

Chapter. 11

kinetics of Condensation
(step growth)
Polymerization

Introduction

Condensation polymerization process

(1)-(6) all reversible reaction, water should be removed to obtain high MW polymer

example

Except for the very small reactants ($n \leq 2$), reactivities are independent of molecular size.

The reactivity of large molecules

Why reactivities are independent of molecular size?

1. The movement of the end group (OH or COOH) is independent of molecular size.

Size affect the overall movement of the molecule (average movement of center can be affected)

2. Liquid cage theory;

In liquid, two reactants will not come together rapidly, while once brought together they will not separated easily. Then reactants in the solvent cage can collide more frequently.

2. Liquid cage theory;

(A + B); reactants in the liquid cage
 k_8 , and k_{-8} ; diffusion rate constant

P; product
 k_9 ; rate constant

(a) Case 1 ; $k_8 \gg k_9$; diffusion is faster than chemical reaction

Rate constant is independent of molecular size

(b) Case 2 ; $k_8 \ll k_9$; chemical reaction is faster than diffusion

Rate constant depends on molecular size

Chemical reaction rate is much lower than diffusion rate,
Rate constant is independent of molecular size

Rates of polycondensation reactions

[acid]; esterification is catalyzed by acid

Case 1: No acidic catalysts added

Eq 24 is only good when $P > 0.8$

Below 80% conversion, reaction medium changes. (see Fig 11.2)

Typical plots for no acidic catalysts added when $P > 0.8$

Unit equivalent/kg not mole/liter

Volume changes according to the reaction

$$k = Ae^{-E/RT}$$

Activation E can be obtained!

Case 2: Acid-catalyzed polyesterification

$k_{\text{cat}} \gg k_3$, and if $k_2 = k_3[\text{H}^+]$

Integration of (27) and substitution of (23)

Time dependence of the average degree of polymerization and the average molecular weight

If water is totally removed throughout the polymerization, the number of COOH groups present is equal to the number of molecule present.

N = total number of molecules, V = the volume

One structural unit from diacid

One structural unit from diol

Therefore total number of structural unit is constant at all the time.

The average degree of polymerization system, \overline{DP} , is defined as the average number of structural units per molecule.

If \overline{M}_0 is the average molecular weight of the structural units, then number average-molecular weight is

For adipic acid ($\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$) and 1,10-decandiol,

12,000 molecular weight is possible when $P > 0.99$

For uncatalyzed system

For catalyzed system

Molecular-weight distributions of linear condensation polymers

P is the fraction of COOH groups that have reacted at time t = the probability that the groups are reacted
 $(1 - P)$ = the probability that the groups are not reacted at time t

The probability that the molecule contains exactly x structural units is,

The number of x -mer in a system of N molecules

The number average molecular weight of x-mer is

Where M_0 is the molecular-weight of the structural unit

The weight average molecular weight of x-mer is

The weight fraction of x-mer, W_x , is the weight of molecules containing exactly x structural units divided by the total weight of the polymer

Definition

Effect of Nonstoichiometric Reactant Ratio on Linear Condensation Polymerization

N_A^0 and N_B^0 are the initial # of functional groups

$$r = N_A^0 / N_B^0 < 1$$

N_{SU} is the total # of structural units possible in the system

P is the fraction of A groups reacted at time t . $P = \Delta N_A / N_A^0$

Then rP is the fraction of B groups reacted at time t .

$$\Delta N_A = \Delta N_B$$