Polymers: Chemistry & Physics of Modern Materials

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CHAPTER 1 Introduction

Polymer → a large molecule, constructed from many smaller structural units called monomers, covalently bonded in any conceivable pattern.

→ or monomer residue → as atoms are eliminated from the simple monomeric unit after polymerization.

→ it is the "building block".

functionality → number of bonding sites of the monomer.

bifunctional monomers → linear macromolecules
polyfunctional monomers → branched / cross-linked macromolecules.

1 species of monomer → homopolymer or polymer
*2 types of monomer unit → copolymer
3 different monomers → terpolymer

* Copolymers prepared from bifunctional monomers can be classified in:

- Statistical copolymers: the distribution of the two monomers is random, but influenced by the individual monomer reactivities.
- Alternating copolymers: regular placement along the chain.
- Block copolymers: substantial sequences or blocks of each.
- Graft copolymers: blocks of one monomer are grafted on to a backbone of the other as branches.

polymerization → process to convert monomer molecules into a polymer.

- step-growth polymerization: used for monomers with functional groups such as -OH, -COOH, -COCl, and typically is a succession of condensation reactions.
  - → a molecule is eliminated from the original monomer in the reaction.
- addition polymerization: (for olefinic monomers) based on the stimulation of opening a double bond with a free radical or ionic initiator.
  - → the product has the same chemical composition as the starting material.

It's unable to assign an exact molar mass to a polymer, since in polymerization, the length of the formed chain is determined by random events. The product is a mixture of chains of differing length

↳ The molar mass can be calculated statistically (a distribution of chain lengths)

- The number-average molar mass $\langle M \rangle_n$ is defined by: (colligative method)

$$\langle M \rangle_n = \frac{\Sigma N_i M_i}{\Sigma N_i} = \frac{\Sigma w_i}{\Sigma (w_i / M_i)}$$

; where: N_i = number of molecules of species i of molar mass M_i
$\langle\ \rangle$ indicates it is an average value
$w_i = \frac{N_i M_i}{N_A}$, N_A is the Avogadro's const.

- The weight-average molar mass $\langle M \rangle_w$ is defined by: (light-scattering)

$$\langle M \rangle_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} = \frac{\Sigma w_i M_i}{\Sigma w_i}$$

- Stadistically $\langle M \rangle_n$ is the 1st moment, and $\langle M \rangle_w$ is the ratio of the 2nd to the 1st moment of the number distribution.

- The higher average (z-average) is given by: (ultracentrifuge)

$$\langle M \rangle_z = \frac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2} = \frac{\Sigma w_i M_i^2}{\Sigma w_i M_i}$$

- The (z+1)-average is often required when describing mechanical properties, and is given by:

$$\langle M \rangle_{z+1} = \frac{\Sigma N_i M_i^4}{\Sigma N_i M_i^3}$$

- The breadth of the distribution can often be gauged by the heterogeneity index:

$\frac{M_w}{M_n}$. Another method to describe the chain length is the average degree of polymerization, given by:

$x = M / M_0$, which represents the number of monomer units in the chain.

M_0 = molar mass of monomer or residue
M = the appropriate average molar mass.

glass transition temperature → the polymer softens and becomes rubberlike
↳ the material may be more easily deformed or become ductile above T_g

melting temperature → at T_m, melting would be observed, and the polymer would become a viscous liquid.

- Fiber Forming Polymers.

nylon = synthetic polyamides
↳ e.g. nylon 6-6 distinguish each polymer by designating the number of carbon atoms in between succesive amide groups in the chain.

dyadic = nylon with two numbers → 2 monomers, prepared with.
↳ it contains both dibasic acid (or acid chloride) and diamine moieties.

monadic → 1 number → 1 monomer, prepared with.

Terylene → polyester
acrylics & modacrylics are based on the acrylonitrile unit $-CH_2CH(CN)-$
↳ acrylic fiber → acrylonitrile content is 85% or higher
modacrylic fiber → acrylonitrile content is between 35 & 85%
Vinyl chloride & vinylidene chloride → comonomers

- Plastics

thermosetting material: become hard when heated above a critical temperature and will not soften again on reheating. (usually cross-linked).
thermoplastic polymer: will soften when heated above T_g, it can be shaped and, on cooling, will harden. However it can be reshaped if required

thermoset plastics: better abrasion & dimensional stability characteristics
thermoplastics: better flexural & impact properties.

Phenolic resins, Amino resins, Polyester resins, Epoxy resins, are thermosetting polymers.

- Elastomers. (caoutchouc / rubber)

styrene-butadiene (SBR) - vehicle tires.
nitrile rubber (NBR) - acrylonitrile + butadiene - resistant to swelling in organic solvents
ABS rubber - nitrile rubber + styrene
butyl rubber (IIR) - isoprene + isobutylene