Chapter 1

Concepts and Nomenclature

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
  - Staudinger ~ polystyrene (1920)
    - ‘Macromolecules are long-chain molecules.’
  - Carothers ~ nylon (1935)
  - Ziegler & Natta ~ polyethylene (1955)

- When is the start of ‘the Plastic Age’?

Nobel prizes

- 1953 (Chemistry) Hermann Staudinger for contributions to the understanding of macromolecular chemistry. Chapt 4
- 1963 (Chemistry) Giulio Natta and Karl Ziegler for contributions in polymer synthesis. (Ziegler-Natta catalysis). Chapt 6
- 1974 (Chemistry) Paul J. Flory for contributions to theoretical polymer chemistry. Chapt 3, 10, 16
- 1991 (Physics) Pierre-Gilles de Gennes for developing a generalized theory of phase transitions with particular applications to describing ordering and phase transitions in polymers. Chapt 16
- 2000 (Chemistry) Alan G. MacDiarmid, Alan J. Heeger, and Hideki Shirakawa for work on conductive polymers, contributing to the advent of molecular electronics. Chapt 8
- 2002 (Chemistry) John Bennett Fenn, Koichi Tanaka, and Kurt Wüthrich for the development of methods for identification and structure analyses of biological macromolecules. Chapt 14
- 2005 (Chemistry) Robert Grubbs, Richard Schrock, Yves Chauvin for olefin metathesis. Chapt 7

Definitions

- macromolecule = large [giant] molecule [巨大分子]
  - with high molar mass [molecular weight]
- 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
  - strictly;
    - A macromolecule is a molecule.
    - A polymer is composed of macromolecules.
    - Polymers are synthesized [polymerized].

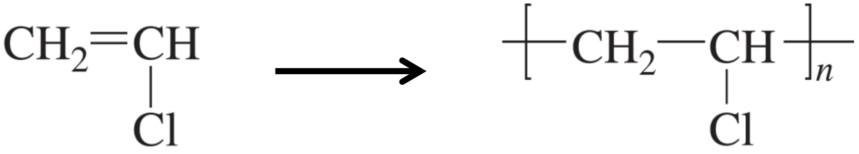
Classification of polymers

- by chemical structure
  - homopolymers ~ with single type of repeat unit
    - chain polymers
    - step polymers
  - copolymers ~ with ≥2 different types of repeat unit
- by skeletal structure
  - linear vs branched vs crosslinked polymers
- by aggregation structure
  - amorphous vs (semi)crystalline polymers
- by (thermomechanical) behavior
  - thermoplastics vs thermosets

Nomenclature of homopolymers

- 2 types of homopolymers and nomenclature
  - chain polymers
    - #1-8, Table 1.1 p7
    - from chain polymerization
    - source-based nomenclature: poly+monomer
    - repeat unit = monomer unit

Memorize Table 1.1!!!



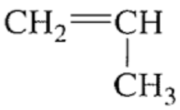
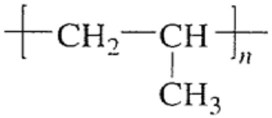
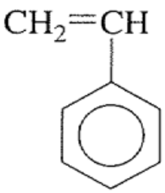
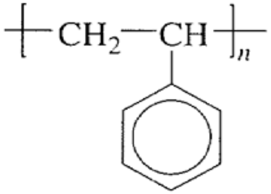
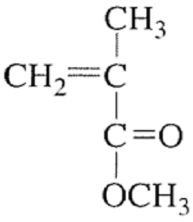
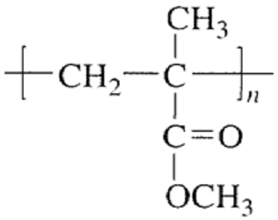
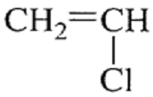
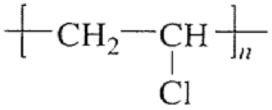
$$CH_2{=}CH(Cl) \longrightarrow \left[CH_2{-}CH(Cl) \right]_n$$

vinyl chloride

poly(vinyl chloride) *or* polyvinyl chloride

( ) for more than 2 words;
omitted conveniently and commonly

Table 1.1

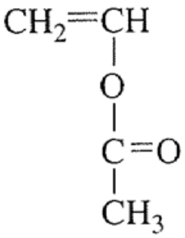
Monomers	**Polymer**
1. Ethylene $CH_2{=}CH_2$	Polyethylene (PE) $\left[CH_2-CH_2 \right]_n$
2. Propylene  $CH_2{=}\underset{CH_3}{CH}$	Polypropylene (PP)  $\left[CH_2-\underset{CH_3}{CH} \right]_n$
3. Tetrafluoroethylene $CF_2{=}CF_2$	Polytetrafluoroethylene (PTFE) $\left[CF_2-CF_2 \right]_n$
4. Styrene 	Polystyrene (PS) 
5. Methyl methacrylate  $CH_2{=}\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}$	Poly(methyl methacrylate) (PMMA)  $\left[CH_2-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}} \right]_n$
6. Vinyl chloride  $CH_2{=}\underset{Cl}{CH}$	Poly(vinyl chloride) (PVC)  $\left[CH_2-\underset{Cl}{CH} \right]_n$

PE > PP > PVC > PS > PMMA ~ 5 GPPs

Monomers

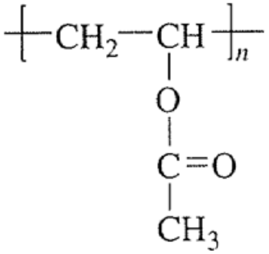
Polymer

7. Vinyl acetate



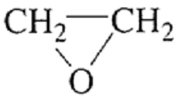
$CH_2{=}\begin{array}[t]{l}CH\\ |\\ O\\ |\\ C{=}O\\ |\\ CH_3\end{array}$

Poly(vinyl acetate)



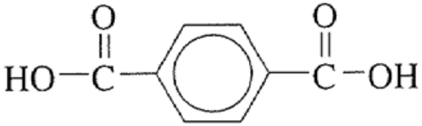
$\left[CH_2-\begin{array}[t]{l}CH\\ |\\ O\\ |\\ C{=}O\\ |\\ CH_3\end{array}\right]_n$

8. Ethylene oxide

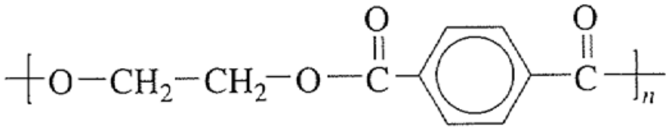


Poly(ethylene oxide) (PEO) $\left[CH_2-CH_2-O\right]_n$

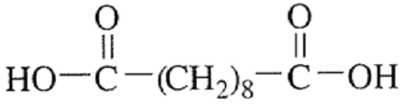
9. Ethylene glycol $HO-CH_2-CH_2-OH$ and terephthalic acid



Poly(ethylene terephthalate) (PET)[a]

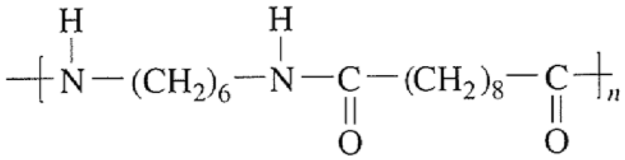


10. Hexamethylene diamine $H_2N-(CH_2)_6-NH_2$ and sebacic acid



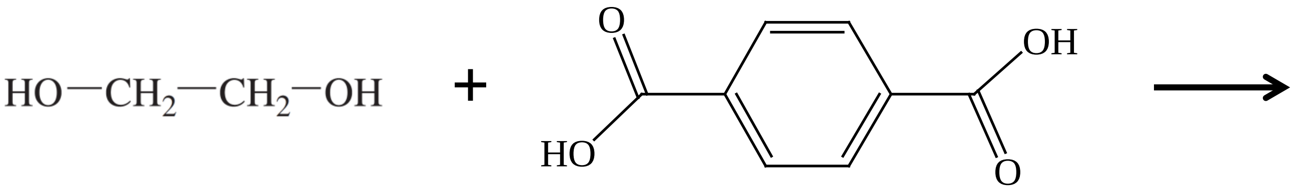
$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH$

Poly(hexamethylene sebacamide) (nylon 6.10)[a]



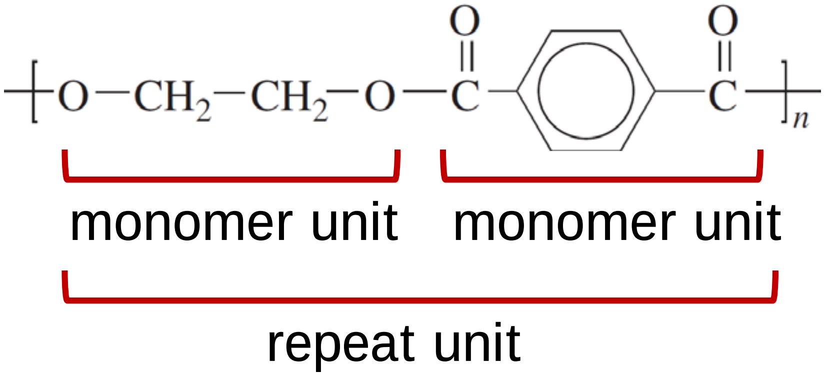
$\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_8-\underset{\underset{O}{\|}}{C}\right]_n$

- step polymers
  - #9,10, Table 1.1 p8
  - from step polymerization
  - structure-based nomenclature: poly+repeat unit
  - repeat unit ≠ monomer unit (structural unit)



poly(ethylene terephthalate)

polyethylene terephthalate



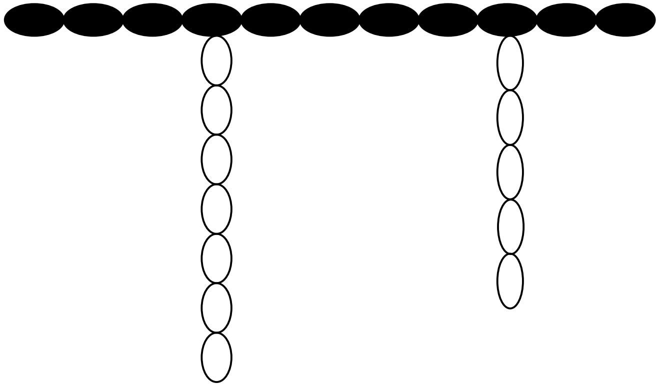
Copolymers

- polymer with ≥2 different types of repeat unit
- types
  - alternating ~ --ABABABAB---
    - poly(A-*alt*-B)

  - statistical
    - Sequence distribution obeys statistical rule.
    - Markov chain ~ dep on previous unit only
    - poly(A-*stat*-B)

  - random
    - Bernoulli distrib'n ~ indep of previous unit
    - poly(A-*ran*-B)

- types (cont'd)
  - block ~ --AAAAAABBBBB---
    - poly(A-*b*-B) or polyA-*block*-polyB
  - graft
    - poly(A-*g*-B) or polyA-*graft*-polyB

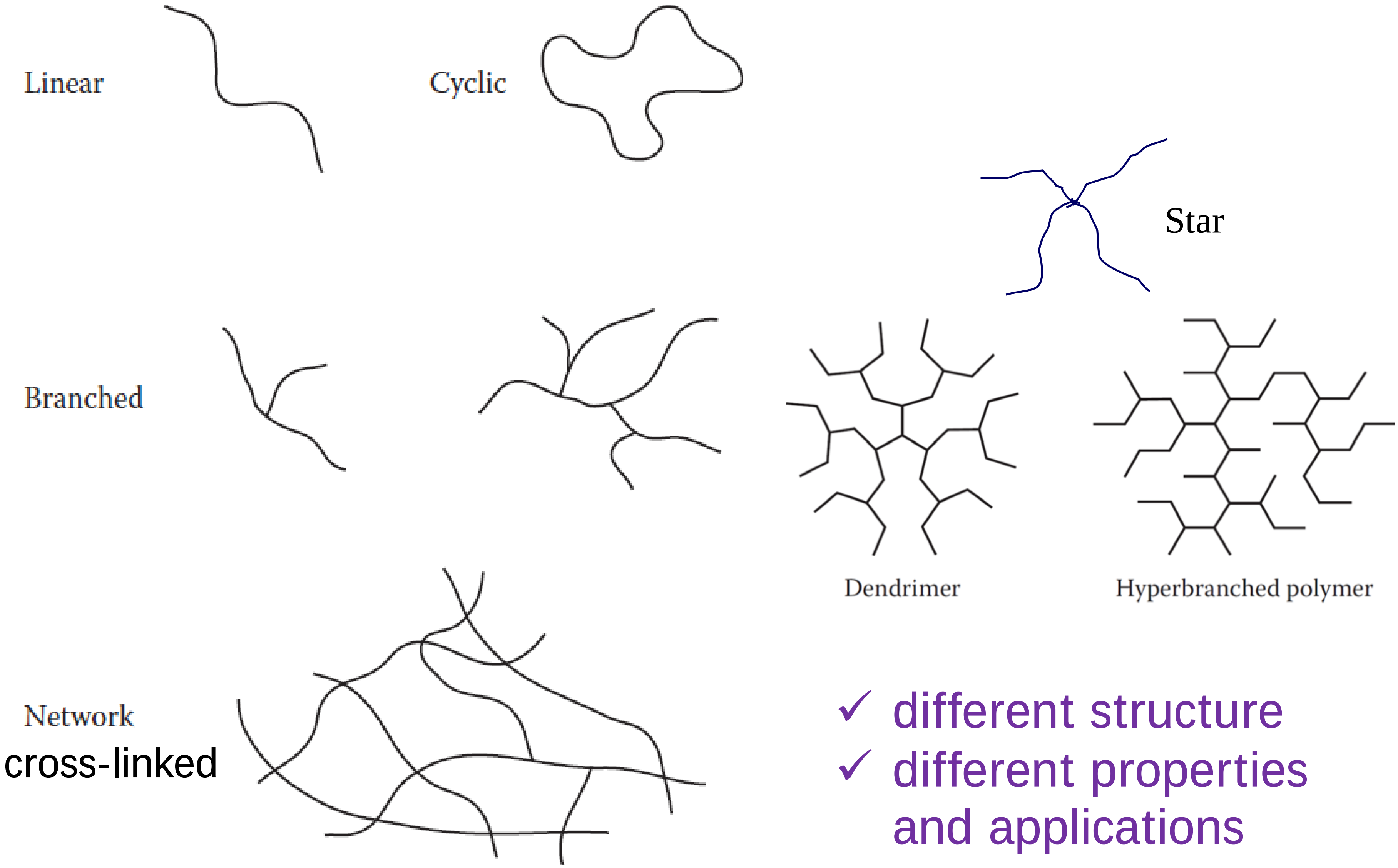


➢ poly(A-*co*-B) ~ unspecified

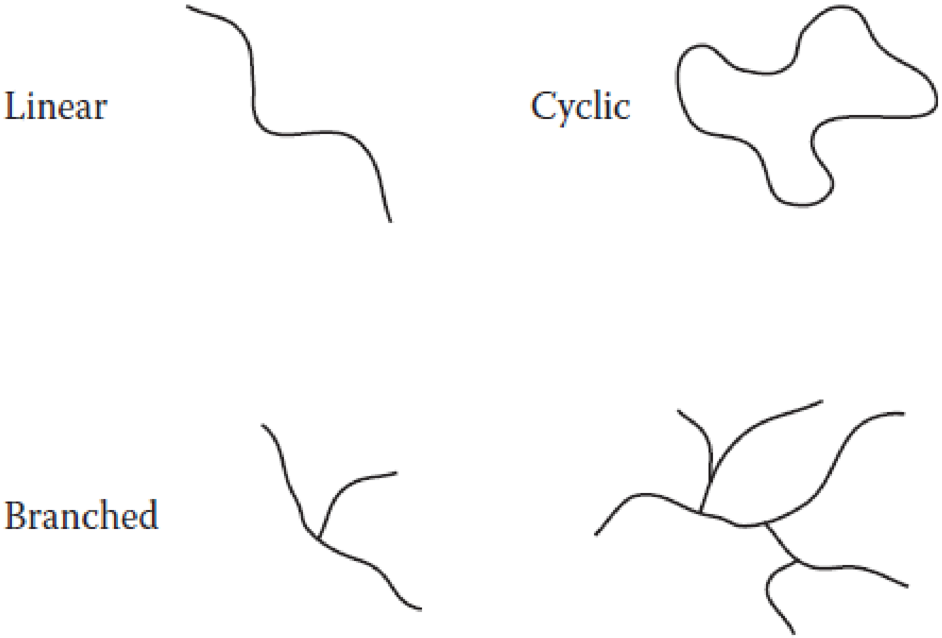
✓ alt, stat, ran ~ no phase separation, avg property

✓ block, graft ~ phase separation, composite property

Skeletal structure

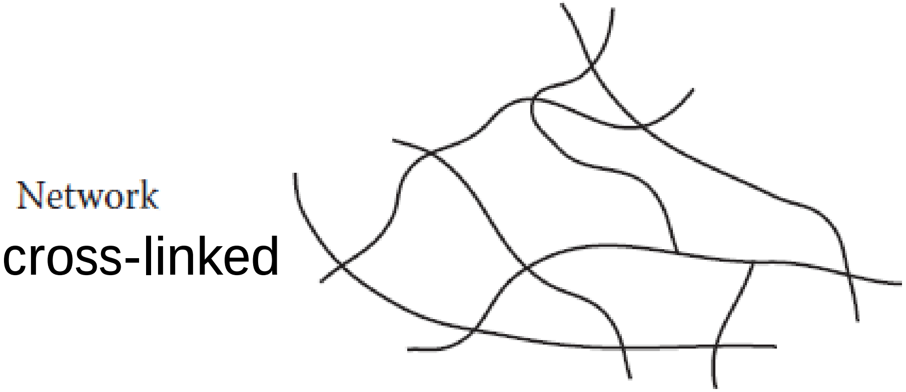


- ✓ different structure
- ✓ different properties and applications



solube in solvent

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

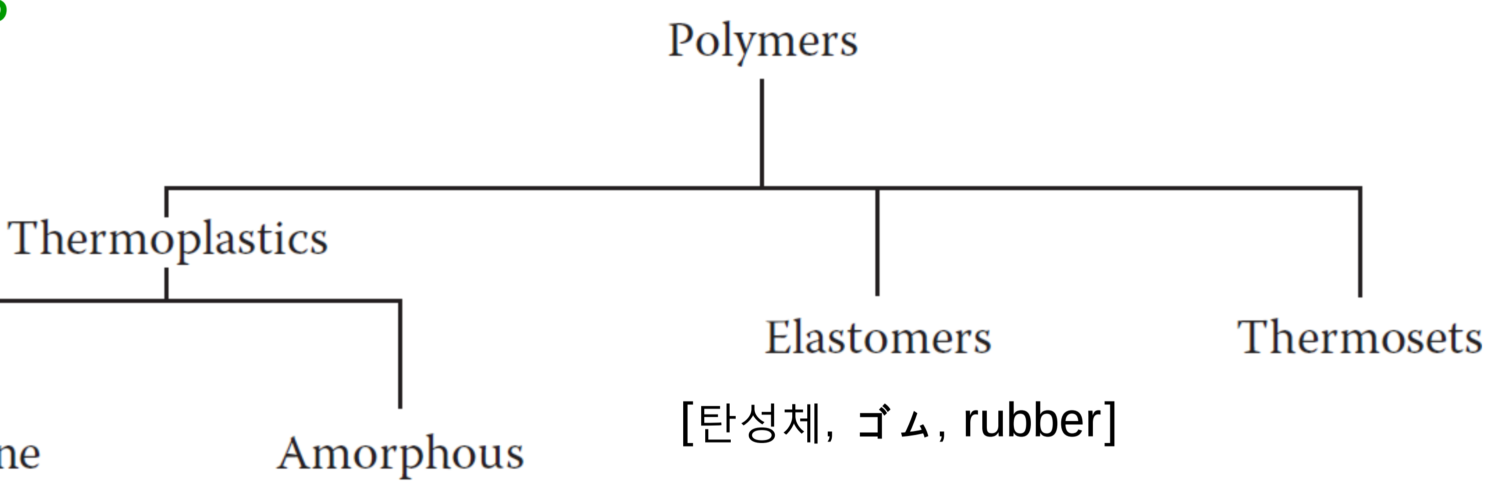


cross-linked

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

Aggregation structure and behavior

Figure 1.3



(semi) Crystalline

[(半)結晶性]

Amorphous

[無定形]

Elastomers

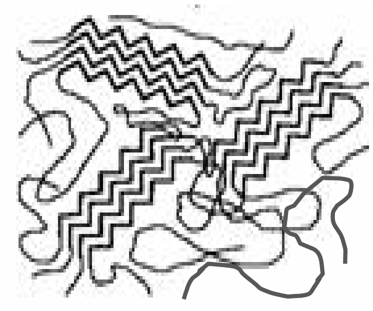
[탄성체, ゴム, rubber]

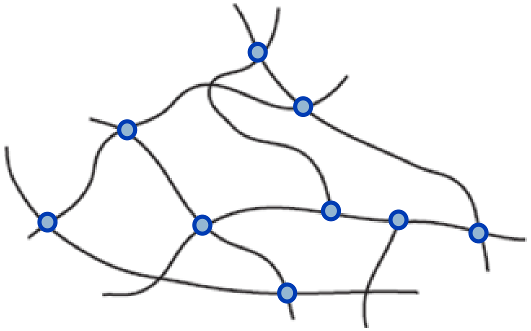
Thermosets

PIP, PDMS, ---

epoxy, PF, ---

- ✓ flexible chain (T > T_g)
- ✓ low Xlink density



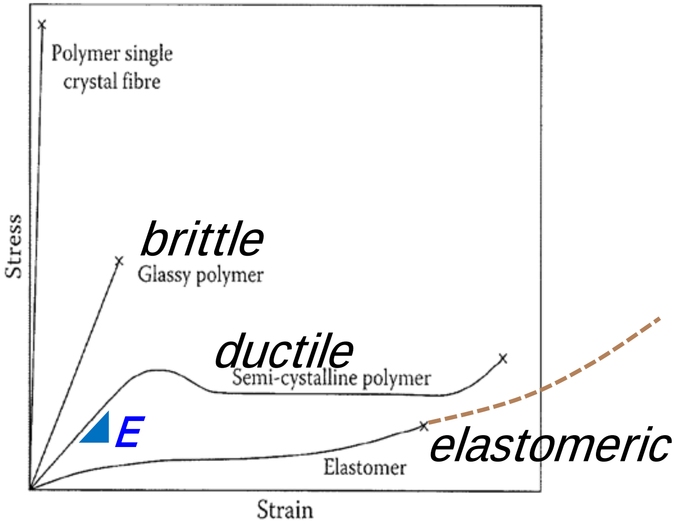


PE, nylon, ---

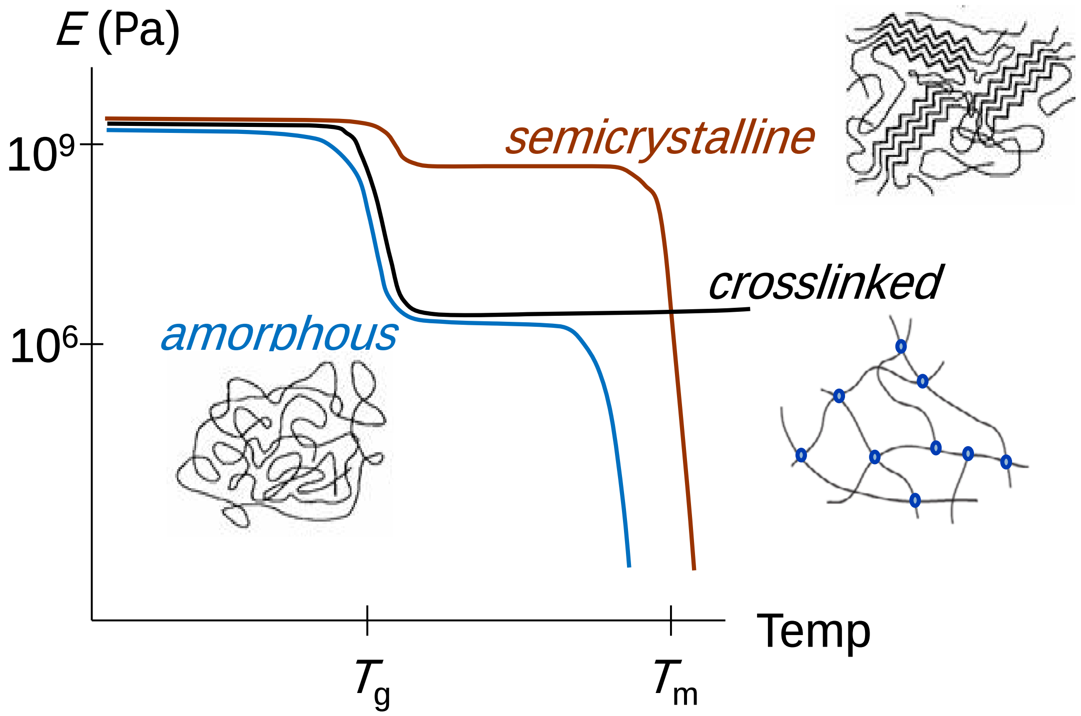
PS, PMMA, PVC, ---

- ✓ depends on chain regularity and cooling rate

Fig 19.4 p477 ~ partly wrong



thermosets	elastomers
- stiff chain ($T < T_g$)	- flexible chain ($T > T_g$)
- high Xlink density	- low Xlink density



glass(-rubber)
transition Temp

(crystal)
melting Temp

T_g and T_m determined by
- chain flexibility
- interchain interaction

Molar mass [分子量]

- polymer is 'molecule with high molar mass'
  - molar mass vs molecular weight
    - [g/mol] vs dimensionless (or [g/molecule])
    - MM preferred over MW
    - still, interchangeable
- polymer is gathering of chains
  - with distribution of molar mass
    - MM distribution [MMD, 分子量分布]
    - polydisperse (not monodisperse)
  - MM should be averages

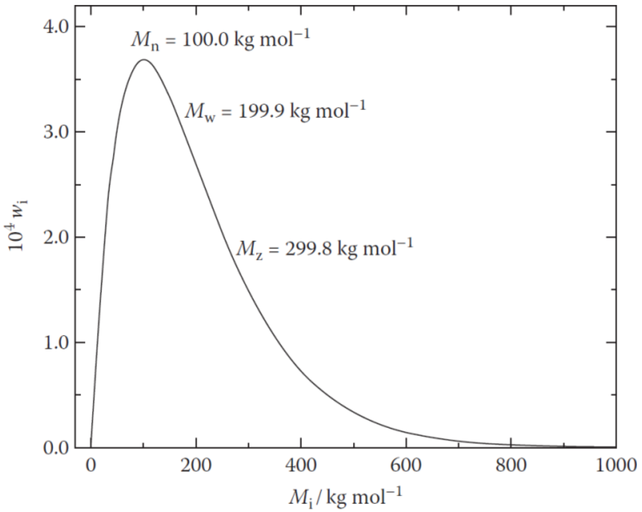
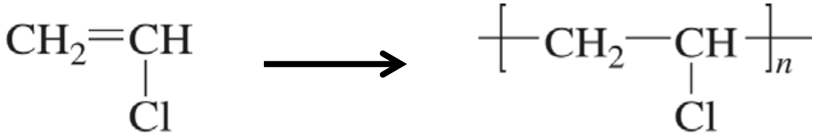
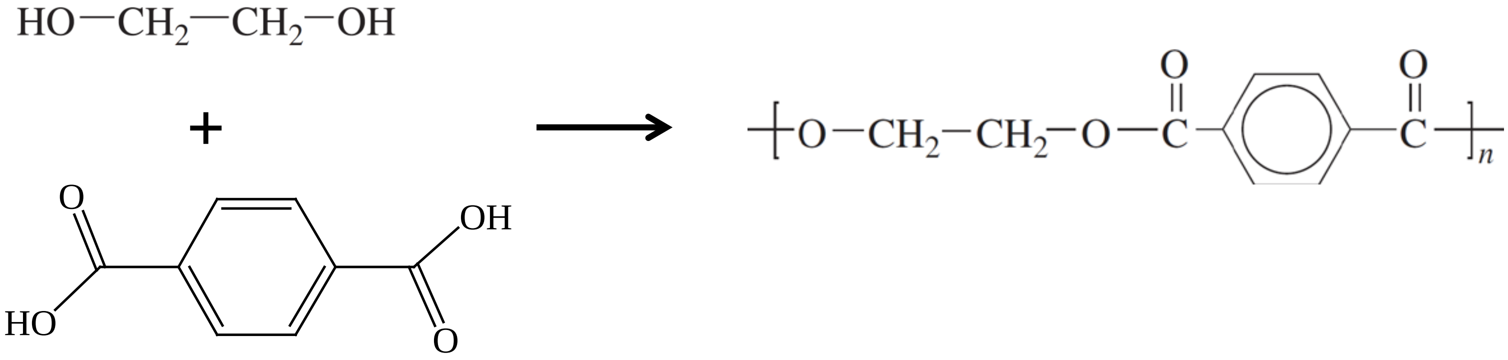


Fig 1.4

- MM of polymer, M = x M_0
  - x ~ (average) degree of polymerization
  - M_0 ~ molar mass of monomer unit (not repeat unit)

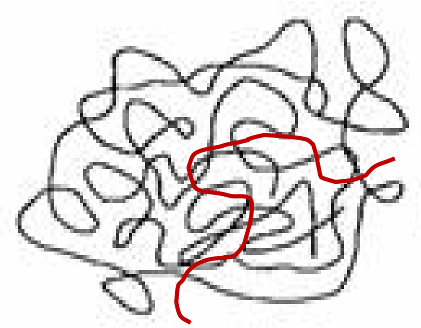




Molar mass averages

- number avg molar mass [數平均分子量]

$$\bar{M}_n = \sum X_i M_i = \frac{\sum N_i M_i}{\sum N_i}$$ = total mass / total #



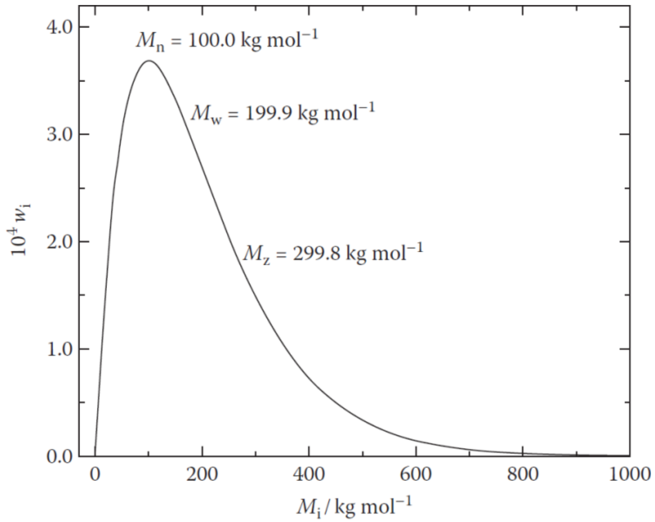
  - N_i = number of molecules having M_i
  - X_i = number [mole] fraction of i = $N_i / \Sigma N_i$
  - $M_n = x_n M_0$
    - x_n = number avg degree of polym'n
- weight avg molar mass [重量平均分子量]

$$\bar{M}_w = \sum w_i M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

  - w_i = weight fraction of i = $N_i M_i / \Sigma N_i M_i$
  - $M_w = x_w M_0$

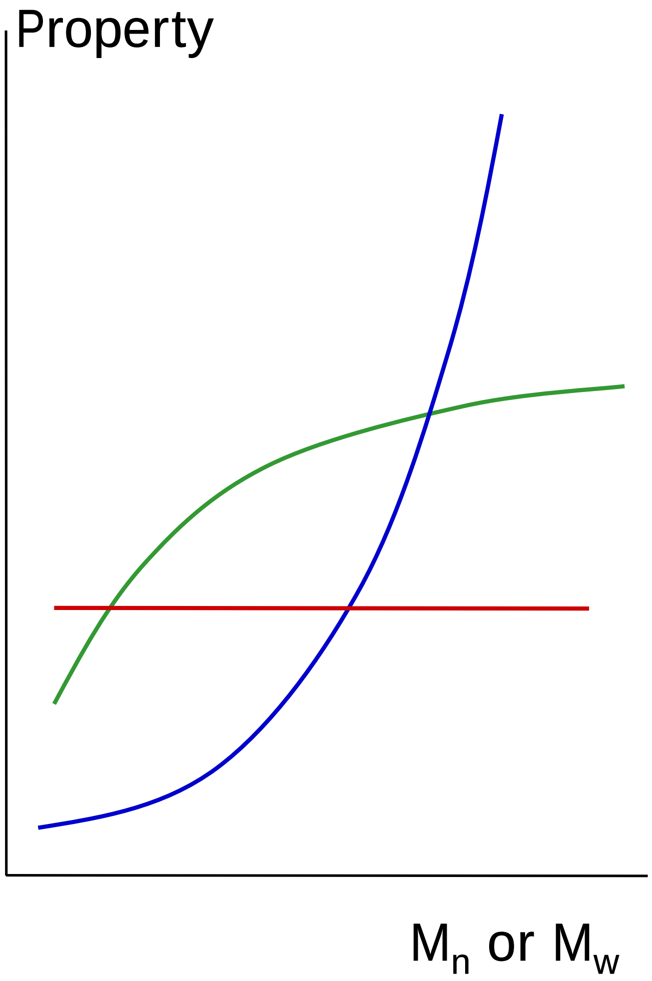
fr	M	N	NM	NM^2
i	1E4	10	1E5	1E9
i+1	2E4	10	2E5	4E9
Σ		ΣNi	ΣNiMi	ΣNiMi^2

- other avg's
  - M_z, M_{z+1}, ---
  - M_v
- MM distribution
  - polydispersity index, PDI = M_w/M_n
  - PDI of 'most probable' distribution = 2
  - PDI can be < 2, mostly > 2
- IUPAC recommended in 2009;
  - polydisperse → non-uniform
  - monodisperse → uniform
  - PDI → D (dispersity)



MM and properties

- Property
  - MM independent
    - property dep on chem structure
    - solubility, refractive index, --
  - M_n dependent
    - property dep on # of molecules
    - strength, T_g
  - M_w dependent
    - property dep on motion of whole chain
    - melt viscosity $\eta = KM_w$ or $KM_w^{3.4}$

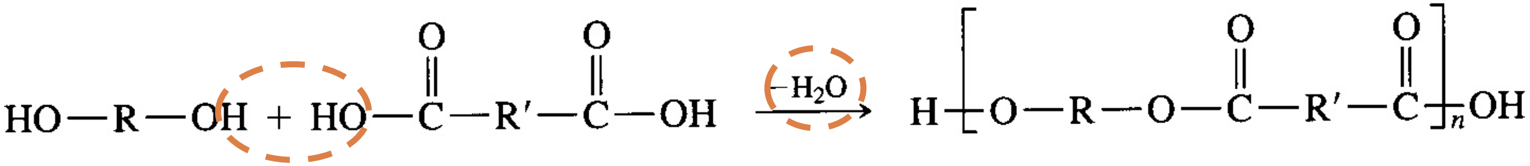


Chapter 2

Principles of Polymerization

Classification of polym'n (1)

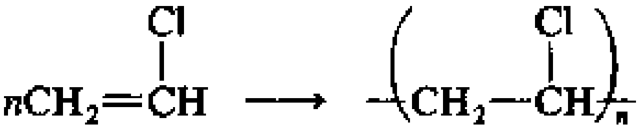
- by type of reaction ~ Carothers' method ~ *older*
  - condensation polym'n
    - #9 & 10, Table 1.1 p7
    - condensation rxn → releasing small molecule like water



$$\mathrm{HO{-}R{-}OH + HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R'{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \xrightarrow{-H_2O} H{+}\!\left[O{-}R{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R'{-}\overset{\displaystyle O}{\overset{\|}{C}}\right]_n\!OH}$$

  - addition polym'n
    - #1 - #8, Table 1.1 p7
    - addition rxn → not releasing small molecule

PU polymerized by addition rxn of functional groups



$$n\mathrm{CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}H}} \longrightarrow \left(\mathrm{CH_2{-}\overset{\displaystyle Cl}{\overset{|}{C}H}}\right)_n$$

Classification of polym’n (2)

- by mechanism Table 2.1
  - step (growth) polym’n [段階重合]
    - reaction of functional groups
    - stepwise growth of the polymer chain
    - n-mer + m-mer → (n+m)-mer
    - #9 & 10, Table 1.1 p7
  - chain (growth) polym’n [連鎖重合]
    - addition of monomer unit to the growing chain
    - chain reaction
    - n-mer + monomer → (n+1)-mer
    - #1 - 8, Table 1.1 p7

Step vs chain polym’n

step polym’n	chain polym’n
Any two species can react.	Reaction of growing chain and monomer
Monomer disappears early.	Monomer concentration decreases steadily.
Polymer molecular weight rises steadily.	High polymer formed at once.
Long reaction time required for high MW.	Long reaction time gives high yield only.
At any stage, species of any MM are present with distribution.	Only monomer, high polymer, and very small amount of growing chain are present.

Ch 3	Step polym’n	
Ch 4	Radical polym’n	chain polym’n
Ch 5	Ionic polym’n	
Ch 6	Coordination polym’n	
Ch 7	Ring-opening polym’n	
Ch 8	Specialized methods	
Ch 9	Copolymerization	
Ch 10-15	Molar mass determination	

Monomer functionality

- functionality of monomer, f
  - the number of chain links the monomer can give rise to
- f and structure
  - f = 2 → linear polymer Figure 2.1
    - a double bond or a ring ~ f = 2
    - diol, diamine, diacid, etc ~ f = 2
  - f > 2 → non-linear polymer (branched, Xlinked)
  - f= 1 → ?

Reactivity of functional groups

- equal reactivity of functional groups
  - reactivity indep of molecular size
  - reactivity of one end irrespective of the other end
  - an assumption proved exp'tally → principle
    - Problem 2.2 p18
- theoretical validation
  - reactivity ∝ collision frequency

1. Rxn is slower than diffusion, esp for step polym'n.
2. If not [If diffusion-controlled], diffusion of ftnal group is much faster than that of whole molecule.
3. If not [If diffusion rate depends on molecular size], large molecules diffuse in and diffuse out slowly.