Chapter. 12

Kinetics of Free-Radical Polymerization

Introduction

Approximation

Kinetic Chain Length

very large ! Monomer consumed in the initiation is negligible

The direction of Radical Addition to the monomer

Head to tail!

Radical Reactivity and size

Reactivity of the propagating radicals is independent of the size

The steady-state approximation

The total concentration (or number) of propagating radicals is constant.

Where $R = \Sigma_n[R_n]$

Since $d[R]/dt = 0$

Steady-state concentrations of the propagating radicals

r_i; rate of initiation **r_t; rate of termination**

For termination

Rate of polymerization, r_p

Definition

Initial rate of polymerization

Normally r_p is constant upto 10 ~ 15 % conversion

Experimental measurement of rates of polymerization

Yield of the reaction (wt % base)

ω_m = weight of monomer

Theoretical rates of polymerization

rate of polymerization $\propto [I]^{1/2}, [M], (r_i)^{1/2}, (1/k_t)^{1/2}$

If r_i is solved (대학원), r_p vs [M] gives $(k_p^2/2k_t)^{1/2}$

If $(k_p^2/2k_t)^{1/2}$ is obtained from several temperatures

T vs $(k_p^2/2k_t)^{1/2}$, Arrenius parameter and $(E_p-E_t/2)$ are obtained. See table 12.2

Kinetic chain length

The average number of monomer molecules polymerized per chain initiated

If $(k_p^2/2k_t)^{1/2}$ is obtained, then υ can be obtained

Without r_i, υ can be obtained (r_p should be obtained)

Average degree of polymerization and average molecular weight

If termination by combination predominant, $k_{tc} >> k_{td}$

If termination by disproportionation predominant, $k_{tc} << k_{td}$

M_o is molecular weight of monomeric unit in the polymer

Distribution of the degree of polymerization and molecular weight

If f_n is defined as the fraction of propagating radicals that have a degree of polymerization, n

Steady state assumption

X_n ; mole fraction of polymer having a $\overline{DP}$ of n

Only by combination

υ= 300
Both combination and disproportionation

Chain transfer

Chain transfer can make DP less than υ
How?

Effect of chain transfer on average degree of polymerization

Chain transfer can occur with monomer (M), polymer (P), solvent (S), initiator (I), or impurity (Y), then;

where $C_i = k_i/k_p$

If C_I***, CY, and*** $C_{polymer}$ ***is very small (it is true)***

$[S]/[M]$ ***vs*** $(\overline{DP})^{-1}$ ***plot ;*** $(\overline{DP})_0^{-1}$ ***and*** C_s ***can be obtained***

Slop is C_s

Intercept is $\overline{(DP)}_0^{-1}$

$C_s = k_s/k_p$, *then*

Effect of chain transfer on the distribution of the degree of polymerization (*exercises for students*)

Without chain transfer

With chain transfer

Example of the effect of chain transfer on $\overline{DP}$ and molecular weight distribution

Polymerization of styrene (1M)
Initiation rate, $r_i = 10^{-8}$ mol/Ls (0.4 M AIBN at 25 ^oC)

Problem 6 in chapter 3, Tables 12-3 and3

Dependence of the degree of polymerization on temperature

Polymerization of styrene Using AIBN

$E_i = 30800$ cal/mol

$E_p - E_t/2 = 6600$ cal/mol

$T\uparrow, \ \overline{DP}\downarrow$

Copolymerization

The copolymer composition equation; reactivity ratios (r_1 and r_2)

γ = the ratio of the number of M_1 to M_2 in the copolymer

Steady state assumption

Copolymer composition equation

Copolymer composition equation

1. **Independent of dilution**
2. **Independent of the initiation rate**
3. **Independent of medium**

f_i ; mole fraction of i molecule in the polymer

F_i ; mole fraction of i molecule in the reactant

$f_2 = 1 – f_{1,}$ $F_2 = 1- F_1$

f_1 vs F_1 at different r_1 and r_2

If $r_1 = r_2$,
then $F_1 = 0.5$ then $f_1 = 0.5$
Azeotropic condition ($\gamma=[M_1]/[M_2]$)
;composition in the polymer is same as that in reactants

Azeotropic condition is possible when $r_1 \neq r_2$,

$F_1/F_2 = f_1/f_2$ in eq (99)

Experimental determination of reactivity ratios (r_1 and r_2)

For polymerization of M_1 and M_2 (M_1/M_2 is known), then get γ (from the chemical analysis polymer), then r_1 and r_2 linear plots can be obtained

r_1 and r_2 for M_1 and M_2

Very tough !

Alfrey-Price Q-e scheme

Q and e values are obtained by simulation of data available
Not exactly accurate, but reasonable correct and very useful

Distributions of the Monomer in a Copolymer

Average sequence length of M_1 and M_2 are $\overline{m}_{M1}$ and $\overline{m}_{M2}$, respectively

P_{11} ; the probability that $M_1^{\cdot}$ react with M_1

The probability that a sequence of *m* units of M_1 forms

The probability that a sequence of *m* units of M_2 forms

Average sequence length of $\overline{m}_{M1}$ and $\overline{m}_{M2}$ are ;

Run number , *R*

Average number of sequences of either type per 100 monomeric units

R = 9 x (100/20) = 45

The rate of sequence formation

The total rate of polymerization

Using equations (95), (114) and (115)

Average number of sequences per 100 monomeric units, R

Copolymer composition

Average sequence length

Run number , *R*