

Lecture 45

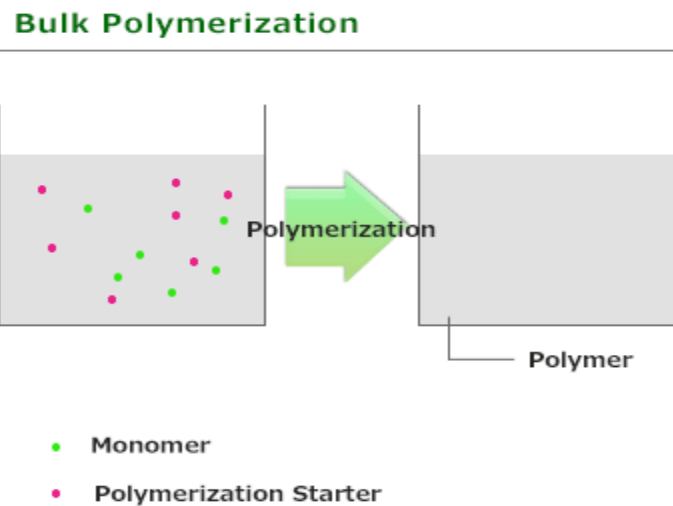
Polymerization techniques

There are four types of polymerization techniques:

1. Bulk Polymerization
2. Solution Polymerization
3. Suspension Polymerization
4. Emulsion Polymerization

Bulk Polymerization:

Bulk polymerization or mass polymerization is carried out by adding a soluble initiator to pure monomer in liquid state. The initiator should dissolve in the monomer. The reaction is initiated by heating or exposing to radiation. As the reaction proceeds the mixture becomes more viscous. The reaction is exothermic and a wide range of molecular masses are produced. This process can be used for Free radical polymerizations and some step-growth (condensation) polymerization.



Advantages:

Bulk polymerization has several advantages over other methods, these advantages are[citation needed]:

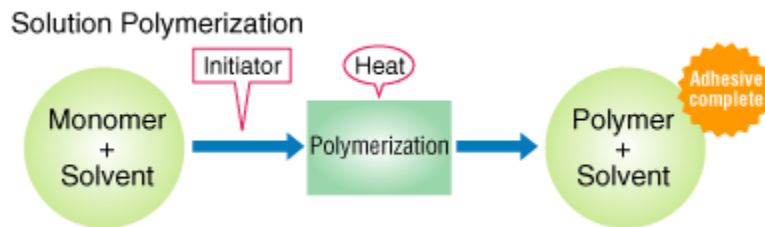
1. The system is simple and requires thermal insulation.
2. The polymer obtained is pure.
3. Large castings may be prepared directly.
4. Molecular weight distribution can be easily changed with the use of a chain transfer agent.
5. The product obtained has high optical clarity

Limitations:

1. Heat transfer and mixing become difficult as the viscosity of reaction mass increases.
2. The problem of heat transfer is compounded by the highly exothermic nature of free radical addition polymerization.
3. The polymerization is obtained with a broad molecular weight distribution due to the high viscosity and lack of good heat transfer.
4. Very low molecular weights are obtained.
5. Gel effect should be there

Solution Polymerization:

This method is used to solve the problems associated with the bulk polymerization because the solvent is employed to lower the. Viscosity of the reaction, thus help in the heat transfer and reduce auto acceleration. It requires requires the correct correct selection of the solvents. Both the initiator initiator and monomer be soluble in each other and that the solvent are suitable for boiling points, regarding the solvent-removal steps.



Advantages:

1. Solvent has low viscosity, reaction mixture can be stirred
2. Solvent acts as a diluent and aids in removal of heat of polymerization
3. Solvent reduces viscosity, making processing easier
4. Thermal control is easier than in the bulk and
5. “Cheap” materials for the reactors (stainless steel or glass lined.)

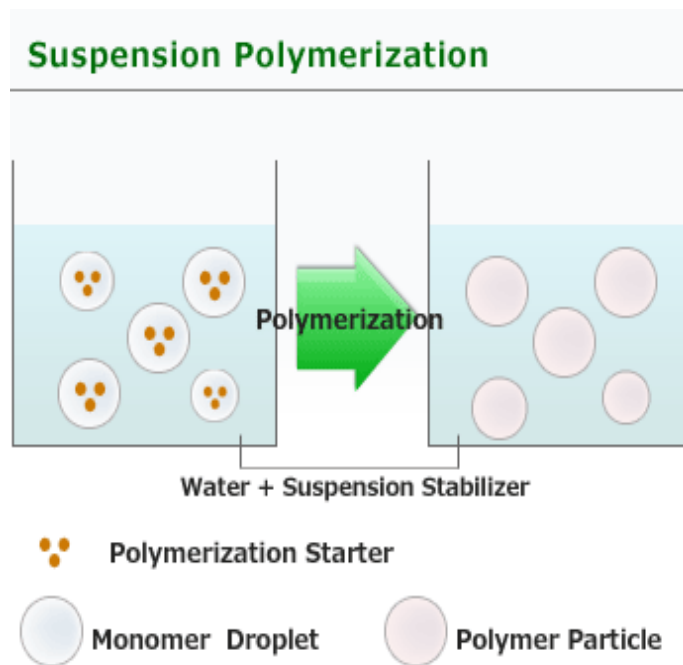
Disadvantages:

1. Reduce monomer concentration which results in decreasing the rate of the reaction and the degree of polymerization
2. Mobility is reduced and this can affect termination events, so the rate of reaction is increased
3. Solvent may terminate the growing polymer chain, leading to low molecular weight polymers
4. Difficult to remove solvent from final form, causing degradation of bulk properties

5. Small yield per reactor volume
6. The requirements for a separate solvent recovery step

Suspension Polymerization:

(Pearl Polymerization) If the monomer is insoluble in water, bulk polymerization can be carried out in suspended droplets, i.e., monomer is mechanically dispersed. The water phase becomes the heat transfer medium. Since it (the water??) is a continuous phase, viscosity changes very little as the monomer converts to polymer, so the heat transfer is very good. In this system, the monomer must be either 1) insoluble in water or 2) only slightly soluble in water, so that when it polymerizes it becomes insoluble in water. The behavior inside the droplets is very much like the behavior of bulk polymerization, but since the droplets are only 10 to 1000 microns in diameter, more rapid reaction rates can be tolerated (than would be the case for bulk polymerization) without boiling the monomer. The advantages are better heat control of the reaction, and separation is much easier than in solution polymerization. The disadvantage is that few monomers are water soluble.

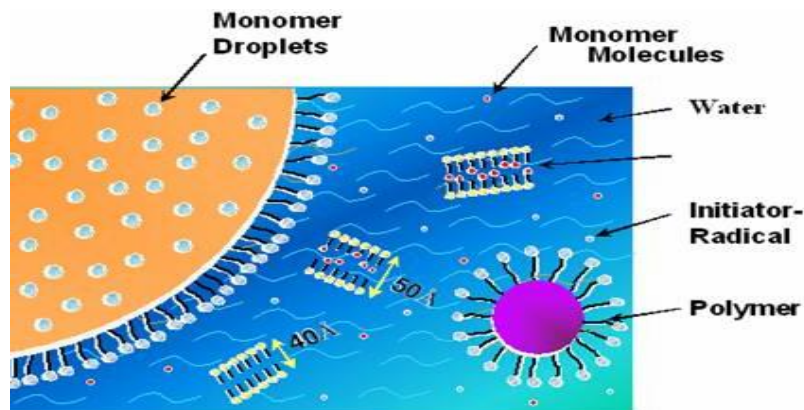


Emulsion Polymerization:

The "ingredients" for an emulsion polymerization include 1) a water soluble initiator, 2) a chemical emulsifier, and 3) a monomer that is only slightly soluble in water, or completely insoluble.

The two differences between emulsion and suspension polymerization are: 1) that a suspension polymerization is a mechanical process, and must have a stabilizing agent until the droplets are far apart, and 2) the emulsion polymerization is a chemical process which requires a surfactant to make the monomer "emulsify."

Its common type is an oil-in-water emulsion. The droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water. Water-soluble polymers, such as certain polyvinyl alcohols Hydroxyethyl celluloses are used to act as emulsifiers/stabilizers.



Advantages of Emulsion Method:

1. High molecular weight polymers can be made at fast polymerization rates.
2. In others lie a tradeoff between molecular weight and polymerization rate.
3. The continuous water phase is an excellent conductor of heat that Allows the heat to be polymer molecules are contained within the particles,so it is method to increase the rate of many reactions.
4. Since polymer molecules contained within water viscosity remains close to that of water and is not dependent on molecular weight.
5. The final product can be used as is and does not generally need to be altered or processed.

Disadvantages

1. For dry (isolated) polymers, water removal is an energy-intensive process
2. They are usually designed to operate at high conversion of monomer to polymer.
3. It may result in significant chain transfer to polymer.

References:

- <http://www.britannica.com/science/solution-polymerization>
- <http://www.nitto.com/sea/en/rd/base/adhesive/composite/>
- <http://www.slideshare.net/Santachem/polymerization-techniques>
- <http://web.stanford.edu/class/cheme160/lectures/lecture13.pdf>
- <http://web.mst.edu/~jstoffer/chem381/chap21.html>