# Chapter 1. Introduction

Polymer(many parts)

: long chain molecule composed of a large number of repeating units

polymer (n>1000) : plastics, fibers and elastomers

oligomer (n<10)

U.S. polymer production (1993)

: plastics(78%), fibers(14%), elastomers(7.4%)

## 1.1 Classification

Thermal processing behavior : thermoplastics & thermosets

Polymerization mechanism : addition & condensation

ex) addition-type polymers derived from substituted ethylene

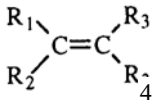

**TABLE 1.2 EXAMPLES OF SOME IMPORTANT ADDITION POLYMERS DERIVED FROM ETHYLENE DERIVATIVES**

| Polymer | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Repeating Unit |
|---|---|---|---|---|---|
| Polyethylene | H | H | H | H | $\{CH_2-CH_2\}$ |
| Polypropylene | H | H | H | $CH_3$ | $\{CH_2-CH(CH_3)\}$ |
| Poly(vinyl chloride) | H | H | H | Cl | $\{CH_2-CH(Cl)\}$ |
| Poly(vinyl alcohol) | H | H | H | OH | $\{CH_2-CH(OH)\}$ |
| Polyacrylonitrile | H | H | H | C≡N | $\{CH_2-CH(C\equiv N)\}$ |
| Poly(vinyl acetate) | H | H | H | $O-C(=O)-CH_3$ | $\{CH_2-CH(O-C(=O)-CH_3)\}$ |
| Polystyrene | H | H | H |  | $\{CH_2-CH(C_6H_5)\}$ |
| Poly(methyl methacrylate) | H | H | $CH_3$ | $C(=O)-O-CH_3$ | $\{CH_2-C(CH_3)(C(=O)-O-CH_3)\}$ |
| Poly(vinylidene chloride) | H | H | Cl | Cl | $\{CH_2-C(Cl)_2\}$ |

Polymerization kinetics : step growth & chain growth

## 1.2 Polymer Structure

Copolymers : random, alternating, block, graft, ...

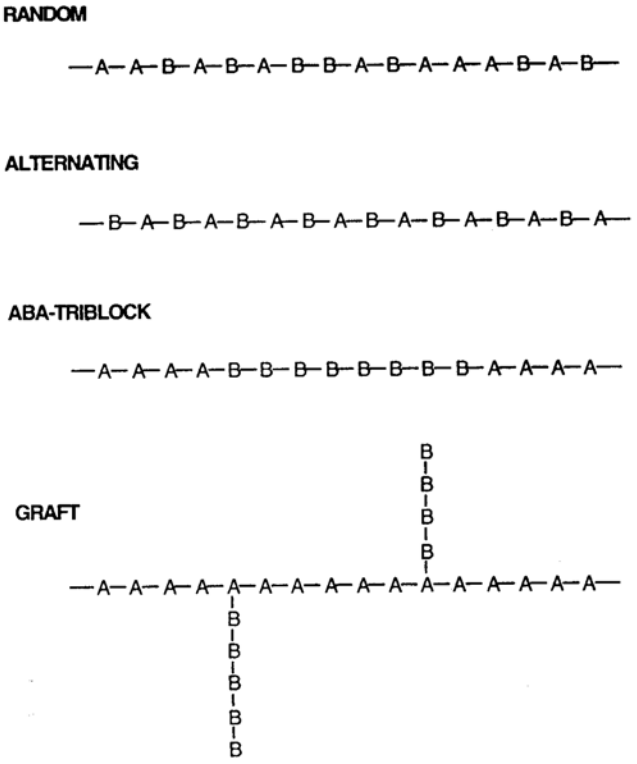


**Figure 1.4.** Possible structures of copolymers containing A and B repeating units.

**TABLE 1.5 SCHEME FOR NAMING COPOLYMERS**

| Type | Connective | Example |
|---|---|---|
| Unspecified | *-co-* | Poly[styrene-*co*-(methyl methacrylate)] |
| Statistical[a] | *-stat-* | Poly(styrene-*stat*-butadiene) |
| Random | *-ran-* | Poly[ethylene-*ran*-(vinyl acetate)] |
| Alternating | *-alt-* | Poly[styrene-*alt*-(maleic anhydride)] |
| Block | *-block-* | Polystyrene-*block*-polybutadiene |
| Graft | *-graft-* | Polybutadiene-*graft*-polystyrene |

[a] A statistical polymer is one in which the sequential distribution of the monomeric units obeys statistical laws. In the case of a random copolymer, the probability of finding a given monomeric unit at any site in the chain is independent of the neighboring units in that position.

Tacticity : isotactic, syndiotactic & atactic

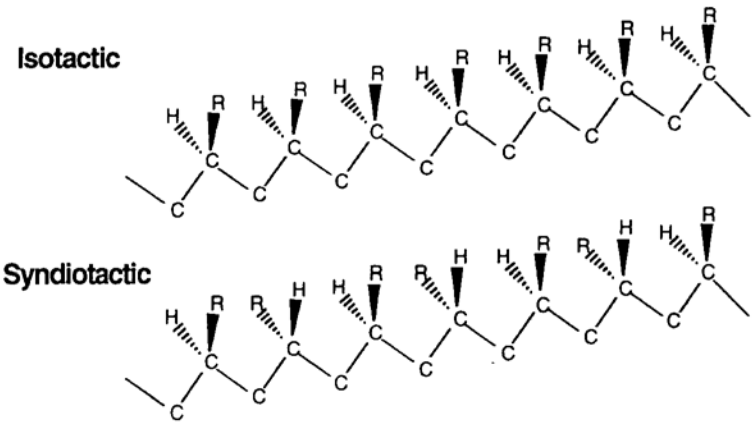


**Figure 1.5.** Two forms of stereochemical configuration of an extended-chain vinyl polymer having a substituent group R other than hydrogen.

Geometric isomers

ex) polybutadiene : vinyl, cis & trans

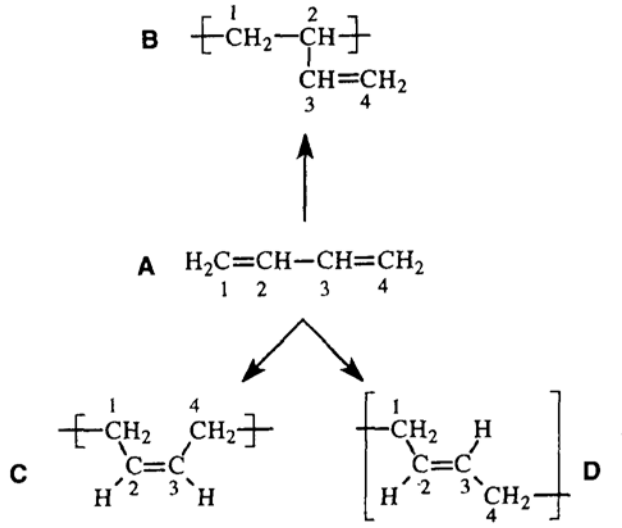


**Figure 1.7.** Alternative pathways for the polymerization of 1,3-butadiene (**A**) to give 1,2-poly(1,3-butadiene) (**B**), *cis*-1,4-poly(1,3-butadiene) (**C**), or *trans*-1,4-poly(1,3-butadiene) (**D**).

Nomenclature

structure-based : poly(CRU) --- IUPAC name

source-based : poly(monomer) --- popular

ex) polystyrene --> poly(1-phenylethylene)

polytetrafluoroethylene --> poly(difluoromethylene)

## 1.3 Molecular Weight

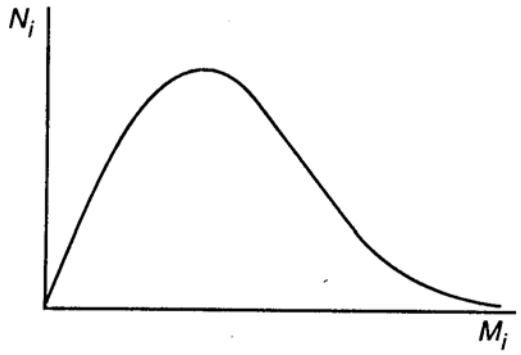


**Figure 1.8.** A typical distribution of molecular weights shown as a plot of the number of moles of chains, $N_i$, having molecular weight, $M_i$, against $M_i$.

Average MW

$$\overline{M} = \frac{\sum N_i M_i^{\alpha}}{\sum N_i M_i^{\alpha-1}} \quad \text{(discrete distribution)} \qquad W_i = N_i M_i$$

$\alpha = 1$ : number avg. MW

$\alpha = 2$ : weight avg. MW

$\alpha = 3$ : z avg. MW

$$\overline{M} = \frac{\int_0^{\infty} NM^{\alpha}\, dM}{\int_0^{\infty} NM^{\alpha-1}\, dM} \quad \text{(continuous distribution)}$$

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PDI (polydispersity index) = $\overline{M_w} / \overline{M_n}$

## 1.4 Thermal Transition

$150K < T_g < 770K$ $\qquad$ $334K < T_m < 675K$

In general, $T_g \approx 1/2 - 2/3$ of $T_m$

**Example problem** 1-1.

A polydisperse sample of polystyrene is prepared by mixing three monodisperse samples in the following proportions:

| | |
|---|---|
| 1g | 10,000 molecular weight |
| 2g | 50,000 molecular weight |
| 2g | 100,000 molecular weight |

Using this information, determine the following: (a) number-average; (b) weight-average; and (c) z-average molecular weight of the mixture.