

## Lecture 42

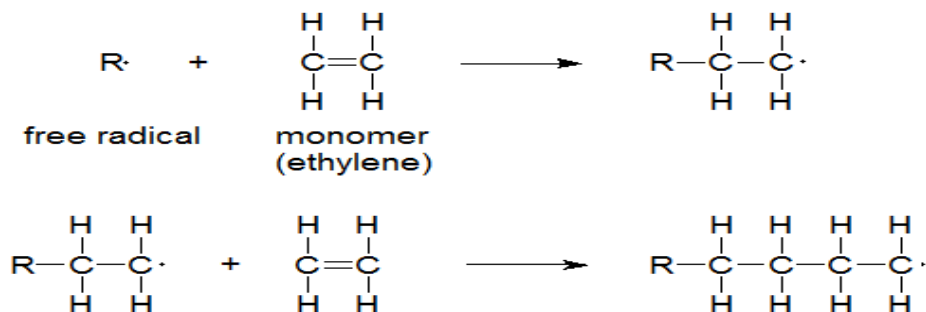
### Polymerization

#### Methods of Polymerization:

There are four types of polymerization reactions Addition or chain growth polymerization, Coordination polymerization, Condensation or step growth polymerization and Copolymerization.

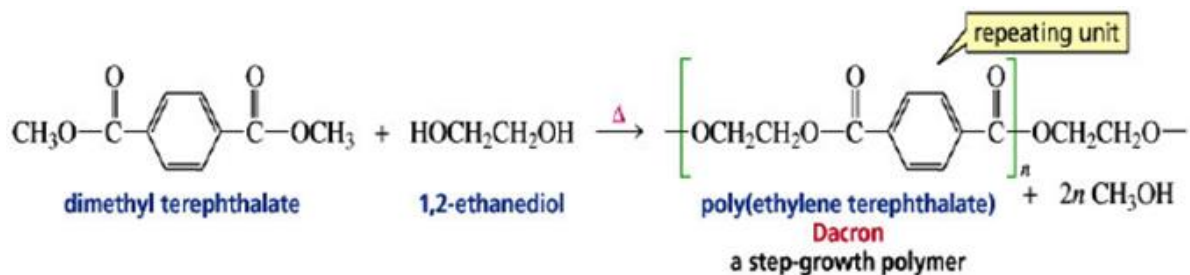
#### Addition Polymerization:

In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers normally employed in this type of polymerization contain a carbon-carbon double bond (unsaturated compounds, e.g., alkenes and their derivatives) that can participate in a chain reaction.



#### Condensation Polymerization:

This type of polymerization generally involves a repetitive condensation reaction (two molecules join together, resulting loss of small molecules) between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.



### **Thermodynamics of Reaction:**

Thermodynamics of polymerization determines the position of the equilibrium between polymer and monomer(s). The well-known thermodynamic expression is

$$\Delta G = \Delta H - T\Delta S$$

It yields the basis for understanding polymerization/depolymerization behavior. Where ' $\Delta S$ ' is the disorder of the system, ' $\Delta H$ ' is heat energy and ' $T$ ' is temperature. For polymerization to occur (i.e., to be thermodynamically feasible), the Gibbs free energy of polymerization  $\Delta G_p < 0$ . If  $\Delta G_p > 0$ , then depolymerization will be favored.

### **Enthalpy and Entropy:**

Standard enthalpy and entropy changes  $\Delta H^\circ_p$  and  $\Delta S^\circ_p$  are reported for reactants and products when Temperature is  $25^\circ\text{C}$  or  $298\text{K}$  then the Monomer is Pure, bulk monomer or  $1\text{ M}$  solution and Polymer is Solid amorphous or slightly crystalline.

### **Thermodynamics of Depolymerization:**

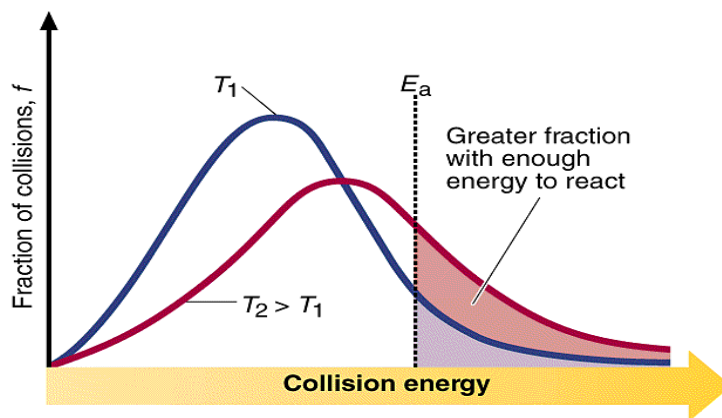
Change in entropy is always less than zero ( $\Delta S_p < 0$ ) for nearly all polymerization processes. Since depolymerization is almost always *entropically* favored. So change in heat energy  $\Delta H_p$  must then be sufficiently *negative* to compensate the unfavorable entropic term. Only then polymerization will be thermodynamically favored by the resulting  $\Delta G_p$  value.

### **Temperature and Thermodynamics:**

Polymerization is favored at low temperatures  $T\Delta S_p$  is small and Depolymerization is favored at high temperatures when  $T\Delta S_p$  is large. When  $T\Delta S_p$  overrides then  $\Delta H_p$  and thus  $\Delta G_p > 0$  thermal instability of polymers results due to which the system to depolymerize.

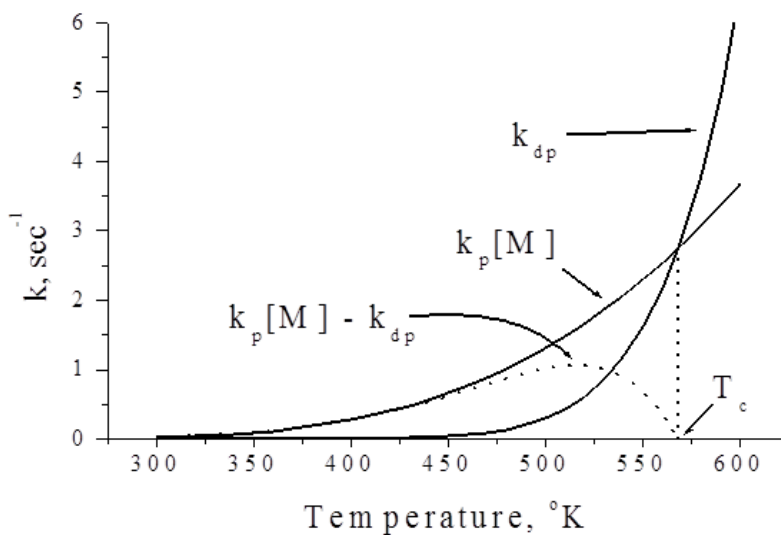
### **Activation Energy:**

It is a minimum amount of energy required to start a chemical reaction. The activation energy for the de-propagation reaction is higher as Compared to depropagation reaction. The rate of depropagation reaction increases with increase in temperature.



### Ceiling Temperature:

Ceiling temperature is a measure of the tendency of polymers to revert to their monomers. When a polymer is at its ceiling temperature, the rate of polymerization and depolymerization of the polymer are equal. Generally, the ceiling temperature of a given polymer is correlated to the steric hindrance of the polymer's monomers. Polymers with high ceiling temperatures are often commercially useful.



### References:

<http://www.ncbi.nlm.nih.gov/pubmed/24825826>

<http://matse1.matse.illinois.edu/polymers/prin.html>

<http://cuiet.info/download/chemistry/Types%20of%20Polymerization%20&%20Techniques.pdf>