

**Polymer Reaction Engineering**  
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**Lecture - 10**  
**Control on Polymer Synthesis-III**

Welcome to the third lecture of control on polymer synthesis under the head of polymer reaction engineering. Up till now we have studied the various parameters associated with synthesis of polymers giving a major overview over the control methodology. And we discussed about the importance of those control methodology in the polymer synthesis, just to control the various properties, just to make the polymer.

Whatever synthesized in due course of time with respect to the processability, with respect to the product overview, with respect to the product desiredness etcetera. So, we have seen that this control protocols are extremely important. Now up to the Lecture Number 1 and 2 of this control methodologies, we discuss about the basic things related to the method of polymerization whether it is a bulk polymerization, immersion polymerization or solution polymerization.

And the different type of ingredient with respect to the reactants etcetera. How they play a vital role. What is the role of significant role of heat etcetera and how this molecular weight distribution plays a vital role etcetera. So, we discussed a lot in this category. Now in this particular lecture we will discuss about the various physical control strategies for polymerization process.

Now for the production of polymer in different industries there are various type of reactors. And if you have any knowledge about the chemical reaction engineering in that case you see that there are three different type of basic reactor, batch reactor, continuous reactor, plug flow reactors. And sometimes the batch reactor is classified or subdivided into the batch and semi batch type of a reactor.

So, all these type of reactors are extremely useful in the polymerization process. And if you recall in the previous lecture we discussed about the beads formation in under the head of suspension polymerization.

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Control strategies for polymerization process

For production of polymers in industries various types of reactors are used such as batch, semi-batch reactor and continuous reactors.

➤ **Control in continuous reactors**

In free-radical polymerization the source of non-linearity is the autocatalytic nature of polymerization reaction i.e. gel effect which causes uncontrollable reactions, excessive temperature rise, rapid conversion and equipment plugging etc. There are four mode of operations With continuous polymerization:

- Startup
- Steady-state operation
- Grade transition
- Shutdown



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There we use the batch reactor with the fitted heating and cooling jacket and agitation assembly etcetera. So, this particular the importance of a reactor in the polymerization process is extremely important. And that reactor should have a proper control methodology, proper control protocols so that the losses can be minimized. Proper efficiency of the reaction can be achieved.

Energy efficient the process may become the more and more energy efficient etcetera. So, this type of thing should be in our mind that we should have a feasible reactor process. We should have a feasible polymerization process not at the cost of the adversity in the polymer final polymeric product. So, based on this particular picture in our mind let us have a discussion about the various kind of control protocols in different type of reactors being used in the polymerization process.

Now first in this category is the control usually control in the continuous reactor. Now obviously because of the offering of more and more easiness and more and more capacity building these continuous reactors are extremely important in all kind of chemical operations and especially in the polymerization process.

But if you see the other things into your cognitions like the reactants, importance of reactant and how these reactants or these monomers and other allied components they play vital role during the formation of the polymerization process. Then it gives you a better choice among

batch, semi batch reactor and continuous reactor. So, let us have a look about the control methodology in the continuous reactor.

Now usually in free radical polymerization the source of nonlinearity is the autocatalytic nature of polymerization reaction. And sometimes it is referred as a gel effects. And gel effect usually causes the uncontrollable reaction. And sometimes because of the exothermicity in the nature sometimes there may be a chance that excessive temperature rise may achieve during the course of polymerization process.

It may create the rapid conversion. And sometimes because you are attributed to the rapid conversion and there may be a chance that equipment plugging may occur. Sometimes, if you are using the impellers or agitators, so the polymeric product may get deposit over the shaft of those impellers etcetera and if you are having because it is a continuous type of reactor.

Sometimes if you are taking the output it may clog this one. This may create further and further problem in the reactor system. So, usually this type of a situation needs to be addressed while we decide the control protocol or control methodology in the continuous type of reactor. Now usually there are four modes of operation with the continuous polymerization.

One is the startup the first and foremost that is very important thing in polymerization process. Because sometimes startup may create a problem as at the start you are having all the reactants the sufficient quantity and then there may be a chance sometimes the rapid shoot up may create. But if you are talking about the autocatalytic type of thing sometimes it may become a little sluggish and then it may enhance the things.

We will discuss this thing in subsequent slides. Then steady state operation. You are always looking for this steady state operation so that you can have a proper control in those continuous reactors. Then grade transition and last one is the shutdown. Because shutdown is again played a very vital role because at what time you are truncating the reaction at what time you are putting or at what time you are extracting the things that is important.

So, shutdown is again very important. Now during the startup and shutdown process of these kind of a reactor the prime objective is safety. The product quality control is also concerning


during the steady state operation and the grade transition. Now the safety sometimes there are several accident in past that took place just because of this improper protocol followed by the people in during the startup and shutdown process of those polymerization process.


Then you need to look into the control objective and strategies protocols. Now these are different in each cases. There are modern strategies involved in two level of hierarchical structure with base regulatory control. Now usually at the first level of control, the process manipulated variables are monomer, flow rate and temperature.

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**Control strategies for polymerization process**

- During the startup and shutdown the primary objective is safety, product quality control is concerning during the steady state operation and grade transition.
- The control objective and strategies are different in each cases.
- The modern strategy involves two level hierarchical structure with base regulatory control.
- At first level of control the process manipulated variables are monomer flow rates and temperatures.
- The set point of these process variables are determined at higher advanced control level to obtained desired product characteristics.





Now remember the at the start if you are taking the start of the monomer concentration probably, they are on the higher side you are having the flow rate that you need to look into. And sometimes because of the exothermicity of the reaction, sometimes endothermicity of the reaction you need to have a proper control over the reaction. Now the set point of these process variables are usually determined at higher advanced control level to obtain the desired product characteristics.

Again, I am repeating that we must have this thing into our consideration that whenever we talk about the polymerization process my focus of attention is my final product. Now there are certain base regulatory control the foremost thing in this base regulatory control is my temperature controller. Now sometimes as I told you that you need to encounter with the problem of exothermic polymerization.

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## Control strategies for polymerization process

### Base regulatory control

#### ❖ Temperature control

- For highly exothermic polymerization process the temperature control (Cascade control with two PID controller used) is universally important regardless of operating mode for safety and polymer properties.
- It is important when reactor operate at unsteady state operation.
- The rate of change of reactor temperature must be carefully monitored when the reaction is highly exothermic in nature and unreacted monomer is present in the reactor.
- The cooling is achieved by fluid flowing outside the reactor in the surrounding jacket or the cooling tube inside the reactors.



So, for highly exothermic polymerization process, the temperature control usually they are attached with the cascade control with two PID controllers. Now the temperature control is universally important regardless of the operating mode of safety and polymer properties. Because a slight variation in the temperature control may create severe problem, that may be catastrophic in nature.

So, this particular thing because exothermicity may create further problem during the course of action now it is important when the reactor operates at unsteady state operation. Now the rate of a change of a reactor temperature this must be carefully monitored when the reaction is highly exothermic in nature. And unreacted monomer is present in the reactor.

So, that is why again it may create a future problem of uncontrolled chains, formation of chains, highly viscous in nature. Because at the time of reaction you will not be able to assess the importance of temperature because the viscosity and temperature both are interlinked so higher the temperature, viscosity would be on the lower side. But when you go for shut down of a reaction then it may create a problem.

So, that is why this particular approach is important. Now cooling is usually achieved by the fluid flowing outside the reactor. Now this is your reactor and usually the cooling jackets are encountered with this reactor. So, this is achieved by the fluid flowing outside the reactor maybe in the surrounding jackets or sometimes cooling tube within the reactor. There may be certain cooling tubes within the circulating cooling tubes within the reactor.


So, by this way you can maintain the proper temperature control. Because this way you are having the things in your hand but sometimes you may not have sufficient things with respect to the reaction mechanism. So, this thing should be kept handy during the things of polymerization.

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**Control strategies for polymerization process**

❖ **Flow control**

- The sum of reactant flow rates has effect on steady state and dynamic behavior of reactor. If the reactor has to be operated at desired steady-state then the total feed rate should be maintained at constant rate.
- The flow rate of monomer and solvent are dominant and the flow rates of chain transfer agent, cross-linking agents and initiators are small relative to dominant rates. These small flow rate have effect on the properties of the polymers obtained as product after the reaction.
- The multiple single loop PID controllers are typically used to maintained the flow rates constant and to set the desired value for small flow rates (manipulated variables).



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Next approach is the flow control. Flow control is again very important. The sum of reactant flow rates they has effect on steady state and the dynamic behavior of reactor. Now if the reactor has to be operated at desired steady state, then sometimes the total feed rate should be maintained at constant level.

See if you are having unsteady feed rate or if you are having the variation in the feed rate, then probably there may be a chance that your polymerization may go on the higher side or sometimes you may have some sticky mass type of a thing which you cannot process further. And if you are having the lesser flow rate, then there may be a chance that your reaction mass may be triggered to the undesired level.

And sometimes there may be a chance that you may have some byproducts etcetera. If you are having dissimilar type of polymerization practice, the flow rate of monomer and the solvent usually they are dominant. Because they are usually having some intimate contact with each other so these two are the deciding factor about the fate of your polymerization process.

The flow rates of chain transfer agent sometimes cross linking agent as I discussed in the previous lecture about the polystyrene and diene. There the diene acts as a cross linking agent. So, the flow rate of chain transfer and a cross linking agent and sometimes the initiator they are having the small relative to the dominance rate although their importance cannot be overlooked.

But they are having the lesser importance towards the fate of this polymerization. So, these small flow rates have effect on the properties of a polymers obtained as product after the reaction. See I told you that about the initiations, cross linking agent. Sometimes the porosity controller like polystyrene diene when you synthesize the bead, the toluene is being used as a porosity controller. Gelatin is used as a particle size controller.

So, they are having very minimal effect in the gross polymerization. So, their flow rate usually their people sometimes if they are using the continuous type of a reactor their flow rate having the minimal effect in the process of polymerization. Now the multiple single loop PID controllers, they are typically used to maintain the flow rate constant and to set desired value of small flow rates and they are referred as manipulated variables.

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### Control strategies for polymerization process

#### ➤ Control in semi-batch/batch reactors

##### ☐ Feedback control

The control characteristics of the process of batch polymerization involve the requirement to track the desired trajectories from start to finish of the run with the objective that the final product has some desired properties.

The effective control strategy involves the following two-steps:

- ✓ Determine the input and output profiles (trajectories) desired to manufacture a product with desired properties.
- ✓ Design a control scheme to track the selected profile as close as possible.



Now let us have a look because in the previous slides we discussed about the continuous reactor control. Now let us have a look small look into the control in semi batch or a batch reactor. See the detailed study we will discuss in due course of time in the different chapters. Now the important aspect in the batch and semi batch reactor is the feedback control, the control characteristics of the process of batch polymerization.

It sometimes involves the requirement to track the desired trajectories from start to finish of the run. This is with the objective that the final product should have the desired properties which you are looking for. Usually, there are various strategies being involved in the feedback control. One is that determine the input and output profiles of trajectories. This is desired to manufacture a product with the desired properties.

See whenever we talk about the desired properties every time you are having the tailor-made properties you are looking for in that particular polymer. Now you need to design a control scheme to track the selected profile as close as possible. Now trajectory monitoring it can be accomplished by two ways.

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### Control strategies for polymerization process

- Trajectory monitoring can be accomplished by two ways: online inspection in a single batch, where input adjustment is made digitally as the batch progresses.
- Run to run control over several batches, where adjustment is not made digitally during the batch, but instead input trajectories are calculated between batches, using the information obtained from previous batches to decide how to operate the next.
- **Run-time outputs**- which evolve with run time of the batch
- **Run-end outputs**- That consists of variable process values at batch end e.g. product quality, batch time and maximum reactor temperature.



One is the online inspection in a single batch where the input adjustment is made digitally as the batch progresses. Second is that run-to-run control over several batches where the adjustment is not made digitally during the batch but instead sometimes the input trajectories they are calculated between the batches. So, using the information obtained from various kind of a previous batches to decide how to operate the next one.

So, these two trajectories are important. Let us have a brief look about these run time output like which evolve with the run time of the batches. And second one is the run and outputs. This consists of variable process values at batch. Sometimes referred as a product quality, sometimes batch time because time is again a very important factor and the maximum reactor




temperature. So, this thing is again very crucial. Apart from this we may look for online control.


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Control strategies for polymerization process

□ **Online control**

- It consists of monitoring the profiles that were predetermined offline for an individual batch.
- The goal is to monitor the profiles that were pre-computed using the nominal models.
- Tracking the pre-computed temperature profile by changing the heating / cooling rate of the reactor with online run time overhead power.
- The molecular weight profile for the drug can also be monitored by changing the chain transfer agent's feed rate. Use of an observer to reconstruct the product's average molecular weight in the reactor form another measurement is required.



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This online control is a very integral part of your control methodologies of the polymerization process. Now it consists of monitoring the profile that we predetermined offline for an individual batch. Now the objective is to monitor the profiles that were pre computed using the nominal model. It is just like that you are having the pre decided polymer properties and you are trying to control the various input in that particular polymerization reactor.

Maybe the flow rate, may be the concentration etcetera. Now tracking the pre computed temperature profile sometimes by changing the heating cooling rate of the reactor with online runtime overhead head power. Now see this is a most common phenomenon. Because you see that if your reaction are exothermic in nature in that case there may be a tendency towards the reaction mass that the temperature inside the reaction mass may go on the higher side.

Some if you are handling with the catalytic reaction, then there is a chances of efficacy of that particular reaction. And if and usually this efficacy works within the domain of our temperature range. So, if it crosses that particular temperature range, then efficiency of that reaction or the conversion factor of the reaction mass is usually adversely affected. So, based on this particular protocol sometimes you may need to incorporate more and more cooling.

And this is most common when there is a thermal runaway reaction in the polymeric system. So, you need to track those kind of a pre computed temperature that you need to work within

that particular temperature range. It is extremely important. The molecular weight profile for the like this can also be monitored by the changing of chain transfer agents feed rate. Now use an observer to reconstruct the products average molecular weight in the reactor from the another measurement is required.

See we are always talking about the molecular weight distribution, MWD, average molecular weight number, average molecular weight etcetera. We are talking about this one. And we have also discussed that this average molecular weight or molecular weight distribution plays a very vital role decide about the deciding the properties of the polymer. So, you need to keep an eye over the products molecular rate distribution throughout.

Now if it crosses the acceptable limit, then you need to take a drastic step to control the things or if it is below the desired level, then again you need to take some drastic step to change the things. So, that is again the under the head of an online control system that is you need to have look into the measurement system and other devices so that you can put some more effort for the control of those molecular weight distribution.


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**Control strategies for polymerization process**

The following diagram showed the online control of the run time outputs  $y$  in a batch reactor.

**Run-to-run control**

The objective of the run-to-run control is to exploit the peculiarities of batch processes such as their repetitive nature like the procedure for controlling the current batch explicitly incorporates relevant information from the previous one.

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Now here you can see the online control of the runtime output  $y$  in a batch reactor. Usually, it is having a small flow diagram this is your batch reactor and here you are having the control device usually the signal. And if this is the output and if it is not having the desired one in that case you may put a signal to here maybe signal maybe plus and or minus so that you can rectify the things accordingly.


So, this is the importance of your online controller the run-to-run control this objective of run-to-run control is to exploit the peculiarities of batch processes such as their repetitive nature like the procedure of controlling the current batch reactor may be explicitly incorporates relevant information from the previous one. So, this is the objective of this one.

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Control strategies for polymerization process

- Here input profiles are not modified online, rather the input profiles and the resulting product output are used at the end of the kth batch to assess the next input profiles.
- Adjustment run to run helps to reach run-end goals and can be applied in a particular way.
- The discrepancy between expected and actual run-end outputs can be used in the instance to modify the process model, and the modified model is then used to adjust the controller parameters.
- Alternatively, it is possible to parameterize the input profiles and to change the input parameters from one run to the next to implement run-end objectives.



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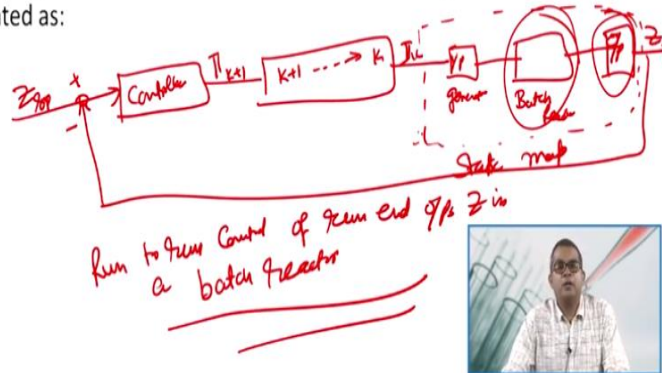
Now here the input profiles they are not modified online. Rather the input profiles and the resulting product output they are used at the end of say the batch to assess the next input profiles. Now sometimes the adjustment to run to run helps to achieve or to reach the run and goals. And it can be applied in a different way which is usually determined by the end product profiling. There may be certain discrepancy in that particular process.

Now these discrepancy between the expected and actual run and output can be used in the instance to modify the process model. And the modified model usually is then used to adjust the controller parameter. Sometimes it is possible to parameterize the input profile and you may change you may need to change the input parameter from one run to the next to implement the run end objective.

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## Control strategies for polymerization process

The flow diagram for run to run control of run-end output in a batch reactor is represented as:



Now here this particular thing is be clear by this particular diagram. Here you are having one controller. Then this is the input and product generator. This is your batch reactor and this is your output. Now this particular thing is the static map. And here we are providing, this is the run-to-run control of run end in a batch reactor. So, this is the flow diagram for run-to-run control of a run end output. This is your run end output. And this is your batch reactor is given here.

Now if any abnormality, then it can easily sensitise to the controller and input stream so that you can alter the things accordingly. So, this is bit alteration. So, in this lecture, we had discussion about the various control protocols used for the polymerization process. And these are the basically related to the product profiling. They are related to the different type of reactors, batch reactor, continuous vector semi batch reactors etcetera.

Their efficacy about the things related to the polymerization process how we can control with the different ingredients or different reactants towards the polymerization reactor and if there is any abnormality in the system, then how we can rectify. In this particular lecture, we discussed that how the temperature controller, how that the control of other things like the different initiators, different type of a porosity controllers, cross linking agents, their things are important.

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## References

- ❖ G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 | DOI:10.1002/047147875X
- ❖ J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1
- ❖ M. Szwarc, Marcel Van Beylen (auth.) - Ionic Polymerization and Living Polymers, Springer Netherlands, (1993)
- ❖ Badi N., Lutz J. Francois., Sequence in polymer synthesis, Chem. Soc. Rev., 2009, 38, 3383–3390 | 3383.



So, we try to give a brief overview about these kind of control methodologies. Now remember these control methodologies are integral part of any kind of a polymerization process. And the fate of the end product is usually determined with the help of these kind of controlled methodology, discussed about the runaway reactions. Runaway variations sometimes may create a problem for the catalytic polymerization reactions etcetera.

So, by this way, we are ending this particular aspect related to the control strategy. And next lecture onward, we will discuss about the morphological aspect of polymerization process and polymer products. Because this thing morphology is again very important thing related to this polymerization process, thank you very much.