

# Physical Chemistry

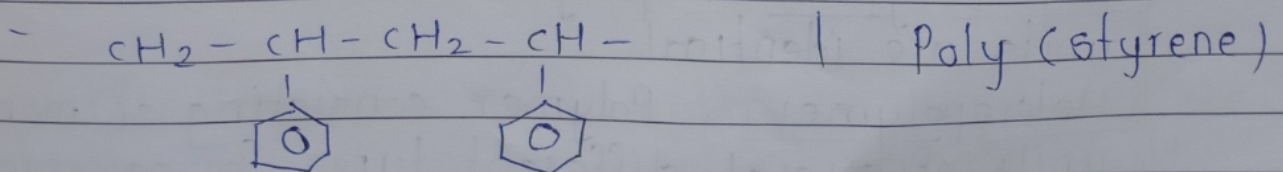
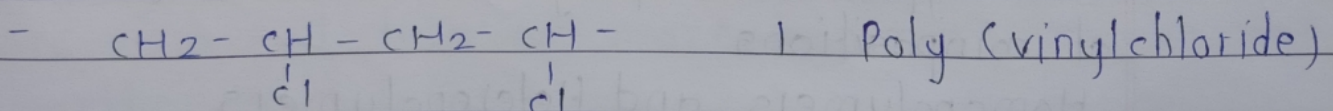
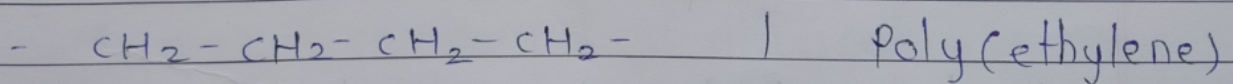
## Macromolecules

24-2-21

### Introduction:

- 1) Melting point : As the length of hydrocarbons get longer then melting point grows weaker. due to this viscosity, hardness, toughness changes in plastics, motor oil, diesel and gasoline respectively.
- 2) Bonding - Covalent in Diamond, Ionic in NaCl, polar in H<sub>2</sub>O respectively
- 3) classification -
  - Inorganic : i) Natural - eg, clays, sand etc.
  - ii) Synthetic - eg, silicones, silanes, phosphazenes etc.
  - organic : i) Natural - eg polysaccharides (carbohydrates), proteins, DNA, Natural rubber, silk etc.
  - ii) Synthetic - eg, polyfins, polyesters, polyethanes

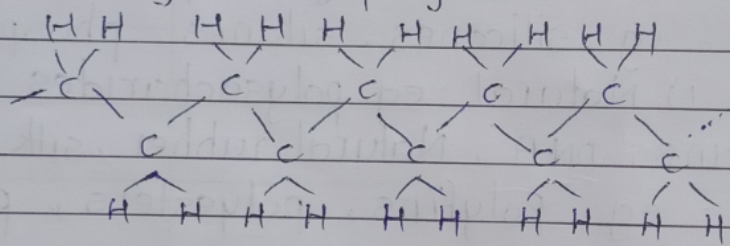
Polymers are long usually linear chains containing of a large number (n) monomer units for synthetic polymers usually  $N \sim 10^2 - 10^4$  for DNA  $N - 10^9 - 10^{10}$





4. Three main factors which governs the physical properties of polymers.

- i) The monomers units are connected into a chain, thus their spatial movements are not independent, contrary to those of the molecules in low-molecular fluids, this is the reason why the polymer systems are anomalously pure in entropy.
- ii) The number of monomer units per chain is large  $N \gg 1$  existence of large dimensionless parameter. ~~eg~~ simplifies radically the construction of the theory.
- iii) Polymer chains are generally flexible
- iv) flexibility of a polymer chain



Rectilinear confirmations of a polyethylene chain shows on the picture, corresponds to minimum of the potential energy. All the monomer units are in the trans position, this confirmation would be an equilibrium one at  $T=0$

5. The types of the polymer molecules on the basis of compositions

Homopolymers and Heteropolymers

Homopolymers: polymer, whose monomer units are identical

Heteropolymers: Polymer consisting of monomer units of several different types. For eg. protein











\* chain growth polymerisation:

1. Typical chain reactions are fast reactions proceeds by three normally distinguishable processes

a) Initiation of the chain

b) Propagation or growth of the chain

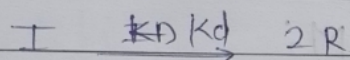
c) termination of the chain

(A fourth process, chain transfer may also be involved)

a) Initiation

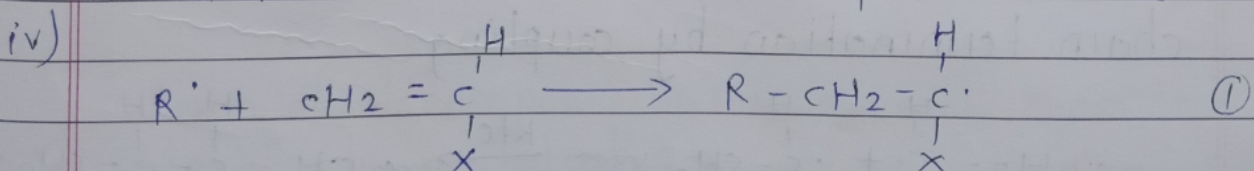
i) The initiation step is considered to involve two reactions

ii) The first is the production of free radicals from the dissociation of initiator

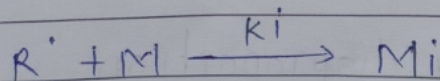


where  $k_d$  is the rate constant for the initiator dissociation. Its magnitude is usually of the order of  $10^{-4} - 10^{-6}$ . (The radical  $R'$  is often referred to as an initiator radical or a primary radical). The second part of the initiation step involves the addition of the radical  $R'$  to a monomer molecule as in

iii) second part of the initiation step addition of radical in a monomer molecule is depicted below



Reaction (1) may be abbreviated and generalised to

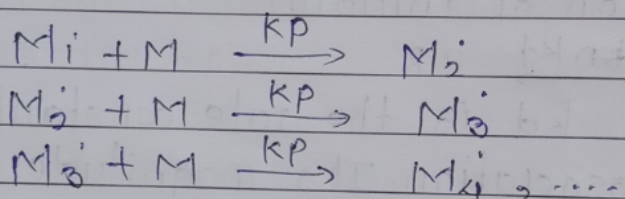




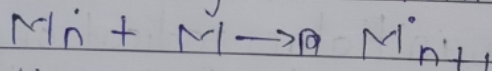
Where M stands for monomer and  $M_i$  actually represents  $RM_i^\cdot$ , that is monomer ended radical containing one monomer unit and an end group R. The rate constant for the reaction is  $k_i$

b) Propagation:

Initiation is followed by chain propagation, which consist of the growth of  $M_i$  by the successive addition of large number of monomer molecules. Each addition creates a new radical which has the same identity as the previous one, except that it is large by one monomer unit. The successive addition may be represented by



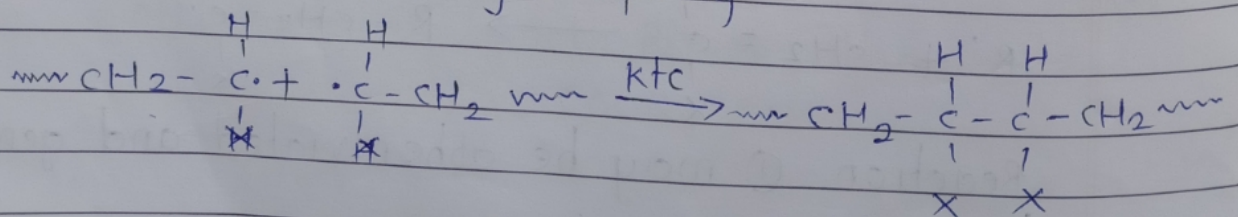
or in general terms



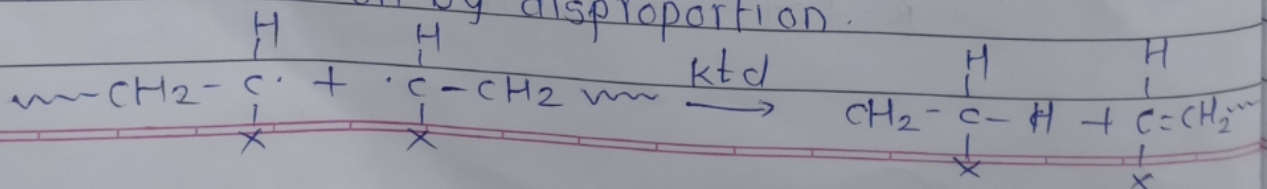
Where  $k_p$  is the rate constant for propagation the value of  $k_p$  for most monomers is in the range  $10^2 - 10^4$  L/mol s.

c. Termination:

chain termination by coupling

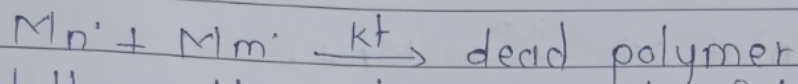
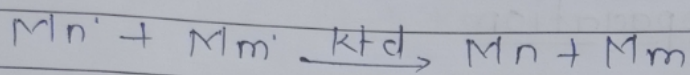
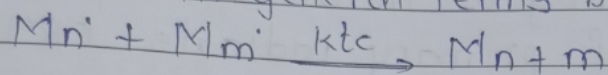


chain termination by disproportionation.





There two different modes of termination can be represented in general terms by,



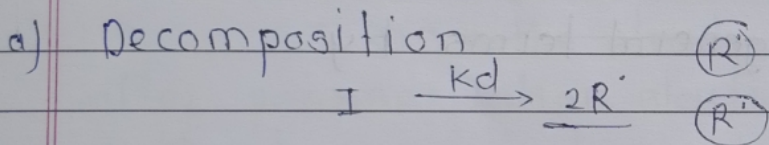
Where the particular mode of termination is not specified and the overall termination rate constant  $k_t$  is given by

$$k_t = k_{tc} + k_{td}$$

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### Kinetics of Radical polymerization (Macromolecules)

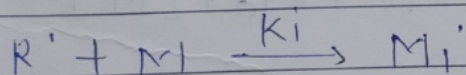
- Initiation



the rate of radical generation being then given

$$d[R \cdot] / dt = 2k_d [I]$$

b) chain initiation



Rate of decomposition is slower than the rate of chain initiation

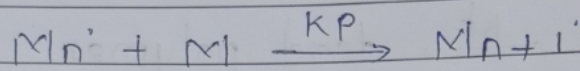
Rate of initiation :

$$R_i = \left( \frac{d[M_i \cdot]}{dt} \right) = 2f k_d [I]$$



where the factor  $f$  is the initiator efficiency or the efficiency of initiation, representing the fraction of primary radicals ( $R\cdot$ )

Rate of propagation



$$R_p = k_p [M] [M\cdot]$$

where  $[M]$  is the monomer concentration and  $[M\cdot]$  is the total concentration of all chain radicals, that is, all radicals of size  $M_1\cdot$  and larger.

Rate of Termination:

By coupling

These two modes of termination can be represented in general terms by

By coupling

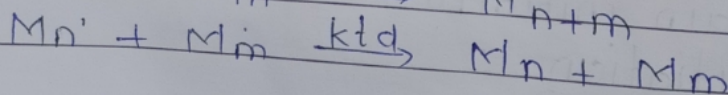
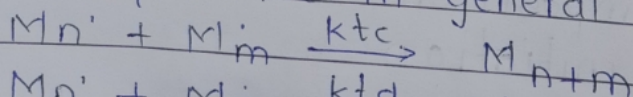
$$R_{tc} = 2k_{tc} [M\cdot]^2$$

By disproportionation

$$R_{td} = 2k_{td} [M\cdot]^2$$

$$R_t = 2k_t [M\cdot]^2 = 2(k_{tc} + k_{td}) [M\cdot]^2$$

These two different modes of termination can be represented in general terms by



Rate of chain polymerization is the rate of monomer disappearance, which is syno-



synonymous with the rate of polymerization, is thus given by

$$-\frac{d[M]}{dt} = R_i + R_p$$

since max number of monomer consumption is in the propagation compared to initiation

$$-\frac{d[M]}{dt} = R_p = k_p [M][M']$$

The assumption that the rate of initiation equals the rate of termination is called the 'steady state assumption'. It is equivalent to the following two statements:

$$R_i = R_t \quad \text{at steady state}$$

$$\text{and } \frac{d[M']}{dt} = 0 \quad \text{at steady state}$$

since the steady state is reached soon after polymerization starts, we can assume without significant error that it applies to the whole course of the polymerization. Substituting  $R_t$  from Eq.

$$R_i = 2k_t [M']^2$$

Rearrangement of eq.

$$[M'] = \left( \frac{R_i}{2k_t} \right)^{1/2}$$

$$R_t = 2k_t [M']^2$$

$$-\frac{d[M]}{dt} = R_p = k_p [M][M']$$

$$= R_p = k_p [M] \left( \frac{R_i}{2k_t} \right)^{1/2}$$

$$R_i = \left( \frac{d[M']}{dt} \right) = 2f k_d [I]$$

$$-\frac{d[M]}{dt} = R_p = k_p [M] \left( \frac{2f k_d [I]}{k_t} \right)^{1/2}$$

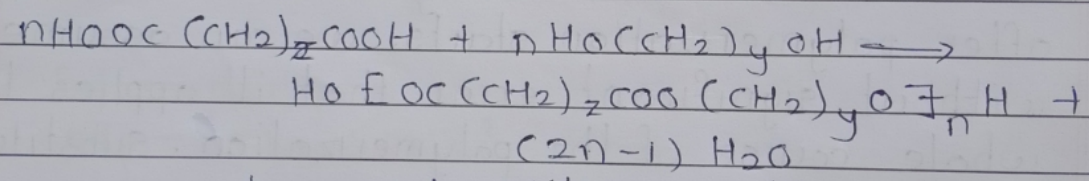


## Condensation (Step-Growth) Polymerization

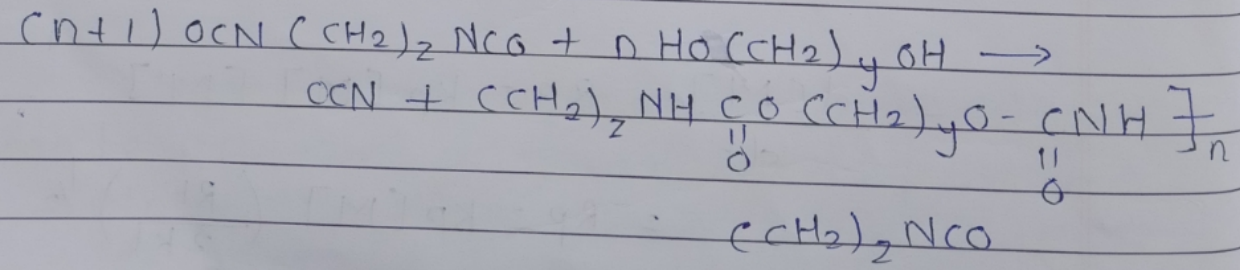
- Bifunctional monomers
- Involves elimination of small molecules
- Polymerization usually proceeds by the reactions between two different functional groups, or isocyanate and hydroxy groups

Step growth polymerization may be described as a stepwise or progressive conversion of a monomer with two reactive end groups to higher molecular weight homologues, which themselves retain two reactive end groups.

It may take place either by a polycondensation reaction, whereby a low-molecular-weight by-product is formed along with the polymer, as is exemplified by polyesterification:



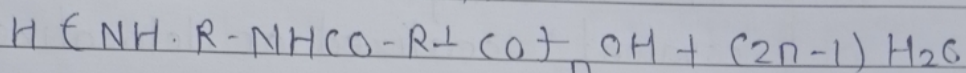
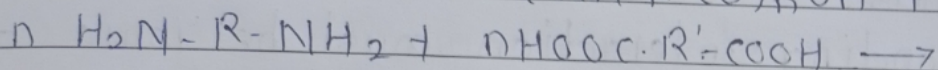
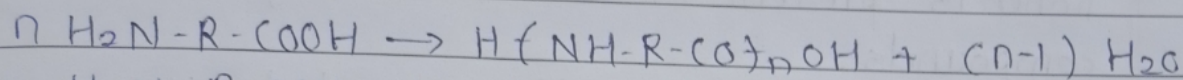
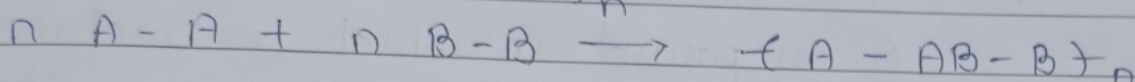
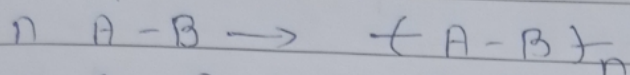
or by a polyaddition reaction in which the total reactants are incorporated in the polymer chain (and no by-products are formed), as is typified by polyurethane formation:



All step polymerization fall into two groups depending on the type of monomers employed. These are represented in a general manner by



The equations:



Step polymerization proceeds by a slow increase in the molecular weight of the polymer. Consider the synthesis of a polyester from a diol and a diacid:

