Chapter 1

Basic concepts

History

- natural polymers like proteins, silk, wood, ---
- empirical developments
  - vulcanized rubber (1840)
  - cellulose polymers ~ Celluloid®, Cellophane®, -- (1850)
  - Bakelite® ~ a PF resin ~ the first fully-synthetic (1910)
- polymer science: the 1st era
  - polystyrene (1920)
    - Staudinger (1953 Nobel prize)
    - 'Macromolecules are long-chain molecules.'
  - nylon (1935)
  - polyethylene (1955)
    - Ziegler and Natta (1963 Nobel prize)
  - When is the start of 'the Plastic Age'?

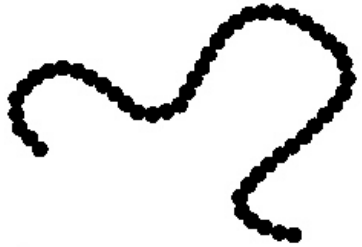
Carothers

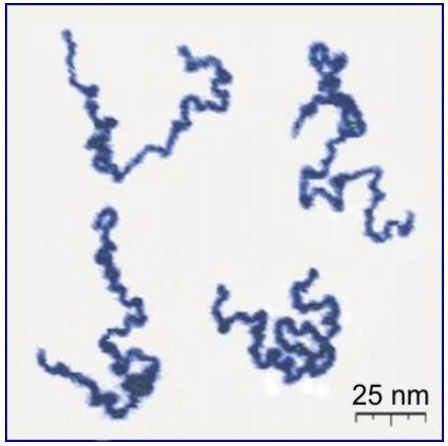
- polymer science: the 2nd era
  - polymer structure in solution (and in bulk)
    - Flory (1974 Nobel prize)
  - behavior of polymer chain in bulk
    - de Gennes (1991 Nobel prize)
- polymer science: the 3rd era
  - conducting polymers
    - MacDiarmid, Heeger, and Shirakawa (2000 Nobel prize)
  - olefin metathesis polymerization
    - Grubbs, Schrock, and Chauvin (2005 Nobel prize)
  - living radical polymerization
    - Matyjaszewski + -- (202? Nobel prize)

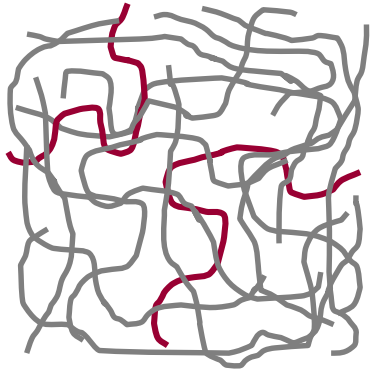
➢ What the next?

Definitions

- macromolecule = large [giant] molecule [巨大分子]
  - with high molar mass [分子量]
- polymer = poly + mer = many + part [高分子]
  - parts linked to form a long sequence [chain]
  - monomer to polymer thru polymerization [重合]
- 'polymer' and 'macromolecule'
  - usually interchangeable
  - long chain molecule comprised of many parts (identical)





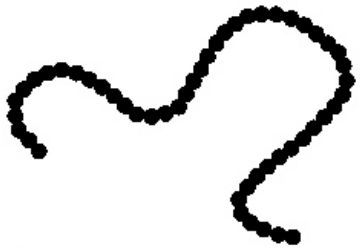


Classification of polymers

- by chemical structure
  - homopolymers vs copolymers
- by skeletal structure
  - linear vs branched vs crosslinked polymers
- by aggregation structure
  - amorphous vs (semi)crystalline polymers
- by thermomechanical behavior
  - thermoplastics vs thermosets (and elastomers)

Homopolymers

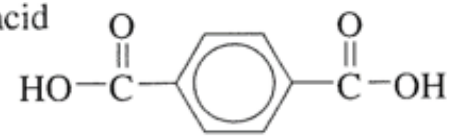
- polymer with single type of repeat unit [反復單位]
- 2 groups
  - chain polymers
    - #1 – 8 of Table 1.1 p7
    - poly+monomer
    - PE, PP, PVC, PS, PMMA, ---
    - GPP [general purpose plastics]
  - step polymers
    - #9 and 10 of Table 1.1 p8
    - poly+repeat unit
    - polyester, nylon, PC, PPO, ---
    - engineering plastics
      - high(er) performance
      - high heat resistance, modulus, strength
      - structural applications



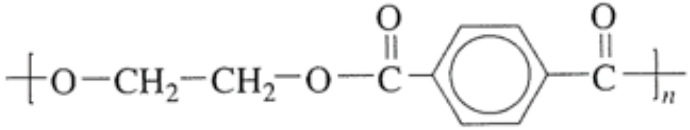
6. Vinyl chloride $CH_2{=}CH(Cl)$

Poly(vinyl chloride) (PVC) $+CH_2-CH(Cl)+_n$

9. Ethylene glycol $HO-CH_2-CH_2-OH$ and terephthalic acid



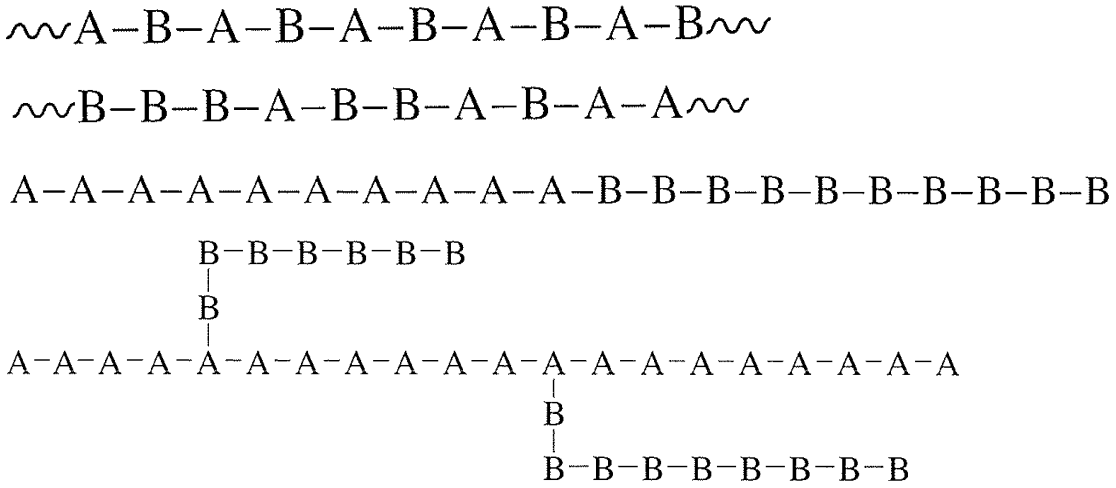
Poly(ethylene terephthalate) (PET)[a]



Memorize Table 1.1!!

Copolymers [共重合體]

- polymer with ≥2 different types of repeat unit
- types
  - alternating
  - statistical or random
  - block
  - graft



- ✓ alt, stat, ran ~ no phase separation → average property
- ✓ block, graft ~ phase separation → composite property

poly(A-*co*-B)
polyA/polyB

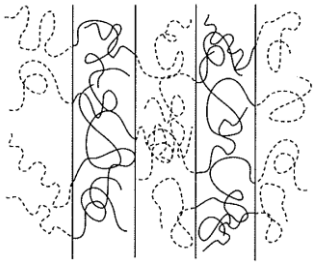
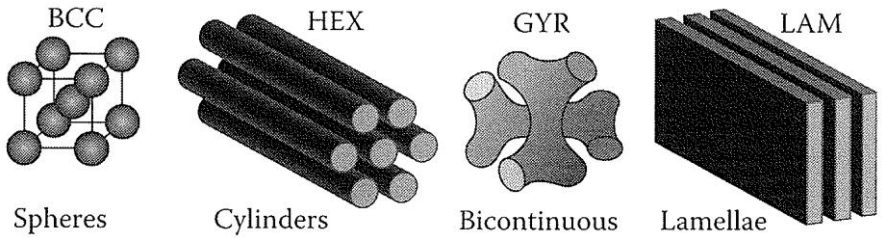


Fig 18.7

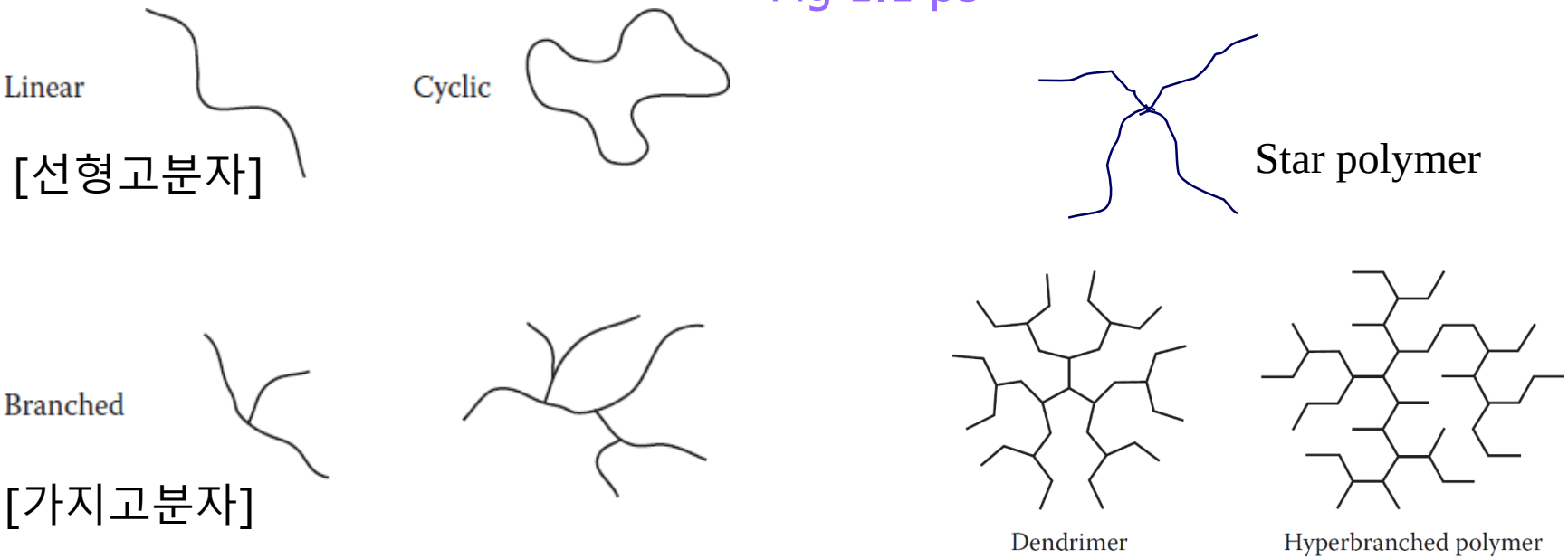
Fig 18.8



- ➢ polymer blend [alloy] ~ mixture of polymers [A/B] ~ also 1 or 2 phase

Skeletal structure

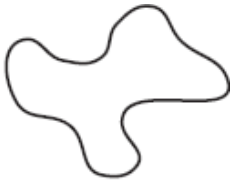
Fig 1.1 p5

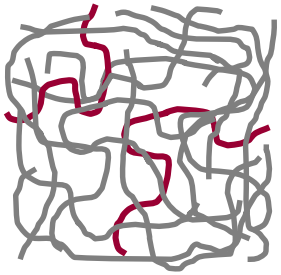


- ✓ different structure
- ✓ different properties and applications

Linear

Cyclic





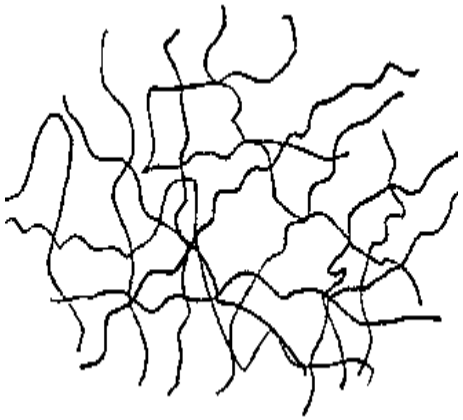
soluble in solvent
fusible [flow] by heat
thermoplastic [熱可塑性]
thermoplastics
[thermoplastic resins, 열가소성 樹脂]

Branched

crosslinked
Network

insoluble and infusible
thermosetting [熱硬化性]
thermosets
[thermosetting resins, 열경화성 수지]

Aggregation structure



irregular
amorphous [無定形]
amorphous polymers
PS, PVC, PC
transparent
soluble in solvents

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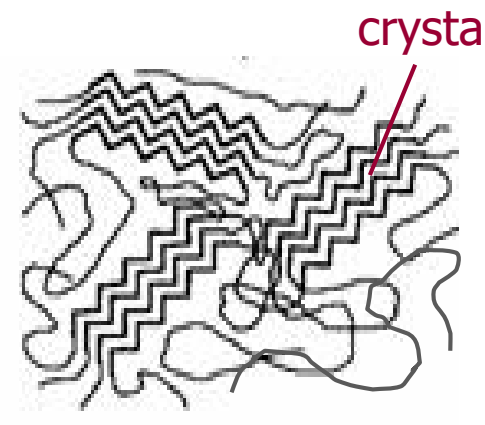
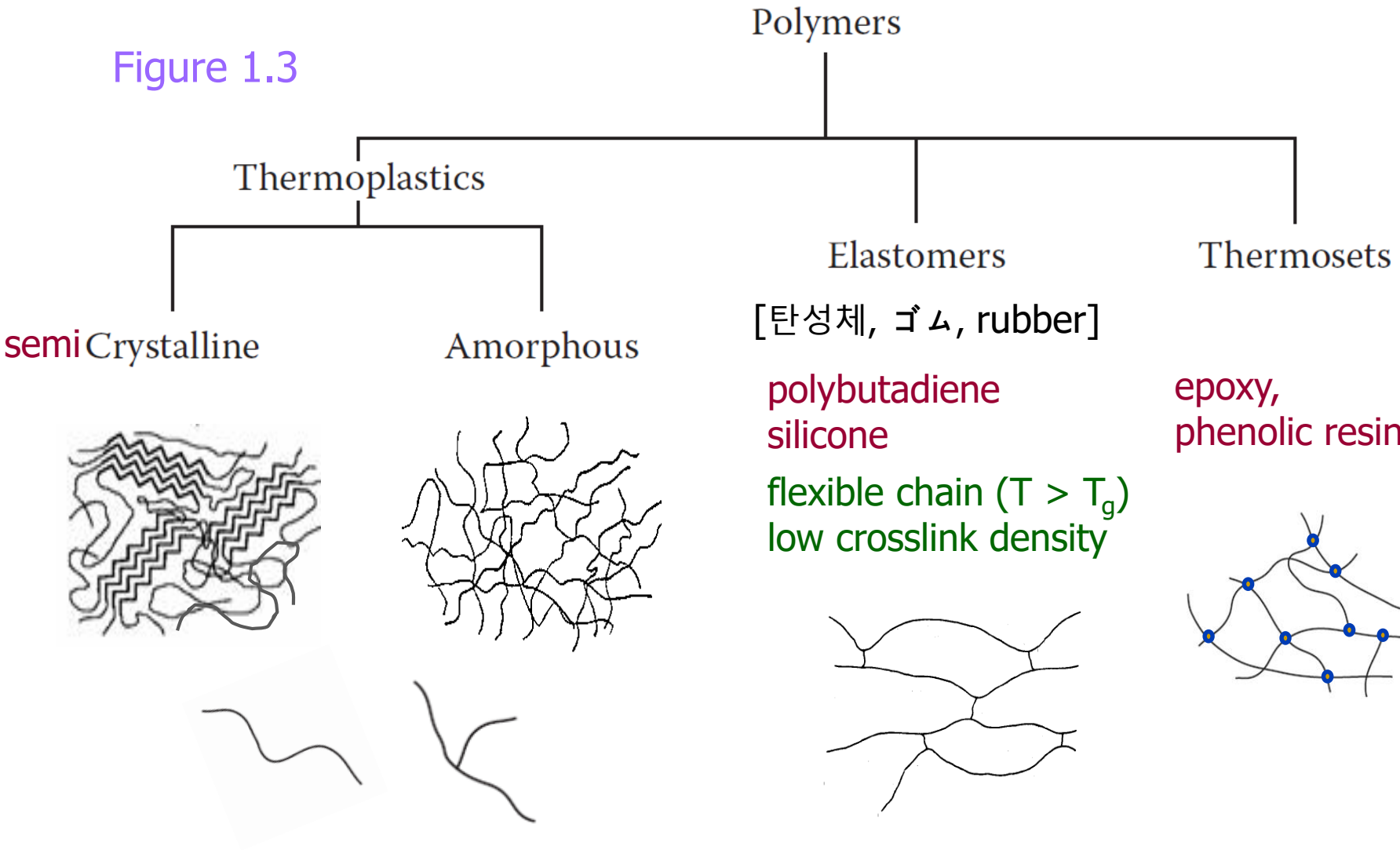
depending on chain regularity and cooling rate



regular (in part)
(semi)crystalline [(半)結晶性]
semicrystalline polymers
PE, PP, nylon, polyesters
opaque
insoluble at RT
(soluble only at high Temp)

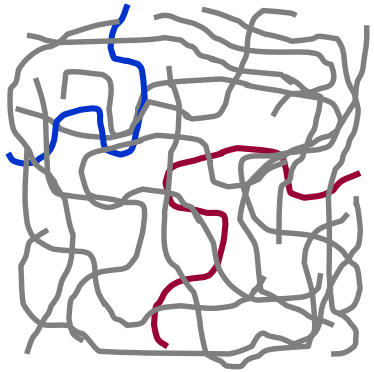
Classification

Figure 1.3



Molar mass [molecular weight]

- Polymer = molecule with high molar mass [MM, 分子量]
  - molar mass vs molecular weight or molecular mass
    - mass/mole vs weight or mass/molecule ~ differ by N_A
    - unit: g/mol vs dimensionless or amu
    - MM more correct, but MW more popular
  - MW or MM = 10000 – 30000 for step polymers
  - MW or MM = ~ 10^5 for chain polymers



- Polymer = gathering of chains
  - with distribution of MW.
    - MW distribution [MWD, 分子量分布]
  - polydisperse not monodisperse
  - MM [MW] should be averages.

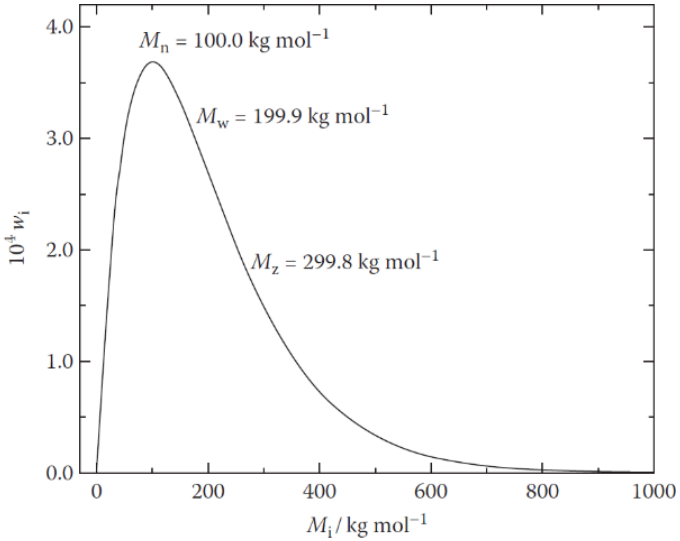
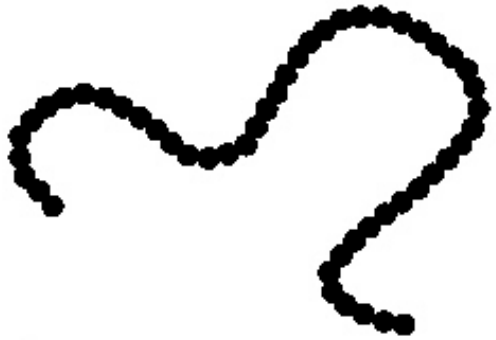


Fig 1.4

Degree of polymerization

- molar mass $M = xM_0$
  - x = degree of polym'n
    = # of monomer units
  - M_0 = MM of the monomer unit



- monomer unit? repeat unit? wrong p11

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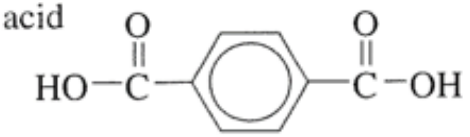
Poly(vinyl chloride) (PVC) $+CH_2-CH(Cl)+_n$

monomer unit = repeat unit
n = x

9. Ethylene glycol $HO-CH_2-CH_2-OH$
and terephthalic acid



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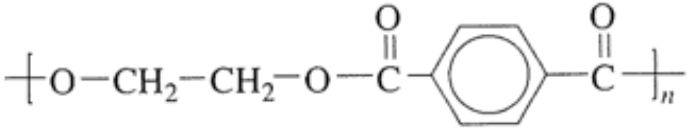
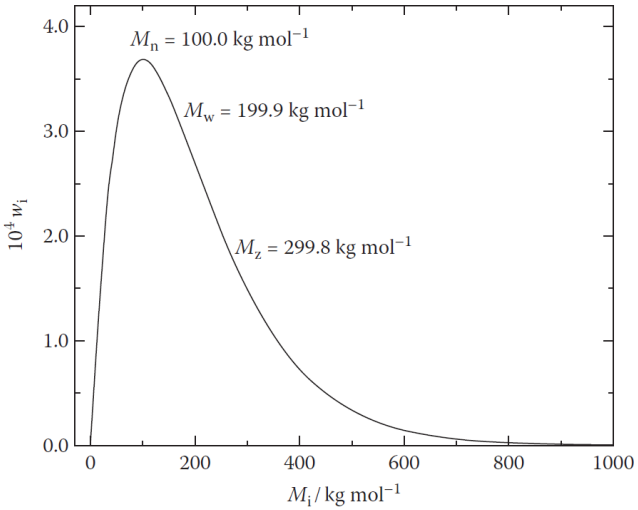


2 monomer units = repeat unit
n = 2x

Molecular weight averages

- number average MW [數平均分子量]
  - $\bar{M}_n = \sum X_i M_i = \dfrac{\sum N_i M_i}{\sum N_i}$ = total mass / total # of molecules
    - X_i = mole fraction of fraction i = N_i / ∑ N_i
    - N_i = # of molecules having M_i
  - #-avg degree of polym'n $\bar{x}_n = \dfrac{\bar{M}_n}{M_0}$
- weight average MW [重量平均分子量]
  - $\bar{M}_w = \sum w_i M_i = \dfrac{\sum N_i M_i^2}{\sum N_i M_i}$
    - w_i = weight fraction of fraction i = $N_i M_i$ / ∑ $N_i M_i$
  - wt-avg degree of polym'n $\bar{x}_w = \dfrac{\bar{M}_w}{M_0}$
- higher averages; M_z, M_{z+1} ---?

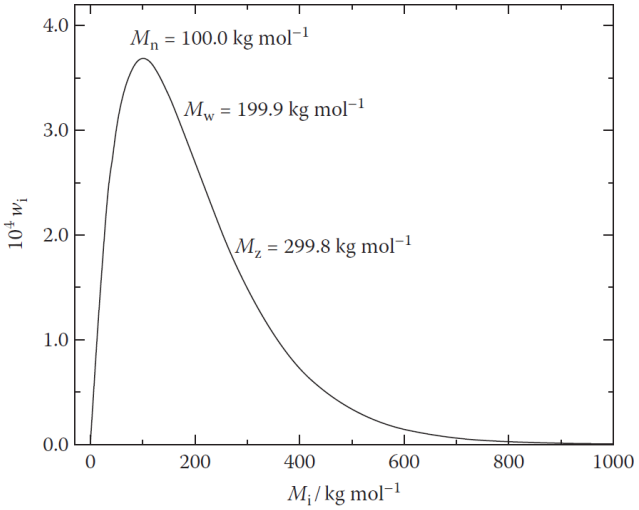
Fig 1.4



MM distribution

- polydispersity index [PDI, 多分散指數]
  - PDI = M_w/M_n
  - higher PDI = broader MMD
  - 2 – 5 for step polymers
  - 5 – 10 for chain polymers

Fig 1.4



MW and properties

- MW-independent properties
  - property depends on chemical structure
  - solubility, refractive index, --
- M_n-dependent properties
  - property depends on # of molecules
  - thermomechanical properties like strength, T_g
- M_w-dependent properties
  - property depends on motion of whole chain
  - melt viscosity

$$\eta = KM_w \text{ or } KM_w^{3.4}$$