potentially improve the safety, lifetime, energy efficiency, and

in a few multiphase polymer systems including hydrogen-bonding brush copolymers,[3c] block copolymers,[3d] and core–shell nanoparticles.[10] Despite these progresses, it remains a challenge to design self-healing materials that are both stiff and tough. Here we report novel self-healing block copolymers to address this problem.

In our previously reported self-healing block copolymer design, a single quadruple hydrogen-bonding motif, 2-ureido-4-pyrimidinone (UPy), was introduced to each diblock copolymer chain end to facilitate

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So, this is a chemical communication paper that has been published in 2014 with a group of zhibin guan and in this particular paper to make the long story short.

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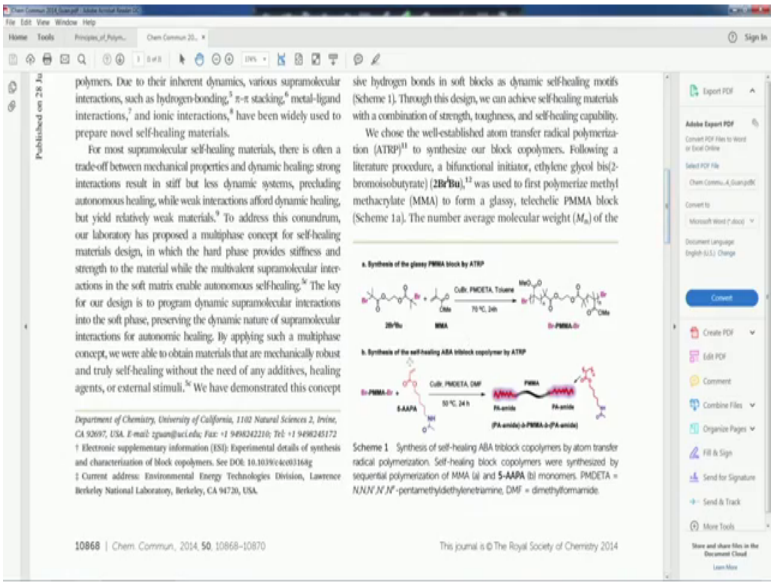

polymers. Due to their inherent dynamics, various supramolecular interactions, such as hydrogen-bonding,[5] π–π stacking,[6] metal–ligand interactions,[7] and ionic interactions,[8] have been widely used to prepare novel self-healing materials.

For most supramolecular self-healing materials, there is often a trade-off between mechanical properties and dynamic healing: strong interactions result in stiff but less dynamic systems, precluding autonomous healing, while weak interactions afford dynamic healing, but yield relatively weak materials.[9] To address this conundrum, our laboratory has proposed a multiphase concept for self-healing materials design, in which the hard phase provides stiffness and strength to the material while the multivalent supramolecular interactions in the soft matrix enable autonomous self-healing.[3c] The key for our design is to program dynamic supramolecular interactions into the soft phase, preserving the dynamic nature of supramolecular interactions for autonomic healing. By applying such a multiphase concept, we were able to obtain materials that are mechanically robust and truly self-healing without the need of any additives, healing agents, or external stimuli.[3c] We have demonstrated this concept

sive hydrogen bonds in soft blocks as dynamic self-healing motifs (Scheme 1). Through this design, we can achieve self-healing materials with a combination of strength, toughness, and self-healing capability.

We chose the well-established atom transfer radical polymerization (ATRP)[11] to synthesize our block copolymers. Following a literature procedure, a bifunctional initiator, ethylene glycol bis(2-bromoisobutyrate) (**2BrⁱBu**),[12] was used to first polymerize methyl methacrylate (MMA) to form a glassy, telechelic PMMA block (Scheme 1a). The number average molecular weight (M_n) of the

Scheme 1 Synthesis of self-healing ABA triblock copolymers by atom transfer radical polymerization. Self-healing block copolymers were synthesized by sequential polymerization of MMA (a) and **5-AAPA** (b) monomers. PMDETA = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, DMF = dimethylformamide.

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You have a methyl methacrylate monomer here, and you have this kind of initiator to start with. Now, this initiator has on both sides you have these 2 bromines here. So, this is basically RX on both sides we have one X unit, now you have Q plus bromide as the catalyst PNDTA already the structure I have written drawn before, now when you are doing the polymerization to ATRP on both sides these groups will be coming and then you have the dormant state introduced on both sides.

So, this particular molecule can now be taken and then so that is Br PMMA Br. So, this block is there. So, basically this block is a hard block because the glass transition temperature is higher, and then you are reacting with what you call as a soft block or a flexible block, where you have this long chain here and you have an (Refer Time: 24:05) unit here which can polymerize.

Again, you are doing an ATRP, now when you are doing ATRP reaction so you have this block here which is PMMA and both sides this rate or the flexible chain is basically this amide unit the a long polymer chains that have been produced here this is the structure say n number of units that come together.

So, basically you have a tri block copolymer say ABA, where this A on both sides, they are soft units and this is the hard unit. So, what you have is the material which has not only the property of stiffness, but that that has also the property that it has a flexibility. So, what you call that as a thermoplastic elastomer; that means, at higher temperature that can be these can become variable, but also this has quite high stiffness as well as high extensibility.

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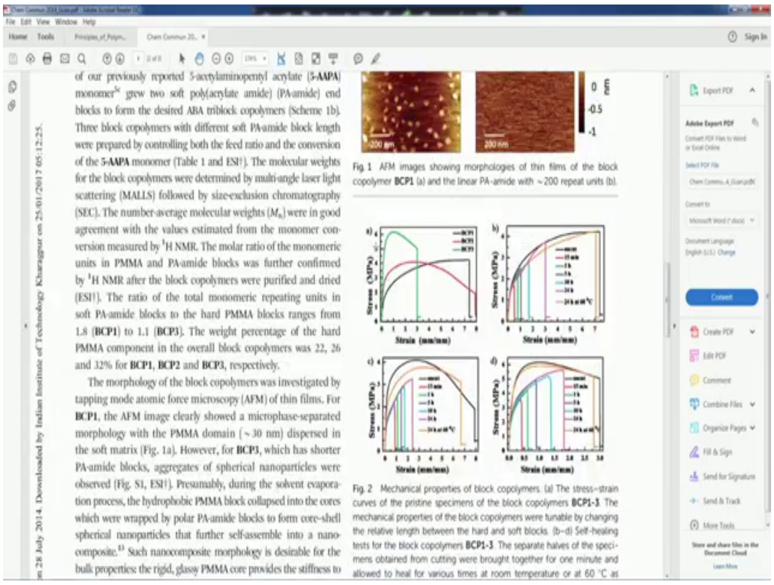

of our previously reported 5-acetylaminopentyl acrylate (**5-AAPA**) monomer[5c] grew two soft poly(acrylate amide) (PA-amide) end blocks to form the desired ABA triblock copolymers (Scheme 1b). Three block copolymers with different soft PA-amide block length were prepared by controlling both the feed ratio and the conversion of the **5-AAPA** monomer (Table 1 and ESI†). The molecular weights for the block copolymers were determined by multi-angle laser light scattering (MALLS) followed by size-exclusion chromatography (SEC). The number-average molecular weights (M_n) were in good agreement with the values estimated from the monomer conversion measured by ^{1}H NMR. The molar ratio of the monomeric units in PMMA and PA-amide blocks was further confirmed by ^{1}H NMR after the block copolymers were purified and dried (ESI†). The ratio of the total monomeric repeating units in soft PA-amide blocks to the hard PMMA blocks ranges from 1.8 (**BCP1**) to 1.1 (**BCP3**). The weight percentage of the hard PMMA component in the overall block copolymers was 22, 26 and 32% for **BCP1**, **BCP2** and **BCP3**, respectively.

The morphology of the block copolymers was investigated by tapping mode atomic force microscopy (AFM) of thin films. For **BCP1**, the AFM image clearly showed a microphase-separated morphology with the PMMA domain (~30 nm) dispersed in the soft matrix (Fig. 1a). However, for **BCP3**, which has shorter PA-amide blocks, aggregates of spherical nanoparticles were observed (Fig. S1, ESI†). Presumably, during the solvent evaporation process, the hydrophobic PMMA block collapsed into the cores which were wrapped by polar PA-amide blocks to form core-shell spherical nanoparticles that further self-assemble into a nanocomposite.[13] Such nanocomposite morphology is desirable for the bulk properties: the rigid, glassy PMMA core provides the stiffness to

Fig. 1 AFM images showing morphologies of thin films of the block copolymer **BCP1** (a) and the linear PA-amide with ~200 repeat units (b).

Fig. 2 Mechanical properties of block copolymers. (a) The stress–strain curves of the pristine specimens of the block copolymers **BCP1-3**. The mechanical properties of the block copolymers were tunable by changing the relative length between the hard and soft blocks. (b–d) Self-healing tests for the block copolymers **BCP1-3**. The separate halves of the specimens obtained from cutting were brought together for one minute and allowed to heal for various times at room temperature or at 60 °C as

So, those kind of things can be actually a gorged by this kind of stress strain graph. So, you see that the stress versus strain graph goes like this. So, this has quite a bit of toughness because the stress by strain this area under the curve actually tells you the toughness or the impact strength. So, let us say of the material and you can actually control the length of these different blocks and correspondingly you can control how the mechanical property will vary. So, that is the power of ATRP now related to this let us come back to our script here.

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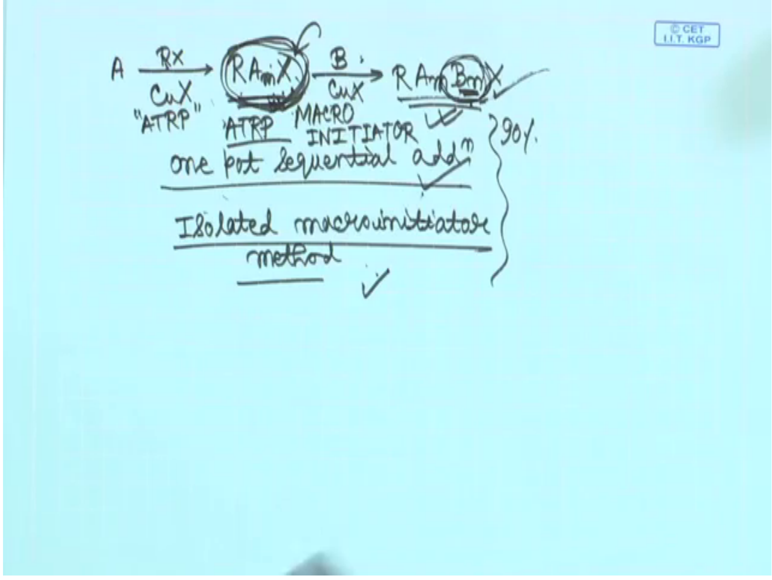

$$A \xrightarrow[CuX]{RX} RA_mX \xrightarrow[CuX]{B,} RA_mB_nX$$

"ATRP" "ATRP" MACRO INITIATOR

one pot sequential addn

90%

Isolated macroinitiator method

So, related to this let me tell you something else also. So, when you have say a monomer like this you are using an initiator and then you are putting along with that initiate or a catalyst say you are using let us say, I do not know say CuX. So, RBr is your initiator and CuX is your catalyst and then your polymerizing doing ATRP reaction. So, this is ATRP reaction. So, in this ATRP reaction you are creative RAmX.

So, you are creating this particular material. So, that is nothing but your this dormant situation, now once you have created that basically it is RAm dot and then that has that has been stabilized. So, this is your dormant species and now you can add your second monomer I have already discussed a research paper similar things they are added here. So, you possibly I will add that paper as a you know kind of reference study material for you.

So, RAm and then you can have Bn, n number of units and then again X, now this can be again used for the reaction for further block formation now so this particular thing that you have created this is your intermediate stage of the block copolymer formation. Now using ATRP you can prepare this kind of block copolymers by 2 processes one is you know a one pot sequential addition method which means, this particular material that you have created you do not isolate that once you have created this you add the second monomer.

Now, these materials basically called they are called macro initiator, even this was the initiator to start with now again you have an X at the end. So, this is another initiator you see here this particular reaction this is not specific to ATRP this is the general thing for this kind of you know reversible termination processes for living polymerization. So, you have this masked system, now when you add the second monomer here what will happen you replace this RZ with RMnz.

So, then this will be the initiator this will break into RMn dot and Z dot and this will now attach the second monomer. So, this is then nothing but a macro initiator, because you have a long polymer chain inside it. So, this is a macro initiator.

So, again this can go to the same process here. So, when your adding the second monomer. So, this is that is why it is the dormant state it is waiting to react and it is just stable thing. So, what you can do is that that macro initiator you do not need to isolate you can add the B. So, this is one pot sequential addition, but here the problem is something else I will talk about it after.

Let us talk about the second process which is your isolated macro initiator method. So, isolated macro initiator method means, you isolate this macro initiator then again you add your B and then you add your copper highlight, cuprous highlight and then you do the next reaction. So, one thing you have to keep in mind here is that you do not go beyond say 90 percent conversion, up to the first reaction is stop at say a 90 percent conversion and then you add the second one whether you go for one pot sequential addition or isolated macro initiator.

Here also isolated macro initiator method suppose you go to say 90 percent conversion, then you isolate it again start the reaction with the fresh batch say in this case fresh batch means, fresh batch of monomer B cuprous allied and this, and if you are doing one part sequential method go up to say 90 percent of conversion and then you are adding the second monomer this is because, if you go to very high conversion then your monomer concentration drops and then your biomolecular termination might become important.

So, if you go to very high conversion then the problem will be like you know you will have you do not have species left for reaction. So, if this will start to get converted to a biomolecular terminated process, because this has an equilibrium you remember this as an equilibrium that can go to our star dot sight. So, if a monomer concentration goes down this will go to that site, equilibrium process reversible process now, when you are considering one pot sequential addition the problem here is that you are adding the monomer B when still there is some a left. So, what can happen is that you basically can have some impurity in this block, where some of the A can be added. So, that is the problem that is not there for isolated macro initiator method, because you have purified that there is un-reacted a in this case.

So, our time is up for this week. So, what we will do in the next week, we have already talked about this atomic transfer radical polymerization. In the next week in the first class we will try to cover the other aspects of living polymerization namely see nitroxide mediated radical polymerization.

So, this ATRP and nitroxide both will constitute this reversible termination way of introducing livingness to radical polymerization; then there is another process called you know reft process, which will be similar to; which will actually illustrate the principle of reversible addition fragmentation which is a basically a reversible chain transfer process that is also a process through which you can ensure the livingness of polymerization.

So, that will be the topic of the next class and we will start with the topic in the next week and then even start talking about chemical reactors and implications they are off in simple chemical reactions followed by polymerization reactions they are after hopefully.

Thank you till then and goodbye.