Chapter. 13

Kinetics of ionic Polymerization

Differences between ionic and free-radical kinetics

1. **Activation E for initiation in ionic poly. is very low**
2. **No termination**
3. **Solvent can produce free ions or ion pairs (solvent effect is very high)**

Anionic Polymerization

Quantitative and instantaneous dissociation of initiator; living polymer

Initiation

Propagation

No termination

Rate of polymerization

Average kinetic chain length

at the completion of reaction

Average degree of polymerization

For sodium naphthalenide initiated polymerization of styrene

Distribution of degree of polymerization

Real system; broader than Fig 13.1
Due to the existence of a propagation-depropagation equilibrium

Rate constant for propagation

Actual situation

Ion pair Free ion

k_p for free ion is much larger than that of ion pair

Free ion concentration ↑, dilution ↑
Then k_p for free ion can be obtained by extrapolation

Apparent k_p is the combination of k_p's for free ion and ion pair

Incomplete dissociation of initiator

Then it is impossible (or very difficult) to obtain the kinetic equation; case by case study

Anionic Copolymerization

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{21}/k_{22}$

Copolymer composition equation

Cationic Polymerization

Rate of cationic polymerization

In principle same as that of anionic polymerization
The only differences could be the charge of the active chain ends.

The rate of polymerization for ion pairs

If steady state approximation is valid, then $r_i = r_t$

Degree of polymerization

where r_{Tr} is the rate of the chain transfer

Mayo equation

$1/\overline{DP}$ vs 1/[M], then $k_{tr,M}/k_p$ and k_t/k_p can be obtained

If the chain transfer occurs with X (solvent, impurity…)

T↑,
chain transfer ↑
Termination ↑

From Arrhenious equation

Effect of temperature

Normally $E_t > E_p$; then T ↑, r_p↓

For radical polymerization, then T ↑, r_p ↑

Temperature effect on DP

If $k_t >> k_{Tr}$

$$\overline{DP}$$

Normally $E_t > E_p$; then T ↑, DP ↓

If $k_t << k_{Tr}$

Normally $E_{Tr} > E_p$; then T ↑, DP ↓

Rate constant for propagation

If the cationic polymerization is initiated by radiation, there is no counter ion, then polymerization is go through free ion.

$C_7H_7SbCl_6^-$ can also induce free ion active site

Cationic Copolymerization

where $r_1 = k_{11}/k_{12}$, $r_2 = k_{21}/k_{22}$

Copolymer composition equation