Principles of Polymer Synthesis

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Lecture – 21
Principles of Living Chain Polymerization (contd.)

Welcome back everyone to this fifth week of lecture of the lecture series on NPTEL course, principle sub synthesis of polymers. So, if you recall what has gone on in the last week, we had started with talking about radical polymerization that was the continuation of previous week, and we were talking about different aspects for example, the initiator efficiency how it can be determined, and also how as a function of temperature the rate of polymerization may or may not change depending on the kind of initiation, that you are using for synthesizing the polymers and afterwards we started talking about chain copolymerization reactions.

We introduced the principle of copolymerization. So, there was a module called terminal module that we used, in order to determine the expressions for the analysis of the reaction the kinetics. So, an from there you also defined things called reactivity ratios of the monomers, we only limited our discussion to the reaction between reaction mixture of copolymerization in which, there are only 2 monomers not more than 2 monomers, and then we also talked about instantaneous copolymer composition.

When you have a very slide conversion from the starting monomer comonomer feed composition, and afterwards we argued that the comonomer feed composition will drift as a function of time, because both the monomers do not have the same reactivity they do not add to the polymer chain to the growing polymer chain with the same propensity. So, ultimately what will happen is that the more reactive monomer will enter the copolymer to a more extent to higher extent, and living it is concentration to be depleted into the comonomer feed mixture.

And hence the comonomer feed mixture that the composition will drift with conversion, and accordingly the composition of the copolymer also will drift it conversion we also tackled that, and finally we talked about microstructure of copolymers. So, the sequence length distribution so, you have 2 monomers m 1 and m 2, to now depending on whether you have alternating perfectly alternating or what you say as you know ideal extremely or what you call as extreme behavior of alteration, or you can consider moderate behavior of alteration extreme behavior of alterations R 1 equals to R 2 equals to 0, both the reactivity ratios are 0.

So, you have perfectly alternating copolymer completely non-random and if your R 1 and R 2 are less than 1, but close to 0 then you have close to being perfect alternation, but it is not exactly perfect, and from there we determined how the sequence length distribution will vary, and we showed from the analysis that even triads tetrads m 1 m 1 triads m 2 tetrads for example, those are also present in a very small quantity because it is not a perfectly alternating copolymer.

So, so on and so, forth, and afterwards we started talking about towards the end of the last week we started talking about living polymerization living chain polymerization, and that is also the topic of today. So, we will continue talking about living chain polymerization today also.

So, if you recall the discussion of the last class of the previous week we told that, although that topic is quite general living chain polymerization. So, that should include say cationic anionic as well as radical, but we concentrating only on radical chain polymerization which we are making into a living version. So, that is also there is also a reason for that because we consider the living radical chain polymerization to be the most important of the all the living chain polymerizations.

Because radicals you know the substrates are less selective as far as reactions in a radical path way are concerned, because the intermediate radical or the propagating species the radicals in the propagating species could be stabilized, whether you have an electron donating group or whether either whether you have electron withdrawing group both ways, both can stabilized that radicals; however, if you have an anion or an cation in a propagating species, corresponding to an anionic or cationic polymerization respectively that is not the case.

So, if you have a electron donating group present then it will destabilize the anion. So, that would mean that particular substrate will be reluctant to undergo anionic polymerization, to rather undergo cationic polymerization and vice versa.

So; that means, that cationic and anionic polymerizations this principles cannot be I mean for example, anionic polymerization you try to make it living typically many of the anionic polymerizations are living, because when you have this negative charge propagating in the species. So, they can actually interact with the solvent and then the negative charge could be taken off from this species, that is one of the viozin verstate polymer could be formed, these does not happen all the time your solvents are typically non-polar that you are using.

So, for all tactical purposes many of these negatively charged species that you generate, in anionic polymerization many of these systems of anionic polymerization they will be basically living polymerizations because the negative charge that you have generated, generally is not taken care of or quenched in the under the reaction condition. So, those things we are not discussing say for example, if you are talking about anionic polymerization applications will be limited, because not all substrates can be subjected to anionic polymerization same is the case with the cation polymerizations, but that is not the case rather with radical polymerizations.

So, that is why we started talking about living radical polymerization the most important of the living chain polymerizations of all, and we will restrict our discussion to only living radical chain polymerization in this particular course.

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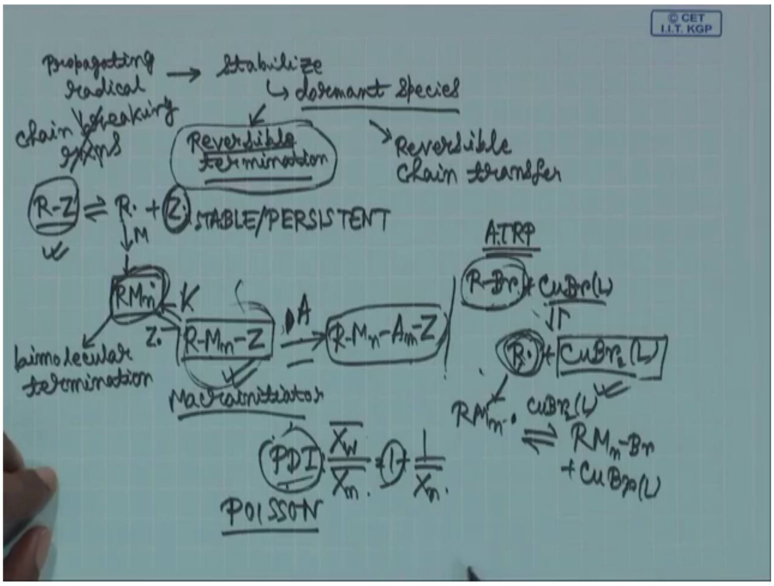

So, to recall we told that we need to have a propagating species, on this case the a propagating radical you want to increase the lifetime of this, you want to stabilize this. So, you actually create a dormant species which will must the radical.

and the way you create this there could be 2 path ways, one is reversible termination and another path way is reversible chain transfer. So, generous scheme we have drawn for the reversible termination. So, the generous scheme is like this, you had this is the recollection of what we had taught the last week, something like this you have an initiator which instantaneously disassociates to form this 2 radicals, and one of them is stable or you can also call that as persistent species, that cannot initiate polymerization.

But the other radical is reactive, and that can initiate polymerization with the monomer. So, several of the monomers can add you can creates RMn dot now this could go to bimolecular termination ; however, this is captured in this kind of reversible reaction, with Z dot to produce RMn Z, this is the dormant species and this equilibrium constant of this reaction is very important, because this concentration of RMn dot should not be too low, because if it is too low then this propagation rate will be hampered, and if it is too high then the bimolecular termination will become predominant. So, the idea is that you want to stop all the chain breaking reactions.

So, be it terminations through coupling disproportionation or it could be chain transfer also. So, these things you want to stop. So, this is the overall aspect of reversible termination, because you are terminating this growing propagating species reversible way and these particular species you can probably isolate after, and once you isolate you can add another batch of monomers, say you are adding say you are adding a monomer 2. And so, aim let us say you are putting A.

So, another monomer you are adding and then you are again add your initiator. So, basically this is your initiator in this case this is was the initiator. So, this becomes a macro initiator and generally you can use a catalyst to disassociate this, to activate this initiator to disassociate. So, that catalyst you will use here again and afterwards. So, this is basically similar to this, but it is a macro version of that. So, macro initiator and then you can add the molecule of A, same number of units and then again Z will be there at the end.

So, this is how you can create specific composition of block copolymers. And so, we had already talked about one of the processes reversible termination, which is ATRP atom transfer radical polymerization, and this atom transfer radical polymerization basically the RZ is your alkyl halide, you are using and you are using a copper halide cypress halide is the catalyst, and this will be reversibly. So, this will actually what will happen, is that in a redox pathway this will activate this thing the RBR electronic transfer will happen, and the bromine transfer will also happen to CUBR. So, this is atomic transfer that is the name the it derives from and you will have CUBR 2. So, on. And so, forth and.

This are dot is and this are dot that can create your RMn dot, and this Z dot is this. So, basically this is not radical, but this is persistent species now this RMn dot could be reversibly terminated by the reaction with this CUBR 2 l, ligand RMn and this bromine again will be transferred here now it will form back CUBR. So, it is a catalyst because CUBR is formed back at the end so on and so forth and you are using a nitrogen-based ligand to stabilize this thing, in a way to solubilize this thing in the particular organic fogram you are using.

So, one thing that remained to be discussed was if you are looking at the molecular weight distribution, Xw by X n because this into m 0 is mw and this into m 0, m n. So, mw by m n is your PDI. So, this is approximately equal to 1 plus 1 divided by X n bar. So, this follows a what you call by as poisson distribution, and if your X n bar is very high, then for all practical purpose this PDI is very close to 1, and that is something that happens because you initiate all the initiator all at once, it will disassociate to form R dot, and not only that this R dot I mean this will initiate the polymerization and that all that chains that will start to grow they will start to grow at the same time, and they will grow for the same length of time.

So, that gives you a very narrow molecular weight distribution and we also discussed one example of ATRP. So, we will also just talk about one more example here, again if you go to the power point we will talk about one more example here. So, this is. So, if you look at.

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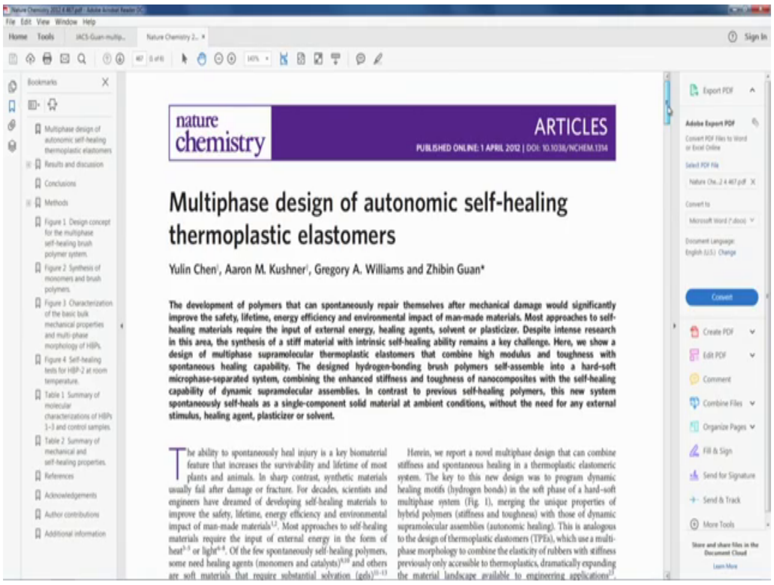

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ARTICLES

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Multiphase design of autonomic self-healing thermoplastic elastomers

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The development of polymers that can spontaneously repair themselves after mechanical damage would significantly improve the safety, lifetime, energy efficiency and environmental impact of man-made materials. Most approaches to self-healing materials require the input of external energy, healing agents, solvent or plasticizer. Despite intense research in this area, the synthesis of a stiff material with intrinsic self-healing ability remains a key challenge. Here, we show a design of multiphase supramolecular thermoplastic elastomers that combine high modulus and toughness with spontaneous healing capability. The designed hydrogen-bonding brush polymers self-assemble into a hard-soft microphase-separated system, combining the enhanced stiffness and toughness of nanocomposites with the self-healing capability of dynamic supramolecular assemblies. In contrast to previous self-healing polymers, this new system spontaneously self-heals as a single-component solid material at ambient conditions, without the need for any external stimulus, healing agent, plasticizer or solvent.

The ability to spontaneously heal injury is a key biomaterial feature that increases the survivability and lifetime of most plants and animals. In sharp contrast, synthetic materials usually fail after damage or fracture. For decades, scientists and engineers have dreamed of developing self-healing materials to improve the safety, lifetime, energy efficiency and environmental impact of man-made materials[1,2]. Most approaches to self-healing materials require the input of external energy in the form of heat[3-5] or light[6-8]. Of the few spontaneously self-healing polymers, some need healing agents (monomers and catalysts)[9,10] and others are soft materials that require substantial solvation (gels)[11-13]

Herein, we report a novel multiphase design that can combine stiffness and spontaneous healing in a thermoplastic elastomeric system. The key to this new design was to program dynamic healing motifs (hydrogen bonds) in the soft phase of a hard–soft multiphase system (Fig. 1), merging the unique properties of hybrid polymers (stiffness and toughness) with those of dynamic supramolecular assemblies (autonomic healing). This is analogous to the design of thermoplastic elastomers (TPEs), which use a multiphase morphology to combine the elasticity of rubbers with stiffness previously only accessible to thermoplastics, dramatically expanding the material landscape available to engineering applications[14].

The power point here this is the actually this is not the power point this is the p d f of the particular paper that I am showing here, published in nature chemistry 2012 multiphase design of autonomic self-healing thermoplastic elastomers.

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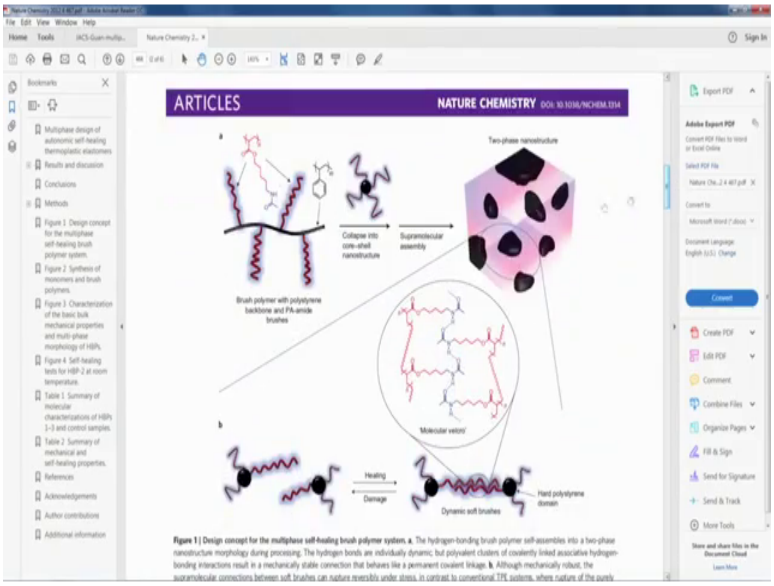

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Figure 1 | Design concept for the multiphase self-healing brush polymer system. a, The hydrogen-bonding brush polymer self-assembles into a two-phase nanostructure morphology during processing. The hydrogen bonds are individually dynamic, but polyvalent clusters of covalently linked associative hydrogen-bonding interactions result in a mechanically stable connection that behaves like a permanent covalent linkage. **b**, Although mechanically robust, the supramolecular connections between soft brushes can rupture reversibly under stress, in contrast to conventional TPE systems, where rupture of the purely

So, basically here the idea is that you have a core chain, which is made of polystyrene and which is basically hard block because the t g or the glass transition temperature is high, and then you create some branches around the length of it. So, these branches that you have they are basically made of this particular polymer which has this long chain, which increases the glass transition which decreases the glass transition temperature, which means the temperature room temperature is basically higher than the glass transition temperature.

So, this becomes more flexible it is not in the glassy state it is more flexible state, but these is in glassy state; so your hard-soft mixture in the system. So, what will happen is that from the solvent, if you precipitate it the solvent evaporates and this particular thing the hard block that will create cross links, and this phase is a soft phase. So, basically these cross links these hard blocks will be dispersed in the soft phase, and they will cross link the soft phase.

So, ultimately these material will be stiff because the stiffness will be derived from this hard block, but this material will be stretchable also, because the softness will be derived from this soft block, and not only that this soft block has hydrogen bounding interactions that are present that are engineered into that.

So; that means, you can actually stretch them and the hydrogen bounds will break and afterwards when you remove the applied force, they may come back to it the original situation by self-healing. So, if you cut the material also into 2 halves when you put them back together because of the hydrogen bounding interactions in this soft matrix, they can come back together now this is the overall principle how do you prepare this kind of material.

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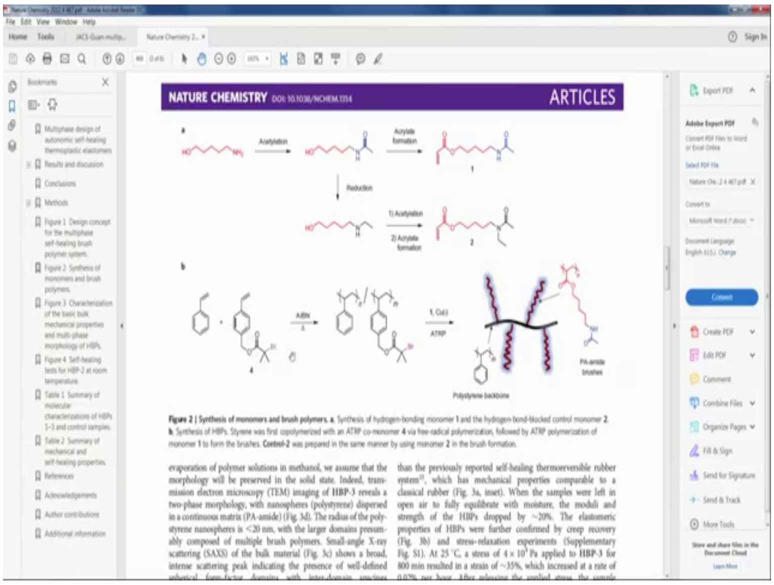

Figure 2 | Synthesis of monomers and brush polymers. a, Synthesis of hydrogen-bonding monomer **1** and the hydrogen-bond-blocked control monomer **2**. **b**, Synthesis of HBPs. Styrene was first copolymerized with an ATRP co-monomer **4** via free-radical polymerization, followed by ATRP polymerization of monomer **1** to form the brushes. **Control-2** was prepared in the same manner by using monomer **2** in the brush formation.

evaporation of polymer solutions in methanol, we assume that the morphology will be preserved in the solid state. Indeed, transmission electron microscopy (TEM) imaging of **HBP-3** reveals a two-phase morphology, with nanospheres (polystyrene) dispersed in a continuous matrix (PA-amide) (Fig. 3d). The radius of the polystyrene nanospheres is <20 nm, with the larger domains presumably composed of multiple brush polymers. Small-angle X-ray scattering (SAXS) of the bulk material (Fig. 3c) shows a broad, intense scattering peak indicating the presence of well-defined

than the previously reported self-healing thermoreversible rubber system[17], which has mechanical properties comparable to a classical rubber (Fig. 3a, inset). When the samples were left in open air to fully equilibrate with moisture, the moduli and strength of the HBPs dropped by ~20%. The elastomeric properties of HBPs were further confirmed by creep recovery (Fig. 3b) and stress-relaxation experiments (Supplementary Fig. S1). At 25 °C, a stress of 4×10^{5} Pa applied to **HBP-3** for 800 min resulted in a strain of ~35%, which increased at a rate of

So, what they did is that they basically have stirring, and this stirring is copolymerized with this particular monomer, you see that here this is kind of an alkyl bromide particularly shooted for ATRP afterwards.

So, with the isobutyl thermal initiation you do the polymerization and you control the amount of this. So, how much of this amount will be in this height chamber will also be controlled, now this is a macro initiator, now and this macro initio initiator you are reacting with a monomer which is this monomer you know, and that is an ATRP reaction you are using copper one. So, with this ATRP reaction basically since these macro initiator the reacting centre, which is massed by the bromide that is at the height chain.

So, at this height chain actually your chains will grow from this soft grash, and then ultimately you get this kind of architecture, and depending on how much of this moiety you are using. So, if you change the ratio you will change the ratio of this how much amount is there, and then if you control the ATRP to what extent this grows also you can control.

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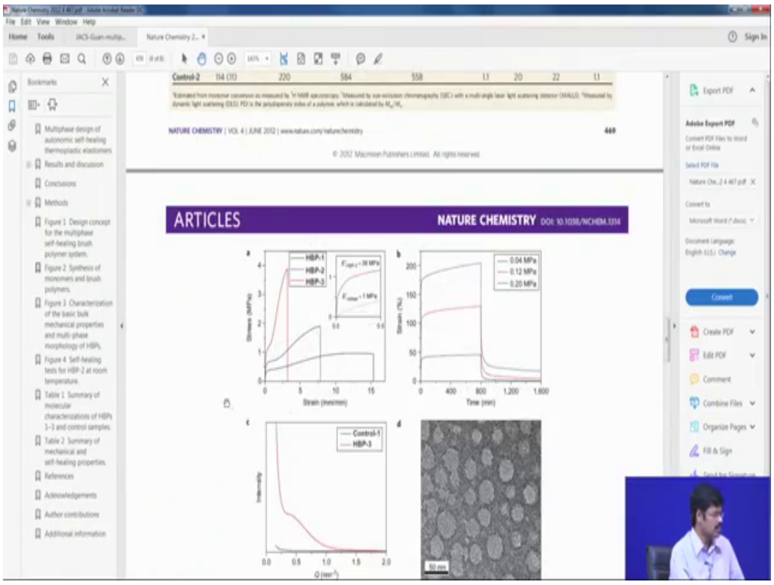

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So, accordingly you can prepare different kinds of material which will respond differently to the stress and strength. So, you make the material tougher; that means, the material can actually stretch to a longer strain to a higher strain, and also stiff enough because the material has this backbone which is your polystyrene.

So; that means, it is a kind of you know and an elastomeric material, and this also this is stiff plus this stretchable. So, both properties are actually present. So, this is an example in which your structure dictates the property, along the way we will discuss more examples after, but this is the power of ATRP that is the take home message from this particular paper. So, we go back to our discussion on the script. So, basically all this I wanted to discuss about ATRP now we will briefly discuss another process another different kind of technique, that uses reversible termination in order to introduce this dormant species.

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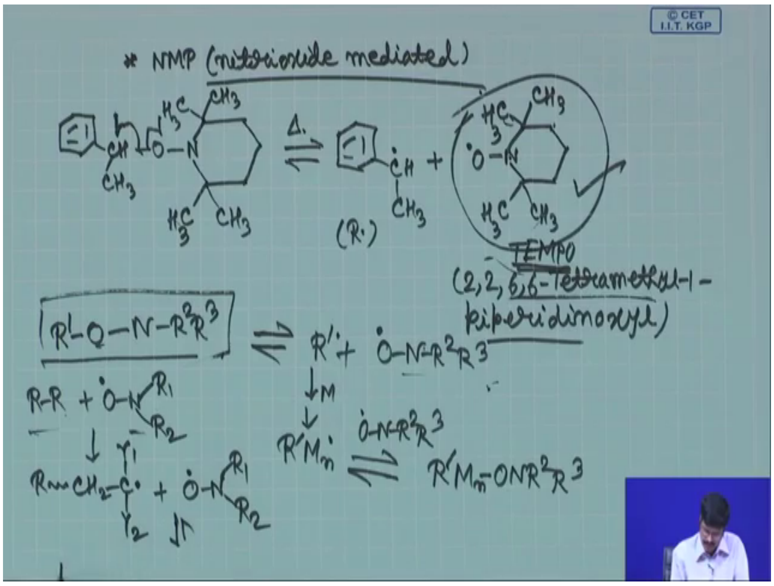

So, another kind of living polymerization which is living radical polymerization which is NMP, which is everywhere it is NMP nitroxide mediated polymerization that is NMP.

So, basically the process is the same this was ATRP for nitroxide mediated polymerization your Z dot basically is nitroxide. So, those nitroxides are stable radicals because of the steady hindrance in the system. So, they can be present there in the system, the from the initiator they will come out, and that these nitroxide then it can reversible terminate the growing propagating species, but they are so, stable that they cannot initiate the polymerization an example should do.

So, basically you can start with this particular molecule, CH CH 3, and then oxygen nitrogen CH 3 CH 3. So, if this material you hit up. So, reversibly it can break and it will create 2 radicals. So, it will break here you know. So, half arrow means one electron moving. So, you will create this 2 radicals, 1 radical is this CH CH 3, which is your reactive radical which is your our basically R dot your R dot is this material. So, which is basically this R dot and this Z dot is your nitroxide radical which will be created from here, that will be this remember.

This is specific example of a nitroxide radical rather nitroxide radicals also available, now this radical is stable because this is steadically hindered. So, it cannot initiate polymerization, but it can reversibly react with the propagating species to terminate the propagating species, this specific radical has a has a name tempo you may here this name tempo this is a very known name. So, basically this radical is 2 2 6 6. So, this is one position 2 3 4 5 6. So, 2 2 2 position 2 methyl 6 positions 2 methyl's 2 2 6 6 tetra methyl 1. So, one position one you have the oxygen radical one. So, this is piperidity in moiety. So, this is pi peri dinoyl dinoxyl sorry.

So, piperidinoxyl so one position. So, this is the name. So, this is tempo. So, this is stable, radical in many situations you will see that this tempo, tempo is used as the persistent radical for nitroxide mediated polymerization. So, basically the general scheme is something like that. So, you may have let us say a nitroxide like this.

So, this is your initiator species, which can de decompose to create disassociate to create nitroxide radical. So, what will happen is that you have R 1 dot, plus ONR 2 R 3 dot. So, this is your nitroxide radical, the same way this can react with monomer and it can create this propagating species, and that can be reversibly terminated by this nitroxide radical, to create this dormant species ONR 2 R 3, now what you could also do is that instead of taking only 1 initiator, I mean this initiator produces a nitroxide radical, what you could have is a bicomponent initiating system.

So, bicomponent initiating system means, you could instead of this what you could take is your normal thermal initiator may be say as your isobutyl nitrate you are taking. So, this along with that you have a stable nitroxide radical, you take it directly because some of this nitroxide radical are also stable they can be sold commercially they are. So, stable. So, so this is a bicomponent initiating system.

So, your bicomponent system so, what will happen is that this will disassociate, and this will form the growing polymer chain. So, your RCH 2 CY1 Y2. So, this is your propagating species, now this propagating species could react with your nitroxide radical reversibly to terminate this so on and so forth; so if it will terminate this and it will create your molecule which is like this. So, this is reversible termination.

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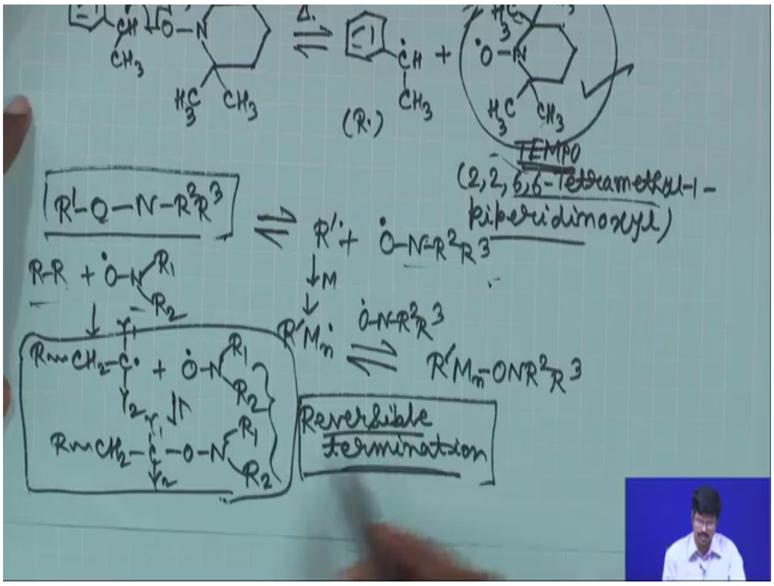

You will have R CH 2 CY 1 Y 2; so R CH 2 CY 1 Y 2 and then you ONR 1 R 2. So, this species is nothing but similar to this particular species here. So, this is the overall principle of. So, this is the activation an reactivation. So, this is the basically your reversible termination, reversible termination step. So, reversible termination step you have now discussed 2 of the examples, ATRP as well as NMP.

So, both of this living radical polymerization processes, the use reversible termination in order to generate your dormant species. So, these dormant species chain can be reacted with another monomer and so on and so, forth. So, finally, what we want to talk about is. So, we have talked about reversible termination process, through which you can make the polymerization living. So, one thing remains to be discussed that is reversible chain transfer process.

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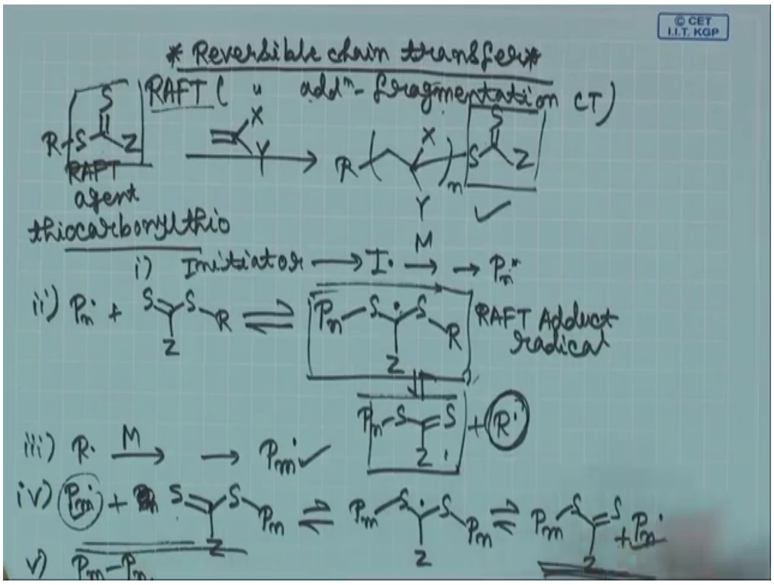

So, because we told that there are 2 ways you can make the polymerization living, one is reversible termination of which we discussed to define 2 classes of reactions ATRP and NMP, another is reversible chain transfer. So, that is this is basically raft polymerization, that that follows under this class this is reversible addition fragmentation chain transfer. So, reversible addition fragmentation chain transfers.

So, the overall reaction is. So, you have a chain transfer that is happening and through that chain transfer you are basically creating the dormant species, and that chain transfer is reversible that is the idea, dormant species is been created through reversible chain transfer unlike in ATRP or NMP, where the dormant species is being created through reversible termination.

So, you basically have a raft agent, which is nothing but this, this raft agent will be a thiocarbonyl thiocompound, and you have your monomer that is reacting a final monomer, and ultimately the product that you will form is something like this, and again then at the end of it you have this thiocarbonnyl thio moiety. So, this can be used as the macro initiator to create another polymeric block after. So, a wide range of functional groups basically are tolerant to raft processes process, say if you have a acrylates acrylamide acrylonitrile tristylites betadines so on and so, forth.

All of them can be used. So, typically the mechanism is something like that you have an initiation step, in which you are using your normal initiator your initiator is decomposing to I dot, and that is initiating your polymerization with the monomer and you have say a growing chain Pn dot, now the second step is basically called a pre equilibration step or reversible it is reversible chain transfer pre equilibration step, where there will of reversible chain transfer of this raft agent with Pn dot. So, this Pn dot can react with your raft agent like this.

And it will create Pn S Z S R dot, now this is your raft adapt radical, this is your persistent species that we are talking about here, in this case this is not reactive enough to react with the monomer itself and start propagation of the chains. So, basically it cannot it does not react with the monomer and transfer the radical and then start propagation, it will basically react with this polymer and create persistent radical like this afterwards. So, it cannot go in this way or that way both ways.

So, this, a stable enough radical so, that it will not initiate the polymerization, and what it can do is that it can decompose in this way Pn S Z double bound S and R dot, now this R dot is the reinitiating species. So, this R dot in the reinitiating process this R dot could again initiate the monomer, and it will create say a polymer chain pm dot. Now in the 4th stage there will be this is the main chain equilibration step.

So, this is pre-equilibration and this is the main chain equilibration step here, now in then main chain equilibration step. So, this Pn dot may be produced from this reinitiating radical, reinitiating species this will react with your this moiety. So, basically, I will just draw this as this.

So, this is the equilibration step, which will establish an equilibration between these 2 species here, and this 2 species here and finally, then this pm dot and Pn dot in the fifth step, could just add up to produce p m Pn which is your trade polymer. So, basically you have this kind of stabled stabilized radical species, which will create what you call as this is your latent or this is your dormant species that is being produced, and this radical species cannot initiate the polymerization with your monomer.

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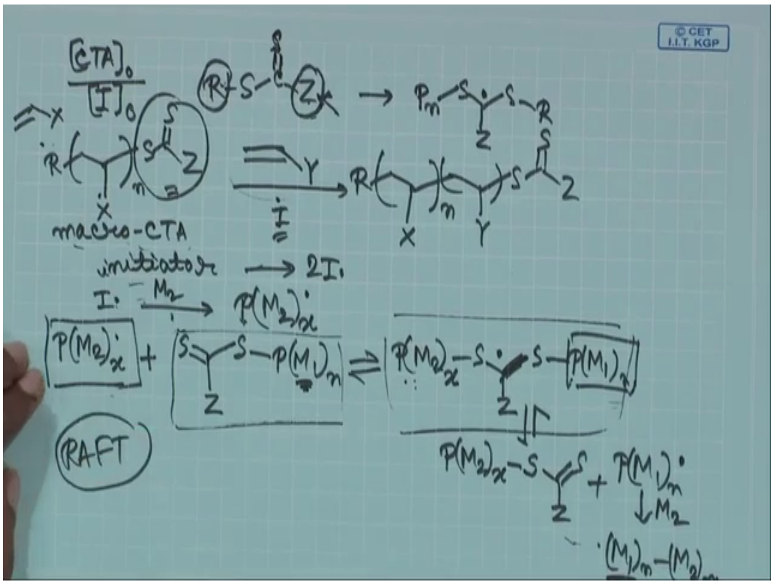

So, specifically say if you certain things you have to keep in mind that this chain transfer agent the concentration of chain transfer agent, that you are starting with the concentration has to be much higher than the initiator in order for this reaction to occur in a proper way, in order for it to be living. So, this has to be higher. So, there will be better control of polymerization, and this thiocarbonyl thiocompound that you are using here this is your raft agent right.

So, the Z that you have this Z has to be. So, C hosen that it will not only stabilize the intermediate radical. So, the intermediate radical is basically something like this Pn S Z S r. So, this stabilize this intermediate radical, but it also helps you know addition to the C double bound S bound, and that is why you your this reaction this particular reaction is will it possible because, Z actually promotes the addition of the Pn dot to C double bound S bound not only that it also stabilizes this radical. So, that is the purpose of Z. So, you have choose it carefully and this R you have to choose it carefully. So, that it is a good homiletic clewing group, because afterwards it will clew off and it will be acting as the reinitiating species here.

So, if you want to create overall say if you want to create a diblock copolymer. So, what you have to do is that you can start with these macro initiator, because you first create this polymer with your chain transfer agent, at the end of it you have this moiety. So, this is your macro initiator macro chain transfer agent, and this can now react with the second monomer of your choice, with a appropriate initiator that you are taking, and it will create the polymer like this. Now something that you have to keep in mind here for this particular reaction, is that the choice of the monomers. So, which monomer to add first and which monomer to add second, in order for a successful raft polymerization reaction.

So, typically for this kind of reactions when you are making a diblock copolymer for example, what will happen is that initially you have an initiator right. So, that will create 2 I dot and then this initiator will react with your monomer 2, remember you have already played your you have already thrown your [die/dice] dice; that means, you have already C hosen your first monomer. So, let us say your first monomer was this monomer.

So, you have C hosen the first monomer you could also choose this monomer first. So, that is very important of which monomer to choose first. So, once you have chosen this monomer you have created this macro chain transfer agent, through the raft addition fragmentation reaction reversible, addition fragmentation reaction, now you are adding the monomer 2 which is m 2 and you are adding another initiator. So, what will happen is that this initiates the polymerization of the second monomer. So, it will create this kind of radical the propagating species p stands for polymerizing system.

now at some point this propagating species can do a chain transfer, with your macro CTA that is very important. So, it can do a chain transfer with your macro CTA. So, I am just drawing here generically. So, pm 1 whole n. So, this was this was your polymer basically at the end of it you have this unit, thiocarbonyl thio unit. So, that this is your macro CTA, I want to add that monomer m 2 as the second block, but what happens is that initially when you have used the initiator, the second block will start to form the propagating species say x number of m 2 units have come together.

So, at some point these particular growing propagating species will do a chain transfer, with this particular molecule with this particular chain transfer agent or macro transient transfer agent. So, when it does that there will be an equilibrium like this you have PM 2 XSZ.

So, basically let me draw this in a so, this is single bound. So, you have this let me split it up into 2 parts pm 1 n this is again a stabilize radical and afterwards it can break like this your pm 2 x, and then you have S double bound S Z, and this will come out as your reinitiating species, now this re initiating species can basically reinitiate your m 2 monomer, and then ultimately you will have at the end of it you have a block of m 1 followed by a block of m 2 same units. So, something that you have to keep in mind is that, these particular monomer that monomer 1 you have chosen in order to create the initial chain transfer agent.

So, once this chain transfer agent has formed, this chain transfer agent should have a high transfer rate constant, with the propagating species of the second monomer. So, that this reversible reaction can actually occur it can go towards this height, and not only that this pm 1 n this has to live in order to create the reinitiating species.

So, the living ability of this polymeric species from this stable radical has to be higher or at least comparable to the living ability of this polymeric species, then only you can have this kind of 2 blocks, that that have been that that are produced in this particular system. So, this is how basically you can use raft process to creates a copolymers block copolymers. So, we will complete the discussion on living chain polymerization in this class by giving you, a one more example of raft chain copolymers. So, you will go back to the desktop and we will show you the particular paper here.

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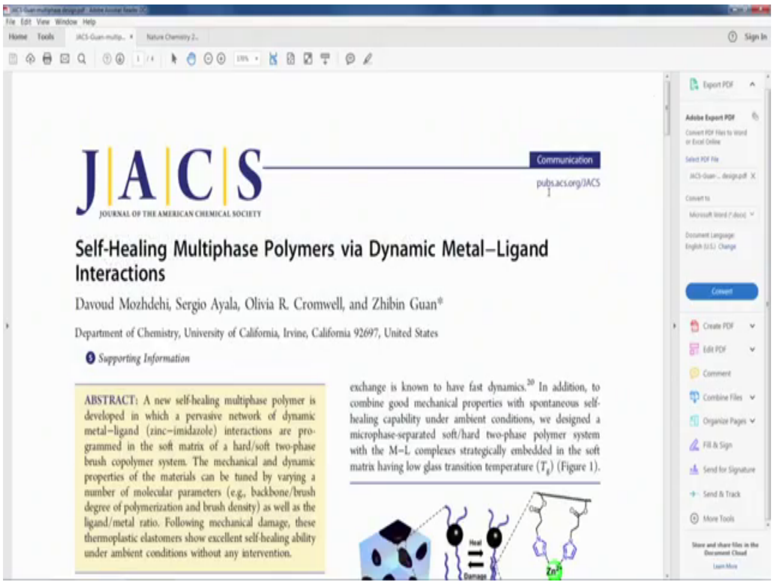

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Self-Healing Multiphase Polymers via Dynamic Metal–Ligand Interactions

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Supporting Information

ABSTRACT: A new self-healing multiphase polymer is developed in which a pervasive network of dynamic metal–ligand (zinc–imidazole) interactions are programmed in the soft matrix of a hard/soft two-phase brush copolymer system. The mechanical and dynamic properties of the materials can be tuned by varying a number of molecular parameters (e.g., backbone/brush degree of polymerization and brush density) as well as the ligand/metal ratio. Following mechanical damage, these thermoplastic elastomers show excellent self-healing ability under ambient conditions without any intervention.

exchange is known to have fast dynamics.[20] In addition, to combine good mechanical properties with spontaneous self-healing capability under ambient conditions, we designed a microphase-separated soft/hard two-phase polymer system with the M–L complexes strategically embedded in the soft matrix having low glass transition temperature (T_g) (Figure 1).

So, self-healing multiphase polymers via dynamic metal ligand interaction.

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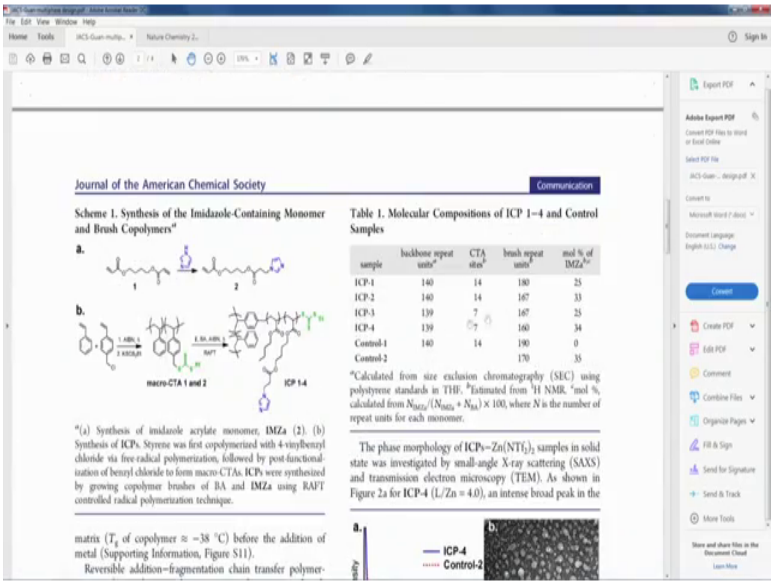

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Scheme 1. Synthesis of the Imidazole-Containing Monomer and Brush Copolymers[a]

[a](a) Synthesis of imidazole acrylate monomer, **IMZa** (**2**). (b) Synthesis of **ICPs**. Styrene was first copolymerized with 4-vinylbenzyl chloride via free-radical polymerization, followed by post-functionalization of benzyl chloride to form macro-CTAs. **ICPs** were synthesized by growing copolymer brushes of BA and **IMZa** using RAFT controlled radical polymerization technique.

matrix (T_g of copolymer ≈ −38 °C) before the addition of metal (Supporting Information, Figure S11).

Reversible addition−fragmentation chain transfer polymer-

Table 1. Molecular Compositions of ICP 1−4 and Control Samples

sample	backbone repeat units[a]	CTA sites[b]	brush repeat units[b]	mol % of IMZa[b,c]
ICP-1	140	14	180	25
ICP-2	140	14	167	33
ICP-3	139	7	167	25
ICP-4	139	7	160	34
Control-1	140	14	190	0
Control-2			170	35

[a]Calculated from size exclusion chromatography (SEC) using polystyrene standards in THF. [b]Estimated from ^1H NMR. [c]mol %, calculated from $N_{IMZa}/(N_{IMZa} + N_{BA}) \times 100$, where N is the number of repeat units for each monomer.

The phase morphology of **ICPs**−Zn(NTf$_2$)$_2$ samples in solid state was investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). As shown in Figure 2a for **ICP-4** (L/Zn = 4.0), an intense broad peak in the

So, what they have basically done here, is that they have created this macro chain transfer agent, now this first reaction is basically your normal radical chain polymerization reaction a I v v is your initiator; so this phenyl 4 phenyl benzyl, benzyl chloride that you are taking. So, you can take this component with respect to this in a certain ratio. So, that you can introduce you can control the amount of C l C a is to C l, that is they are and then you are using this ligand in order to replace this C l with this particular moiety, and you can immediately recognize then this becomes the chain transfer agent as per our discussion before. So, this is thiocarboning thio moiety basico.

Basically, this tri thio carbonate moiety, this can also be a chain transfer agent you can have 2 sulfurs 3 sulfurs together, and after that you can do in the in the second step is that you can put n butyl acrylate. So, this the raft reaction actually you put n butyl acrylates in this is this thing is coming out of the site chain, you create a brash of n butyl acrylate from this this unit. So, it was here. So, you create a brash of n butyl acrylate, and in this n butyl acrylate moiety that you are taking you mix only not only n butyl acrylate you are taking along with that you mix another monomer, which is of this variety at the end of it you have an imidazole moiety.

So, if you take a certain ratio of butyl acrylate 2 a butyl acrylate which is functionalized with this this imidazole moiety, then in that particular ratio they will add to the site chain in the raft polymerization. So, this here if it is m and here it is n number of units this m and n you can actually control, by taking the monomer mixture in that particular ratio mixture. So, this becomes another macro raft agent, but the idea here is that you have created a polymer with this kind of height chain, where you have imidazole unit again this is your hard block and this is your soft block because of this long chain in the soft block at the end, you have imidazole unit which can interact with metal ions.

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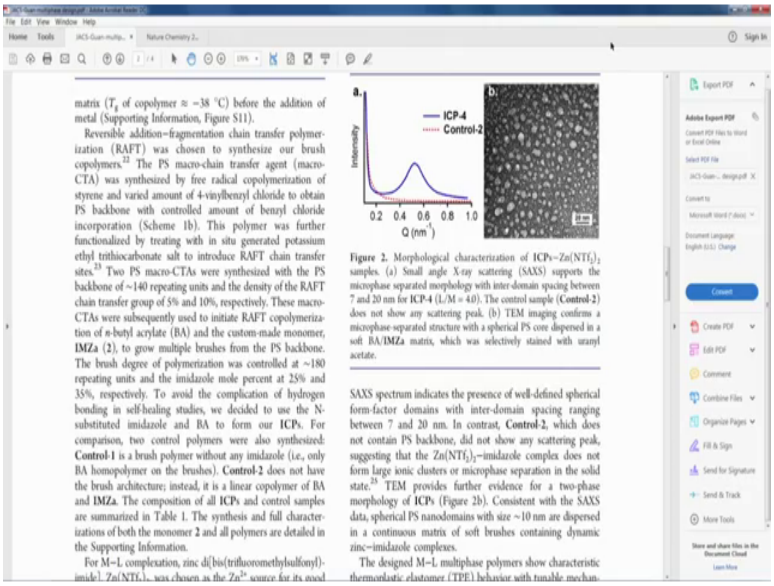

matrix (T_g of copolymer ≈ −38 °C) before the addition of metal (Supporting Information, Figure S11).

Reversible addition−fragmentation chain transfer polymerization (RAFT) was chosen to synthesize our brush copolymers.[22] The PS macro-chain transfer agent (macro-CTA) was synthesized by free radical copolymerization of styrene and varied amount of 4-vinylbenzyl chloride to obtain PS backbone with controlled amount of benzyl chloride incorporation (Scheme 1b). This polymer was further functionalized by treating with in situ generated potassium ethyl trithiocarbonate salt to introduce RAFT chain transfer sites.[23] Two PS macro-CTAs were synthesized with the PS backbone of ∼140 repeating units and the density of the RAFT chain transfer group of 5% and 10%, respectively. These macro-CTAs were subsequently used to initiate RAFT copolymerization of *n*-butyl acrylate (BA) and the custom-made monomer, **IMZa** (**2**), to grow multiple brushes from the PS backbone. The brush degree of polymerization was controlled at ∼180 repeating units and the imidazole mole percent at 25% and 35%, respectively. To avoid the complication of hydrogen bonding in self-healing studies, we decided to use the N-substituted imidazole and BA to form our **ICPs**. For comparison, two control polymers were also synthesized: **Control-1** is a brush polymer without any imidazole (i.e., only BA homopolymer on the brushes). **Control-2** does not have the brush architecture; instead, it is a linear copolymer of BA and **IMZa**. The composition of all **ICPs** and control samples are summarized in Table 1. The synthesis and full characterizations of both the monomer **2** and all polymers are detailed in the Supporting Information.

For M−L complexation, zinc di[bis(trifluoromethylsulfonyl)-imide], $Zn(NTf_2)_2$, was chosen as the Zn^{2+} source for its good

Figure 2. Morphological characterization of **ICPs**−$Zn(NTf_2)_2$ samples. (a) Small angle X-ray scattering (SAXS) supports the microphase separated morphology with inter-domain spacing between 7 and 20 nm for **ICP-4** (L/M = 4.0). The control sample (**Control-2**) does not show any scattering peak. (b) TEM imaging confirms a microphase-separated structure with a spherical PS core dispersed in a soft BA/**IMZa** matrix, which was selectively stained with uranyl acetate.

SAXS spectrum indicates the presence of well-defined spherical form-factor domains with inter-domain spacing ranging between 7 and 20 nm. In contrast, **Control-2**, which does not contain PS backbone, did not show any scattering peak, suggesting that the $Zn(NTf_2)_2$−imidazole complex does not form large ionic clusters or microphase separation in the solid state.[25] TEM provides further evidence for a two-phase morphology of **ICPs** (Figure 2b). Consistent with the SAXS data, spherical PS nanodomains with size ∼10 nm are dispersed in a continuous matrix of soft brushes containing dynamic zinc−imidazole complexes.

The designed M−L multiphase polymers show characteristic thermoplastic elastomer (TPE) behavior with tunable mechan-

So, if you add metal salts say in this case Zinc triphnimite, they are adding and from the solution you evaporate the solvent then you can create this kind of material, where you have a soft matrix which is basically cross linked by your hard backbone of the styrene, and then you can again create what you call as thermo plastic elastomeric materials. So, this this conclude our discussion on living radical polymerization. So, we will leave the radical polymerization behind and in the next class we are going to start talking about the design principles of chemical reactors.

So, till then thank you and goodbye.