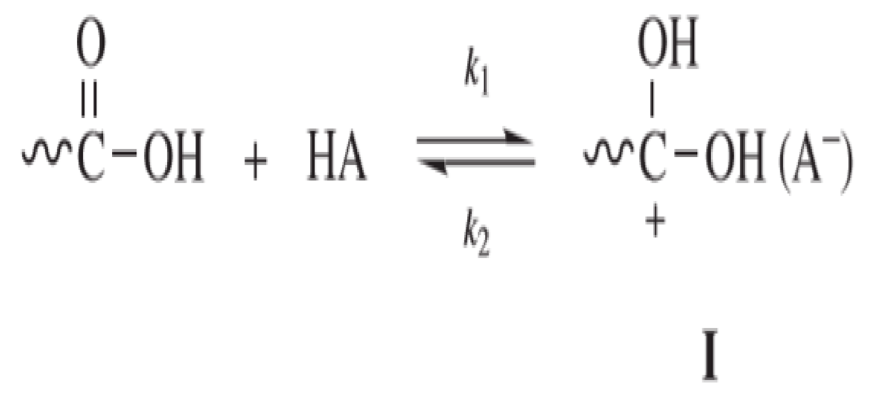
KINETICS OF CONDENSATİON OR STEP GROWTH POLYMERIZATION-2

The kinetics of the step-growth polymerization can be described with Flory’s equal reactivity principle. Flory assumed that all steps, that is, the formation of dimers, trimers and so forth, have equal rate constants.

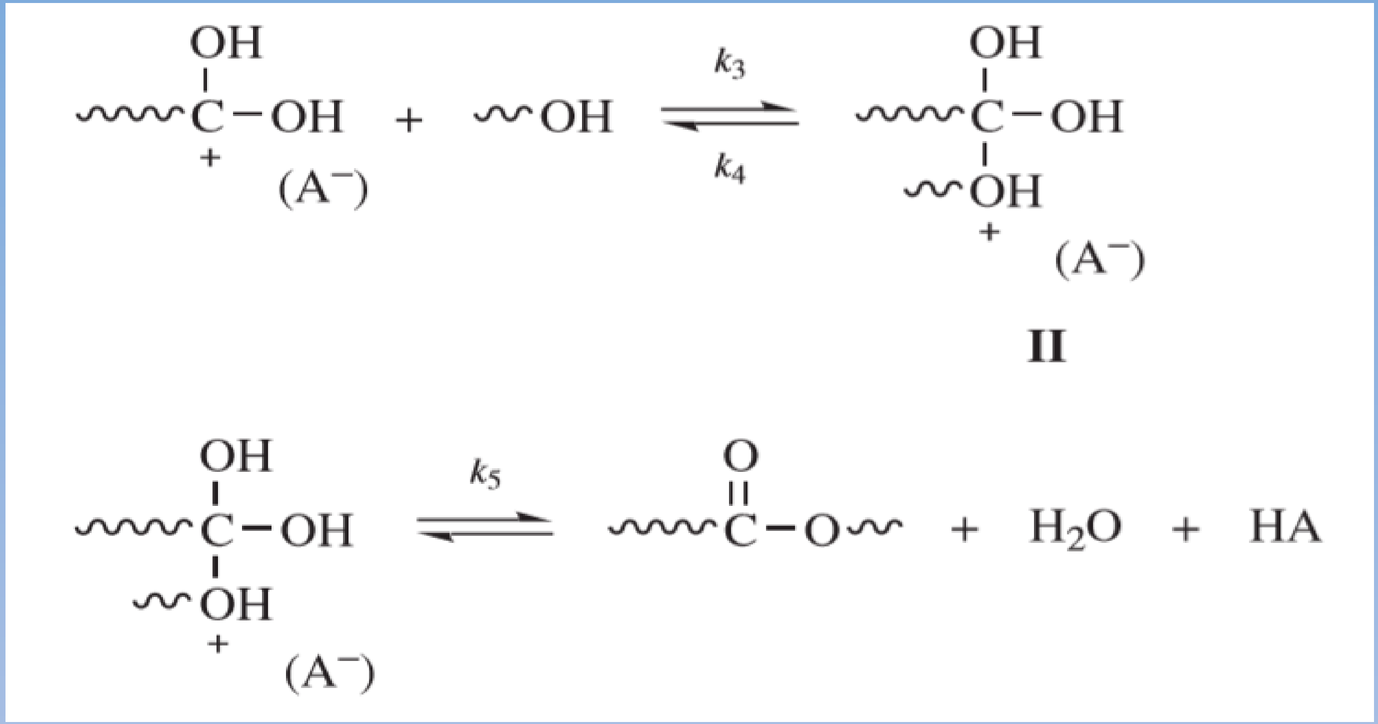
A classic example of a step-growth polymerization is the esterification reaction between an alcohol and a carboxylic acid. The progress of the polyester-forming reaction can be easily followed by titration of the unreacted acids in the samples removed from the batch at different times. Simple esterification reactions are known to be catalyzed by acids.



$$\sim\overset{\overset{\displaystyle O}{\|}}{C}-OH + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim\underset{+}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH\,(A^-)$$

I

Polyesterifications, like many other step polymerizations, are equilibrium reactions.



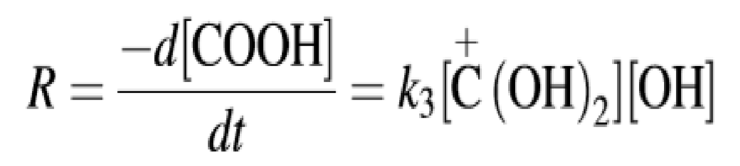
$$\sim\sim\underset{+}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH\ (A^-) + \sim OH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \sim\sim\overset{\overset{\displaystyle OH}{|}}{C}-OH \quad \text{with } \underset{|}{}\sim\underset{+}{OH}\ (A^-)$$

II

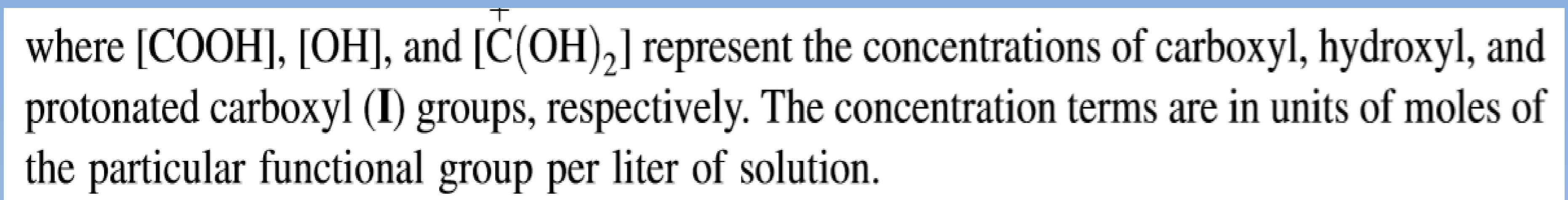
$$\sim\sim\overset{\overset{\displaystyle OH}{|}}{C}(\sim\underset{+}{OH})-OH\ (A^-) \overset{k_5}{\rightleftharpoons} \sim\sim\overset{\overset{\displaystyle O}{\|}}{C}-O\sim + H_2O + HA$$

high yields of high-molecular-weight product such polymerizations are run in a manner so as to continuously shift the equilibrium in the direction of the polymer.

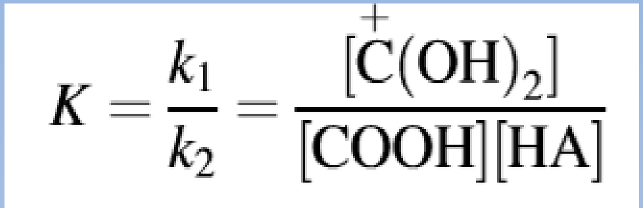
The rate of a step polymerization is conveniently expressed in terms of the concentrations of the reacting functional groups. Thus the polyesterification can be experimentally followed by titrating for the unreacted carboxyl groups with a base.



$$R = \frac{-d[\mathrm{COOH}]}{dt} = k_3[\overset{+}{\mathrm{C}}(\mathrm{OH})_2][\mathrm{OH}]$$



where [COOH], [OH], and $[\overset{+}{\mathrm{C}}(\mathrm{OH})_2]$ represent the concentrations of carboxyl, hydroxyl, and protonated carboxyl (**I**) groups, respectively. The concentration terms are in units of moles of the particular functional group per liter of solution.



$$K = \frac{k_1}{k_2} = \frac{[\overset{+}{\mathrm{C}}(\mathrm{OH})_2]}{[\mathrm{COOH}][\mathrm{HA}]}$$

$$\frac{-d[\mathrm{COOH}]}{dt} = k_3 K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]$$

Polymerization with Strong Catalyst

If the polymerization is carried out in the presence of a strong acid (sulfonic acids) and if the catalyst concentration is kept constant throughout the process, the polymerization follows the kinetics of a second-order reaction: If the polymerization reaction is first order with respect to each functional group reactant, A and B, then the rate of reaction can be expressed by:

where k = k[catalyst]

$$\overline{DP} = \frac{1}{1-p}$$

High-yield reactions and an exact stoichiometric balance are necessary to obtain a high molecular weight linear polymer.

At any particular time, t, in the polymerization process, $\overline{DP}$ is equal to the ratio of monomer molecules present initially to the total number at that time; that is,

$$\overline{DP} = \frac{[A_o]}{[A]}$$

$$-\frac{d[A]}{dt} = k[A]^2$$

or, by integration,

$$\frac{1}{[A]} - \frac{1}{[A_o]} = kt$$

For high molecular weight polymer, we need $[A] = [B]$, then the rate of reaction becomes

At any particular time, t, in the polymerization process, $\overline{DP}$ is equal to the ratio of monomer molecules present initially to the total number at that time; that is,

$$\overline{DP} = \frac{[A_o]}{[A]}$$

$$[A] = [A_o](1 - p)$$

$$\frac{1}{[A_o](1-p)} - \frac{1}{[A_o]} = kt$$

Since $\overline{DP} = 1/(1-p)$,

$$\frac{\overline{DP}}{[A_o]} - \frac{1}{[A_o]} = kt$$

or

$$\overline{DP} = [A_o]kt + 1$$

DP increases linearly with the reaction time, which is a much more favorable situation for obtaining high average molecular weight polymers than the weak-acid catalyzed third-order reaction.

Polymerization with Self-Catalyzed

In the absence of an externally added strong acid the diacid monomer acts as its own catalyst for the esterification reaction

$$\frac{-d[\mathrm{COOH}]}{dt} = k[\mathrm{COOH}]^2[\mathrm{OH}]$$

the important characteristic of the self-catalyzed polymerization — the reaction is third-order overall with a second-order dependence on the carboxyl concentration.

$$\frac{-d[\mathrm{M}]}{dt} = k[\mathrm{M}]^3$$

or

$$\frac{-d[\mathrm{M}]}{[\mathrm{M}]^3} = k\,dt$$

where [M] is the concentration of hydroxyl groups or carboxyl groups.

$$2kt = \frac{1}{[\mathrm{M}]^2} - \frac{1}{[\mathrm{M}]_0^2}$$

where $[\mathrm{M}]_0$ is the initial (at $t = 0$) concentration of hydroxyl or carboxyl groups.

$$p = (M_0 - M) / M_0$$

The extent or fraction of reaction p defined as the fraction of the hydroxyl or carboxyl functional groups that has reacted at time t. p is also referred to as the extent or fraction of conversion.

$$[\mathrm{M}] = [\mathrm{M}]_0 - [\mathrm{M}]_0 p = [\mathrm{M}]_0 (1 - p)$$

The concentration [M] at time t of either hydroxyl or carboxyl groups is then given by and after substitution of M with this expression the rate of the polymerization equation reads

$$\frac{1}{(1-p)^2} = 2[\mathrm{M}]_0^2 kt + 1$$

In the esterification reaction, p can be directly calculated from the carboxyl group titer. If we plot $1/(1\text{-}p)^2$ against time, t,