**Polymer notes**

**Unit III & IV**

**Mechanism of polymersation reaction**-

Polymerization reactions are of following types-

1. **Addition polymerization reaction**
2. **Condensation polymerization reaction**
3. **Addition polymerization reaction**- Addition polymerization reaction are of following types-
4. **Free radical addition polymerization**
5. **Anionic addition polymerization**
6. **Cationic addition polymerization**
7. **Free radical addition polymerization-** free radical addition polymerization is carried out in three steps-
8. **Initiation-** In this step the hemolytic fission of peroxide initiator is done to generate free radicals. This free radical is then reacted with a monomer to form a monomer free radical.

R-O-O-R → R-O o + R-O o

Peroxide free radicals

R-O o  + M → R-O-Mo

Monomer monomer Free radical

1. **Propogation**- In this step n numbers of monomers are further added to the monomer free radical to form a long chain monomer free radical.

R-O-Mo + nM → R-0-(M)n-Mo

Where ‘n’ is the number of monomers.

1. **Termination**- in this step the termination of growing monomer chain is done by two methods-
2. **By coupling**-When the two free radical radical growing chains combine together, the two free radicals combine to form a new bond, and thus the chain is terminated.

R-O-Mo + oM-O-R → R-O-M-M-O-R

1. **By chain transfer method**- In this method the free radical growing chain is reacted with a compound ‘HX’ to terminate the chain. In this method the free radical is transferred on the ‘X’ and no further addition of monomer is possible.

R-O-Mo + HX → R-O-MH + Xo

1. **Mechanism of Anionic addition polymerization**-:

Anionic addition polymerization is carried out in three steps-

1. **Initiation**- in initiation step the dissociation of a base is done to generate an anion. This anion is reacted with a monomer having a electron withdrawing group an unsaturated bond, to form a carbanion.

**KNH2 K+ + NH2-**

Base Anion

**KNH2  + CH2=CH**  NH2-CH2-CH-

R

R

Carbanion

Where ‘R’ is a electron withdrawing group like –OH, CN, COOH, Cl etc.

1. **Propogation-**In this step ‘n’ numbers of monomers are further added to the carbanion to form a long chain carbanion.

NH2-CH2-CH- + n **CH2=CH**  NH2-(CH2-CH)n-CH2-CH-

R R R R

Long chain carbanion

1. **Termination-** Termination is done by reacting the long chain carbanion with trace amount of water.

NH2-(CH2-CH)n-CH2-CH- + H2O NH2-(CH2-CH)n-CH2-CH-H + KOH

R R

R R

The anionic addition polymerization is also called Living polymerization because the negative charge remains stable on the carbanion, when all the monomers are consumed during the reaction the propagation temporarily stops without termination and on further addition of more number of monomers the addition of monomers again starts.

1. **Mechanism of Cationic addition polymerization-**

Cationic addition polymerization is also carried out in three steps-

1. **Initiation**- In this step the dissociation of a acid or a Lewis acid is done to generate a cation. This cation is reacted with a monomer having an electron donating group and an unsaturated bond.

H2SO4 H+ + HSO4-

BF3  + H2O H+ + BF3OH-

Lewis acid

H+ + CH2= CH H-CH2-CH+

**R R**

**Carbocation**

Where ‘R’ is a electron donating group like CH3 C2H5 groups.

1. **Propogation**- in this step n numbers of monomers are further added to the carbocation to form a long cahin carbocation.

H- CH2-CH+ + nCH2-=CH H-(CH2-CH)n-CH2-CH+

R R R R

Long chain carbocation

1. **Termination**- Termination is done by reacting the long chain carbocation with trace amount of water.

H-(CH2-CH)n-CH2-CH+ + H2O H-(CH2-CH)n-CH2-CH-OH + H2SO4

R R R R

1. **Condensation polymerization**- It is also called step growth polymerization. In this method the monomers are added on step wise manner and there is elimination of small by product molecules in each and every step. Formation of Nylon- 6,6 is the best example of step growth polymerization