Polymeric Materials

Chemical and Biological Engineering
458.645
2nd semester, 2019

Textbook

- Plastic Technology Handbook
  - 5th Edn, 2018
  - Chanda, M
  - 7 chapters, 1012 pages
  - Covers everything of polymeric materials
    - properties, processing, materials

Chapters

1 Characteristics

3 Properties and testing

2 Fabrication = processing

4 Industrial polymers = structural polymers

5 Polymers in special uses = functional polymers

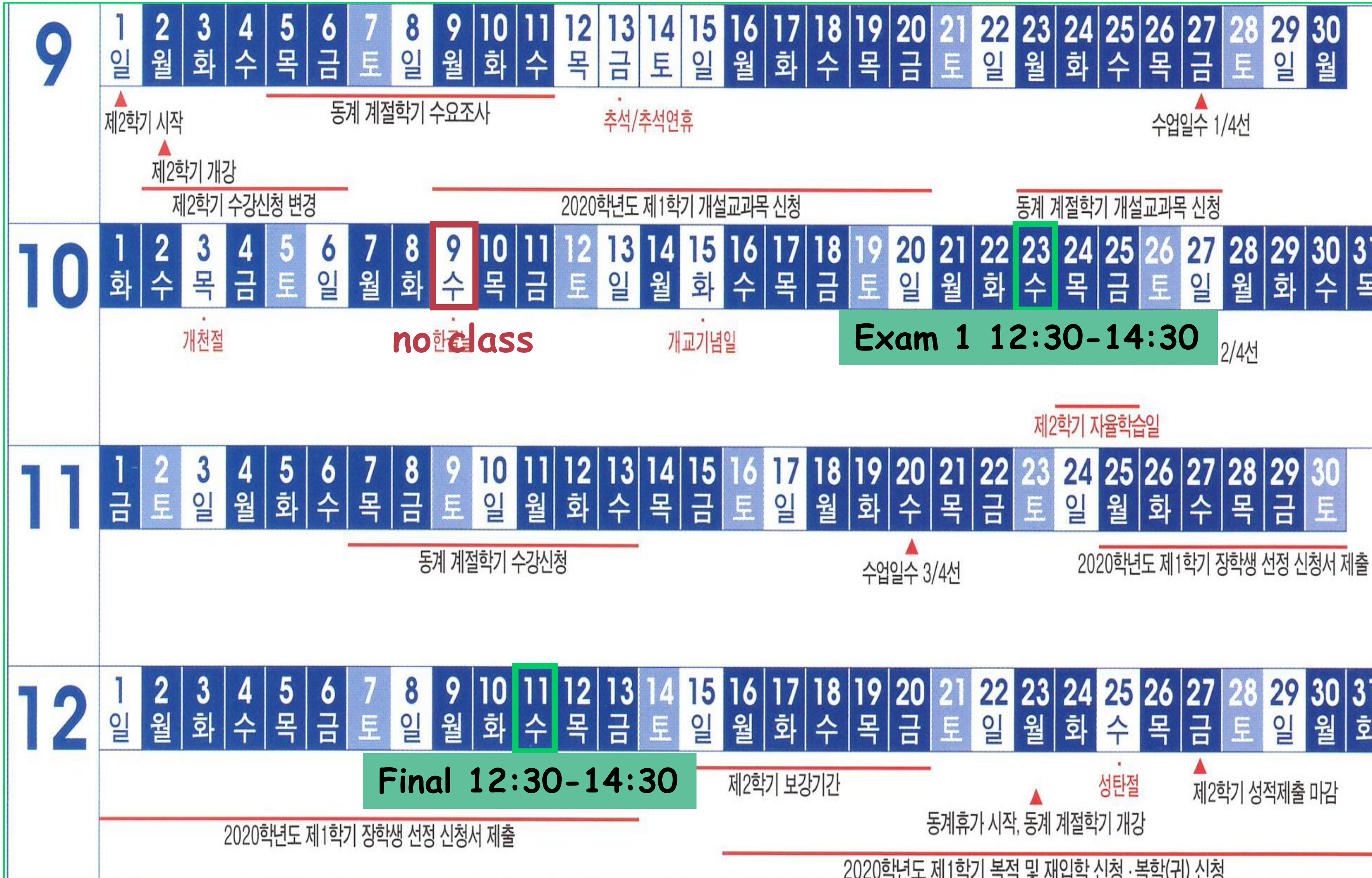
6 Recycling

7 Trends in applications

Grading

- total 220 points
  - 2 exams x 100 = 200 points
    - midterm, Chapt 1 – 3
    - final, Chapt 4 – 7
  - 2 homework assignments x 10 = 20 points
    - past years' exam problems

Schedule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제2학기 시작
제2학기 개강
동계 계절학기 수요조사
추석/추석연휴
수업일수 1/4선
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2020학년도 제1학기 개설교과목 신청
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Exam 1 12:30-14:30
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11
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12
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Final 12:30-14:30
제2학기 보강기간
성탄절
제2학기 성적제출 마감
동계휴가 시작, 동계 계절학기 개강
2020학년도 제1학기 장학생 선정 신청서 제출
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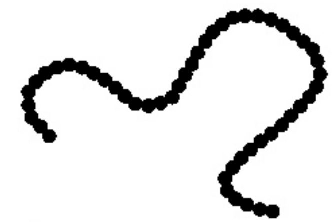
Chapter 1

Characteristics

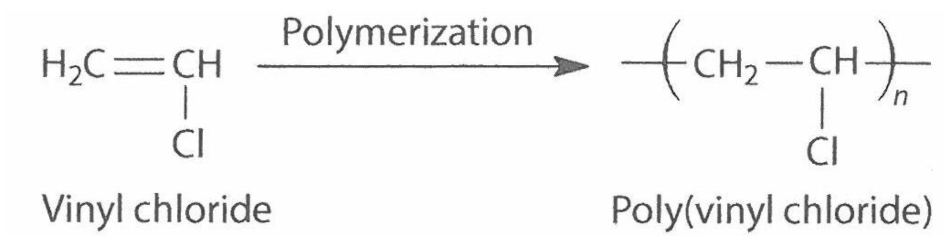
molecular characteristics
structure-property relations
additives

Polymer

- polymer
  - polymer = poly + mer = many parts
  - macromolecules = giant molecule



- polymerization



  - monomer to oligomer to polymer
  - degree of polymerization [DP]
    - mol wt of monomer [M_0] x DP = mol wt of polymer
    - molecular weight = molar mass [g/mol]
  - distribution of mol wt; average mol wt

Mol wt averages

- number-average mol wt, M_n

$$\bar{M}_n = \frac{W}{N} = \frac{\sum N_i M_i}{N} = \sum n_i M_i$$

$$\overline{DP}_n = \frac{\bar{M}_n}{M_0}$$

- M_n determination
  - end-group analysis
  - colligative property measurements
    - ebulliometry (← bp elevation)
    - cryoscopy (← fp depression)
    - membrane osmometry [MO]
    - vapor phase [pressure] osmometry [VPO]
  - none used these days

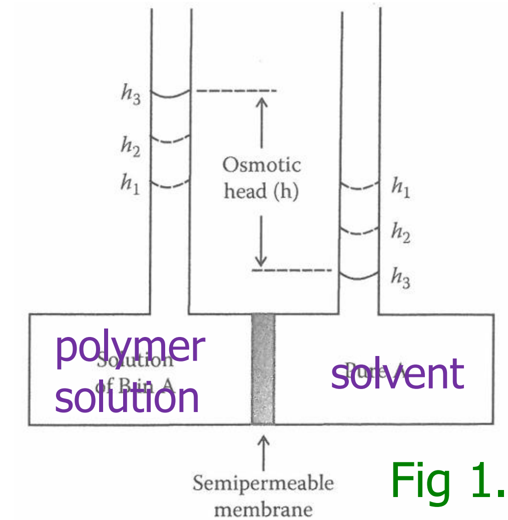
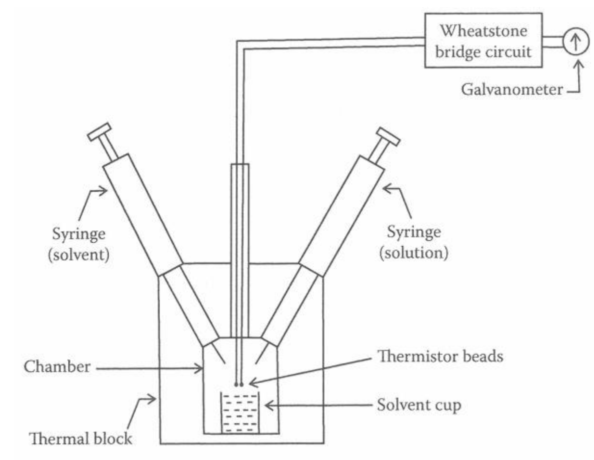


Fig 1.3

Fig 1.5

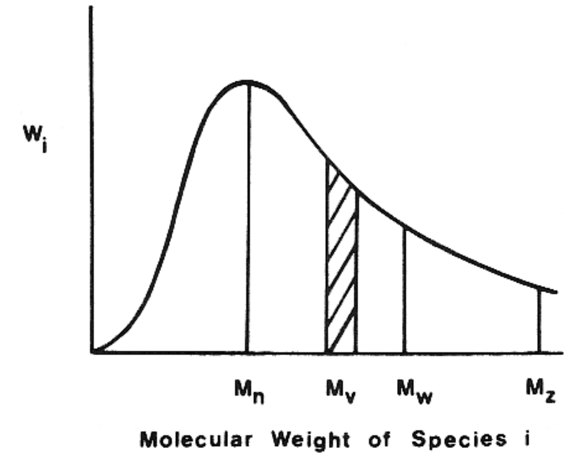


- wt-avg mol wt, M_w

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

= W

  - weighted on the larger; $M_w \geq M_n$
  - M_w determination
    - light scattering [LS]
      - intensity of scattered light ∝ (mass of molecule)^2 and concentration of solution
      - LALLS used
      - more for dynamics



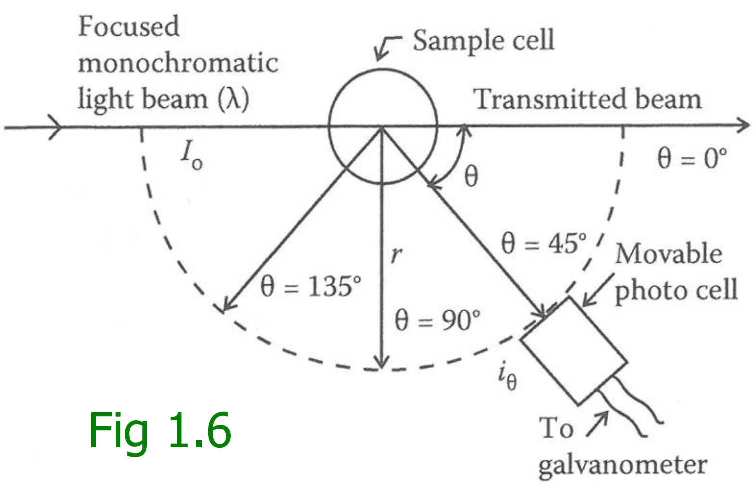
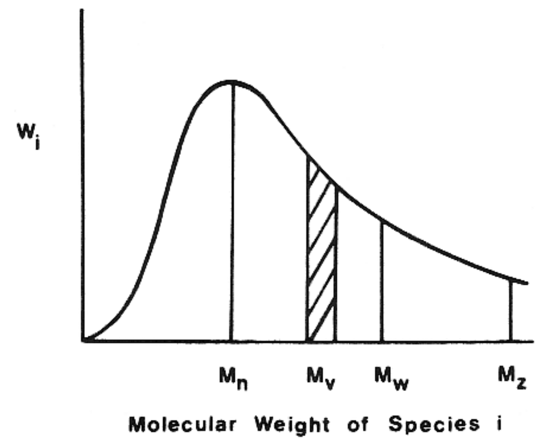


Fig 1.6

- viscosity-avg mol wt, M_v

$$\bar{M}_v = \left[\sum w_i M_i^a\right]^{1/a} = \left[\sum N_i M_i^{1+a} / \sum N_i M_i\right]^{1/a}$$



  - a relative method ← size not mass
- M_v determination
  - dilute solution viscometry [DSV]
    - intrinsic viscosity $([\eta]) = \lim_{c \to 0} \frac{1}{c}\left(\frac{\eta}{\eta_o} - 1\right)$
    - Mark-Houwink-Sakurada [MHS] eqn
      - relates size and mass $[\eta] = K\bar{M}_v^a$
      - K and a from handbook
    - popular (in the lab)

$$\frac{\eta}{\eta_o} = \frac{t}{t_o}$$

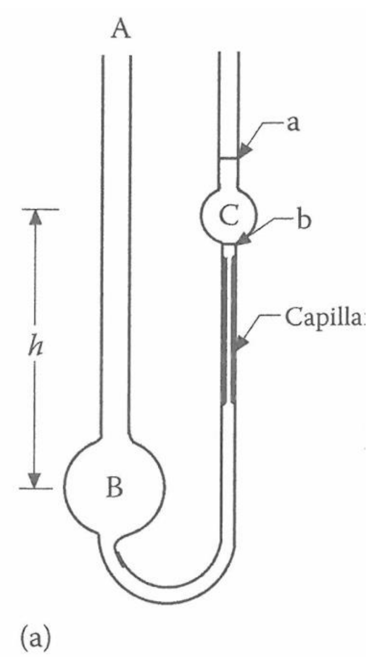
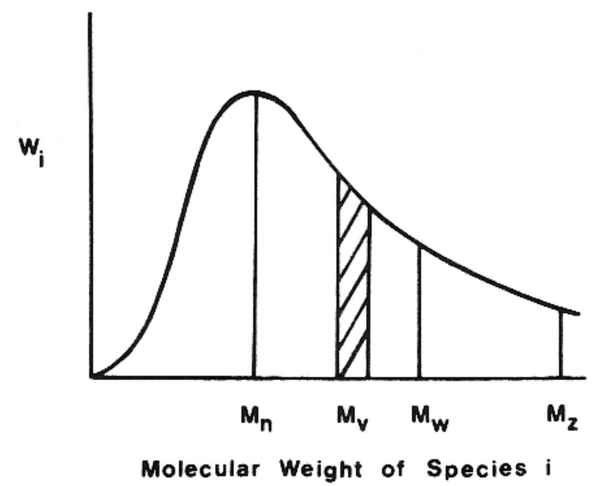


Fig 1.8

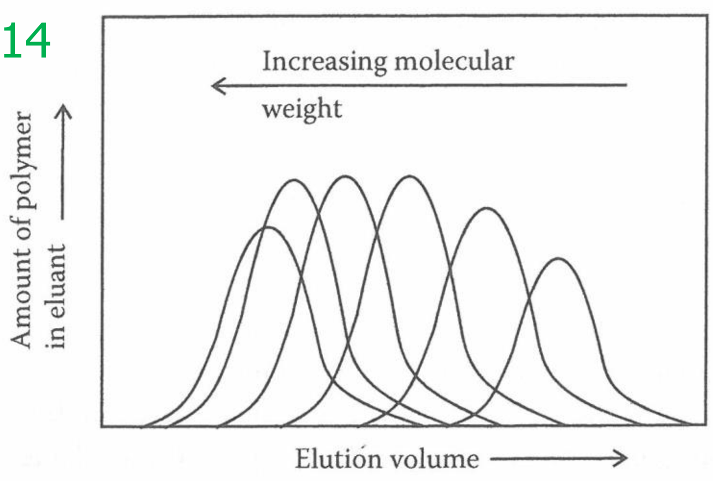
Mol wt distribution

- polydispersity index [PDI]
  - PDI = M_w/M_n
    - measure of width of distribution
    - PDI = 1 ~ monodisperse
    - PDI = 2 - 3 for step polymers
    - PDI = 2 - 10 for chain polymers

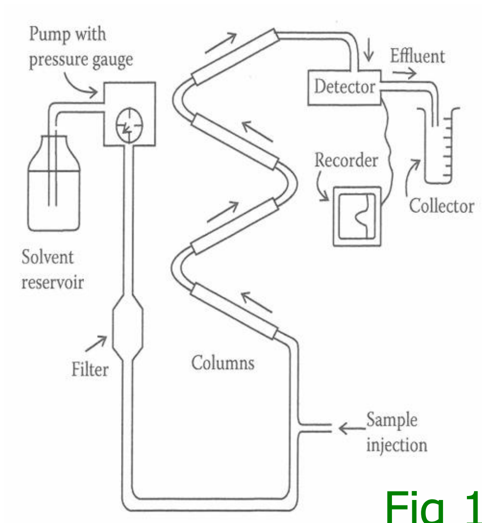


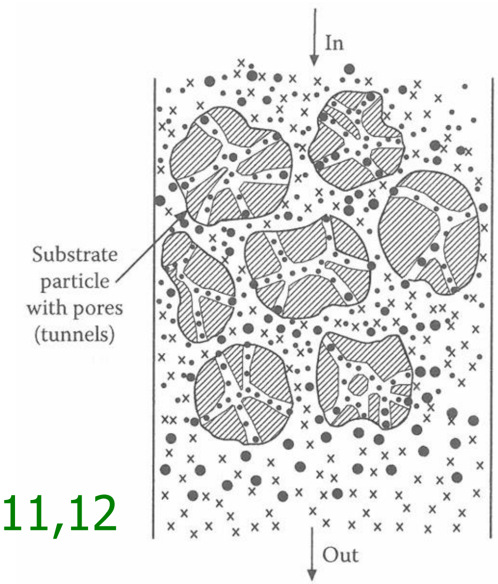
- determination of MWD
  - fractionation
  - gel permeation chromatography [GPC]
    - most popular
  - *Example 1, 2, 3*

Fig 1.14



- gel permeation chromatography [GPC]





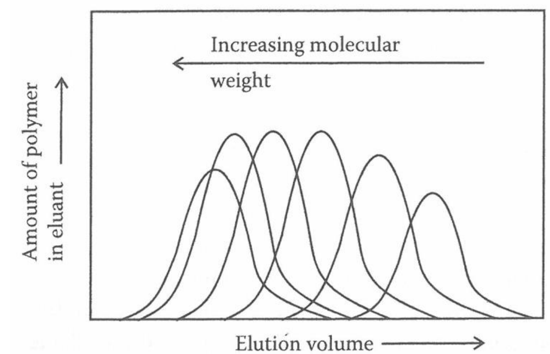


Fig 1.11,12

  - universal calibration

$$\log([\eta]_x M_x) = \log([\eta]_s M_s)$$

$$[\eta] = K\bar{M}_v^a$$

$$\log M_x = \left(\frac{1}{1+a_x}\right)\log\frac{K_s}{K_x} + \frac{1+a_s}{1+a_x}\log M_s$$

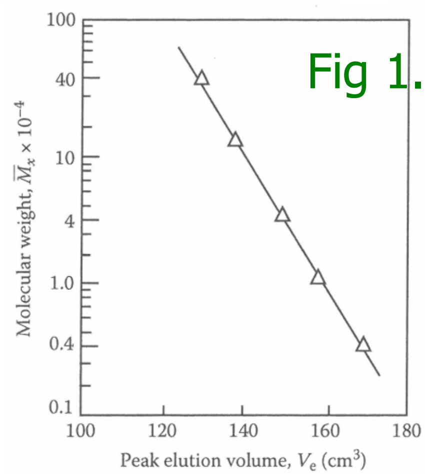
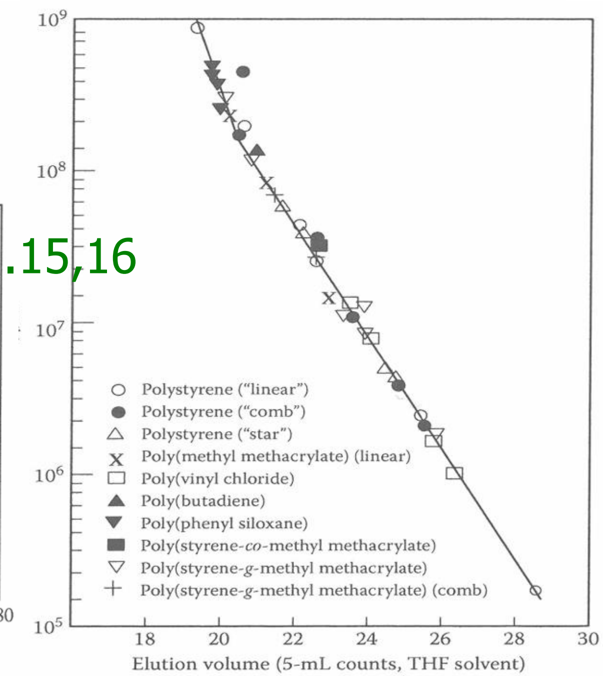


Fig 1.15,16



MW and properties

- threshold MW
  - gas to liquid to wax to solid
  - depends on type of polymers
    - small for step polymers
- dependence
  - MW independent
    - dep on chemical structure
  - M_n dependent
    - $T_g = T_g(\infty) - A/M_n$
    - most thermomechanical prop's
  - M_w dependent
    - $\eta = B\, M_w^x$

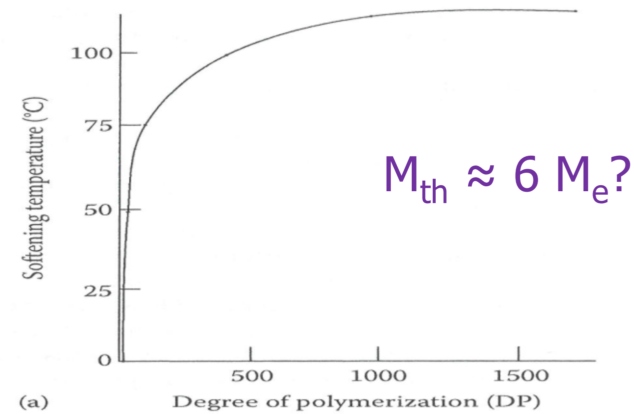
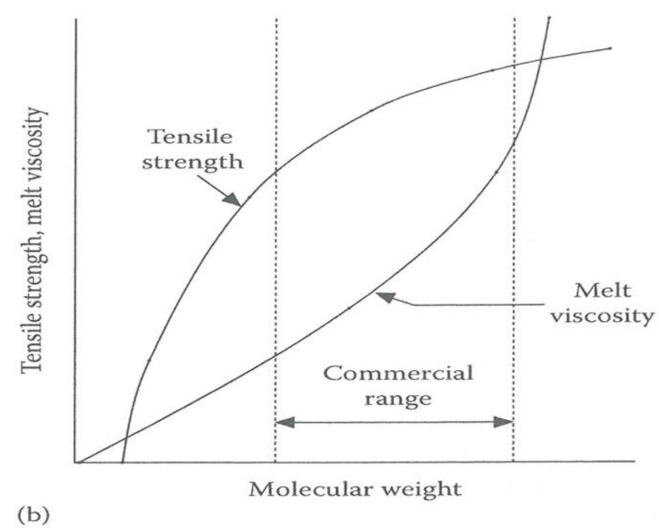


Fig 1.2 p2

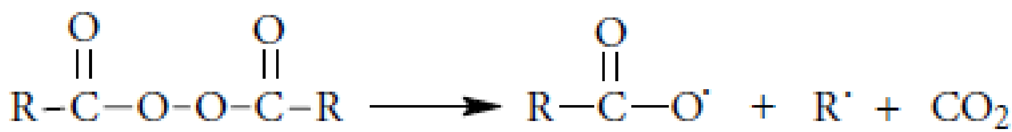


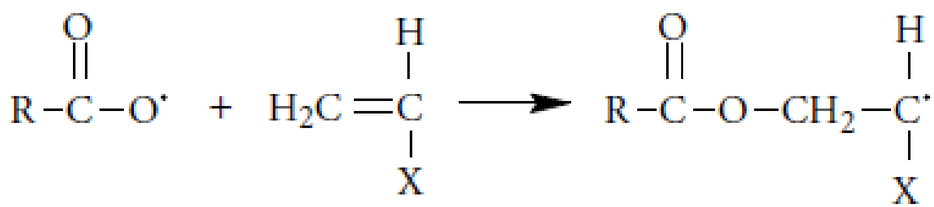
Polymerization

- classification
  - addition vs condensation polym'n ~ old
    - by monomer type ~ C=C or ring vs functional group
  - chain vs step polym'n ~ current
    - by growth mechanism ~ chain rxn vs step rxn
- chain polym'n
  - $I \rightarrow I^* \rightarrow IM^* \rightarrow IMM^* \rightarrow \text{---} \rightarrow IM_n^* \rightarrow IM_{n+1}^*$
  - *; active center
    - * = • [free-radical] → radical polym'n
    - * = ⊕ [cation] → cationic poym'n
    - * = Θ [anion] → anionic poym'n
    - * = coordination site → coordination polym'n

Radical polym'n

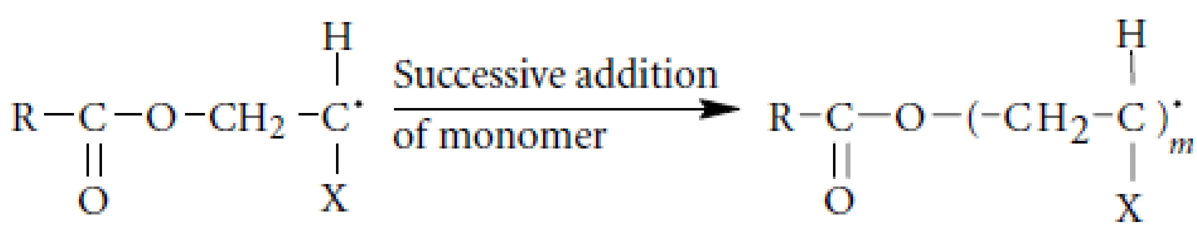
- mechanism
  - initiation



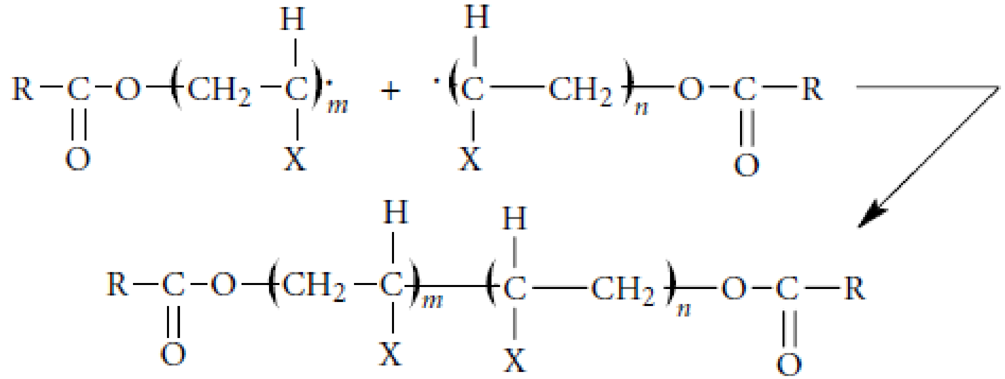


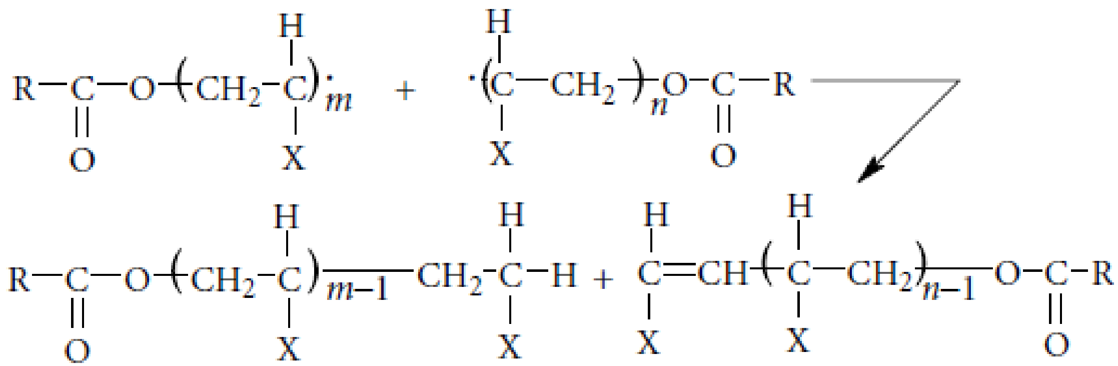
(X = ~~CH_3~~, C_6H_5, Cl, etc.)

  - propagation

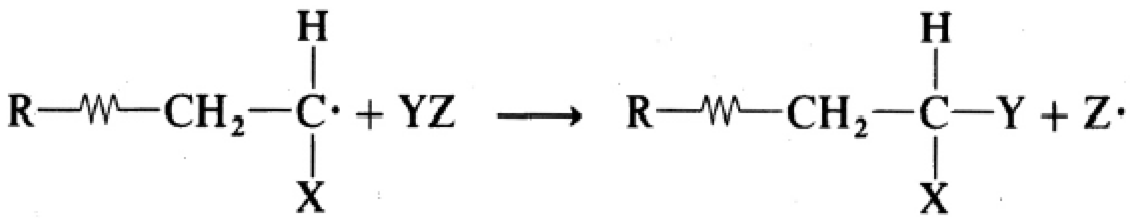


- termination
  - death of active center stopping chain growth
  - through either coupling or disproportionation





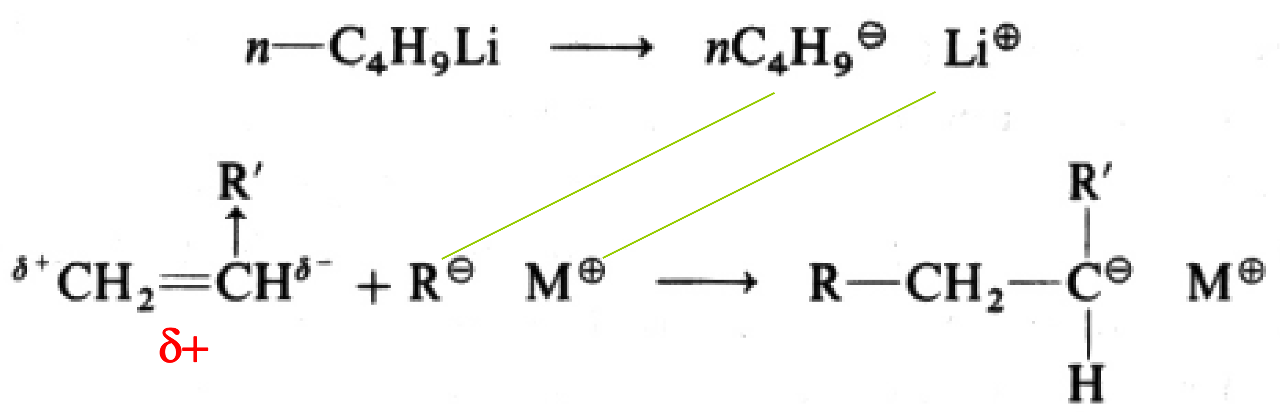
- chain transfer



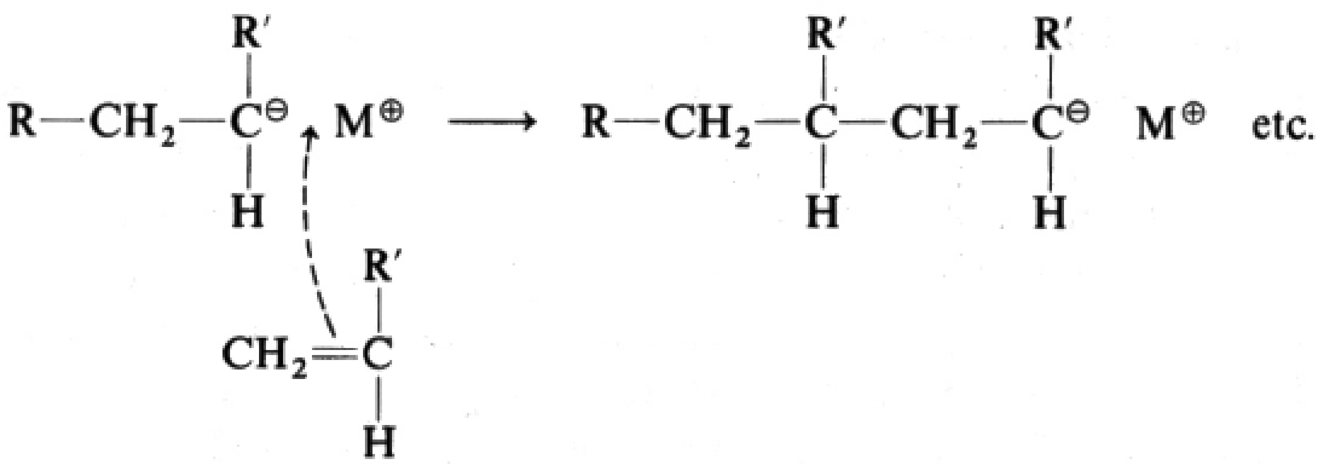
  - to initiator, monomer, solvent, and/or polymer
  - CT to I, M, S lower mol wt
  - CT to polymer enlarge PDI
- retardation and inhibition
- autoacceleration
  - increase of polym’n rate at later stage [high conversion]
  - make PDI even larger

Ionic polym'n

- selective to monomer
  - e-withdrawing substituent ~ anionic polym'n
  - e-donating substituent ~ cationic polym'n
  - radical? ~ not selective, most monomers
- mechanism
  - initiation



- propagation

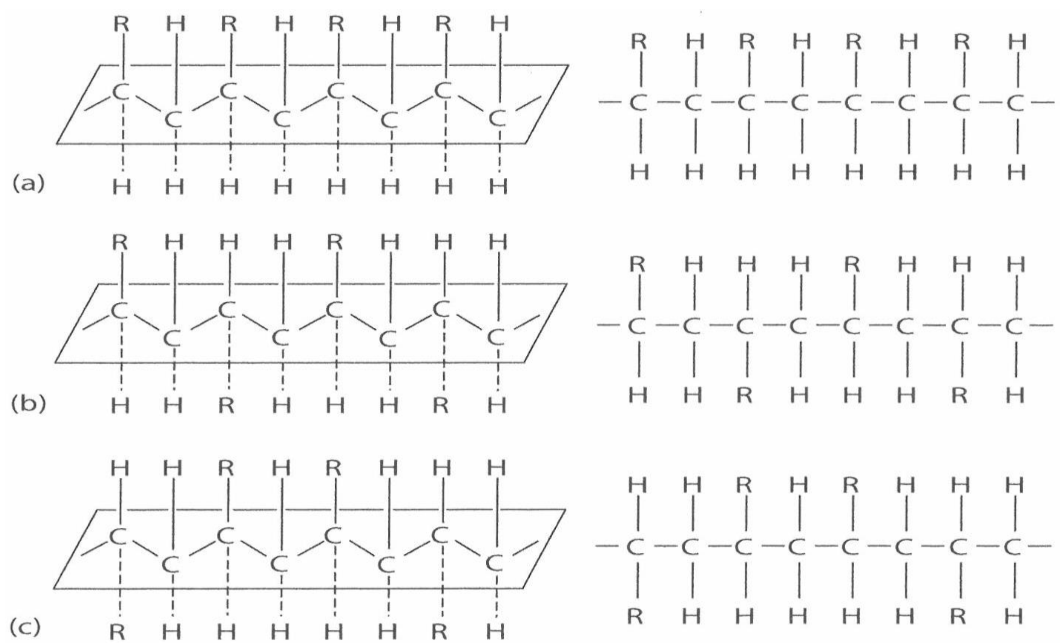


- no bimolecular termination
  - living polym'n; in anionic, hardly in cationic
  - termination by impurity
- narrow MWD
  - living nature + fast initiation

Coordination polym'n

- for stereoregular polymer synthesis
- tacticity
  - isotactic, syndiotactic ~ stereoregular
    - crystallizable → higher strength
  - atactic ~ not stereoregular

Fig 1.46 p59



- Coordination polym'n for
  - HDPE ← Radical polym'n of E gives only LDPE.
  - α-olefin like PP ← autoinhibition in radical polym'n

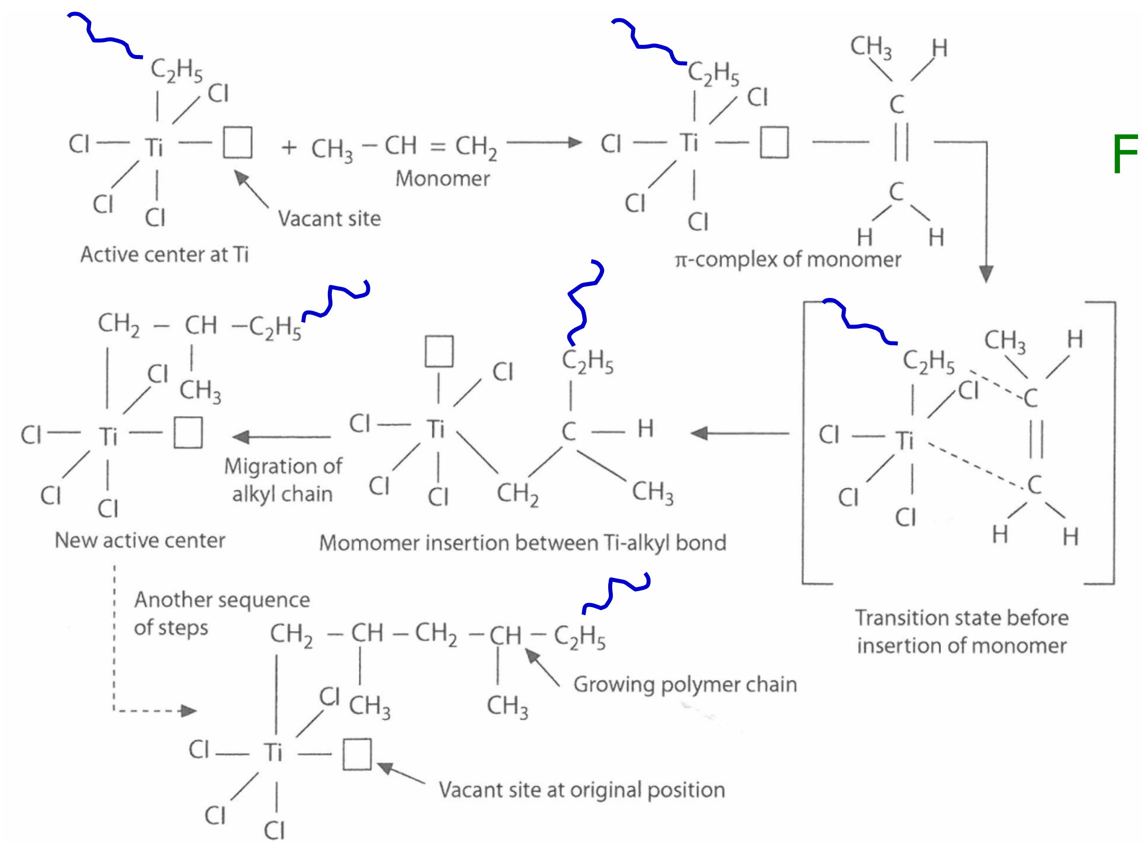
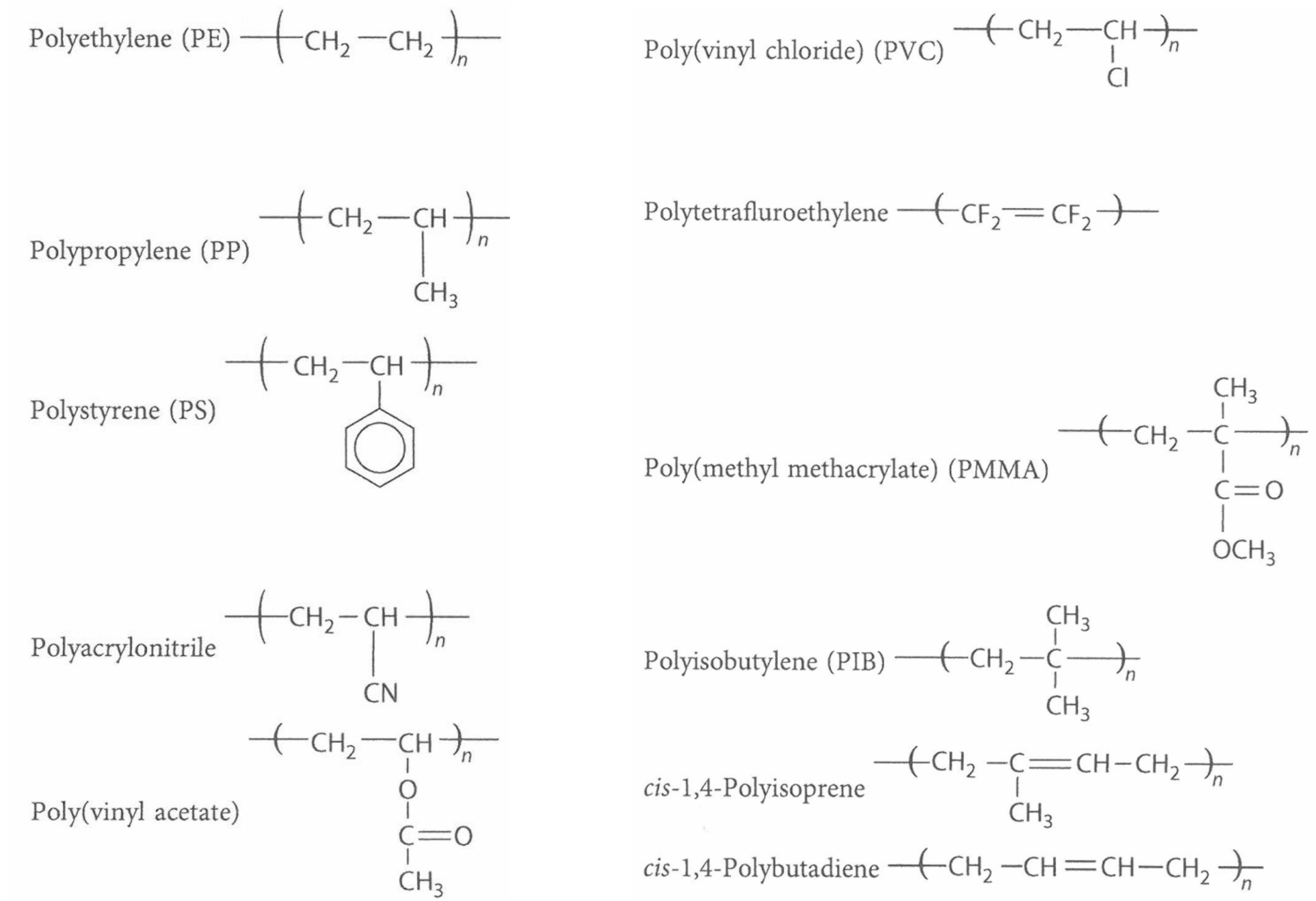


Fig 1.21 p27

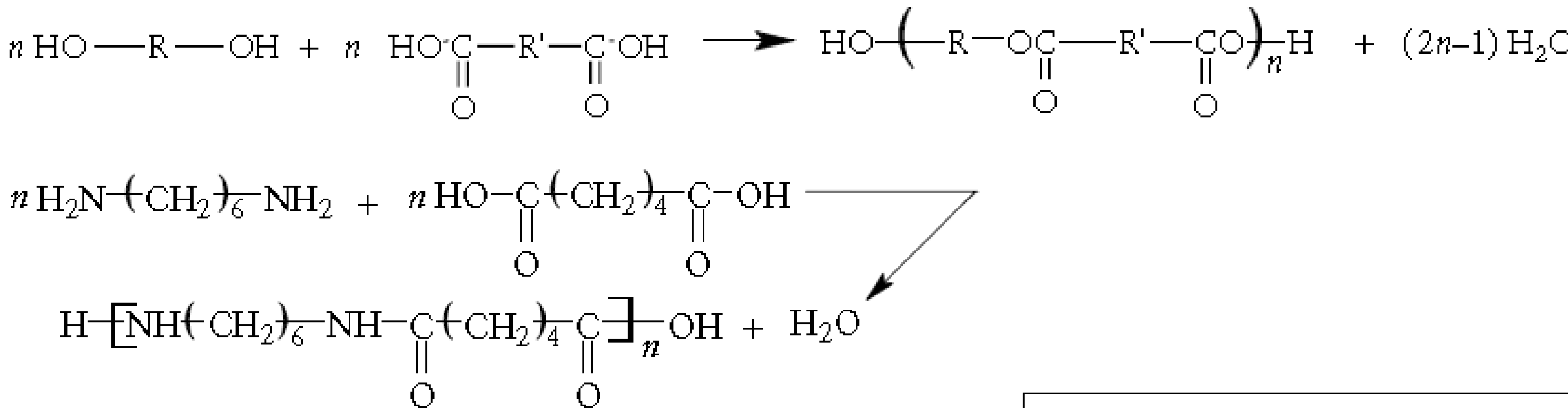
Chain polymers

- Table 1.1 p22-23
  - PE, PP, PVC, PMMA, PS, --- ~ general purpose plastics



Step polym'n

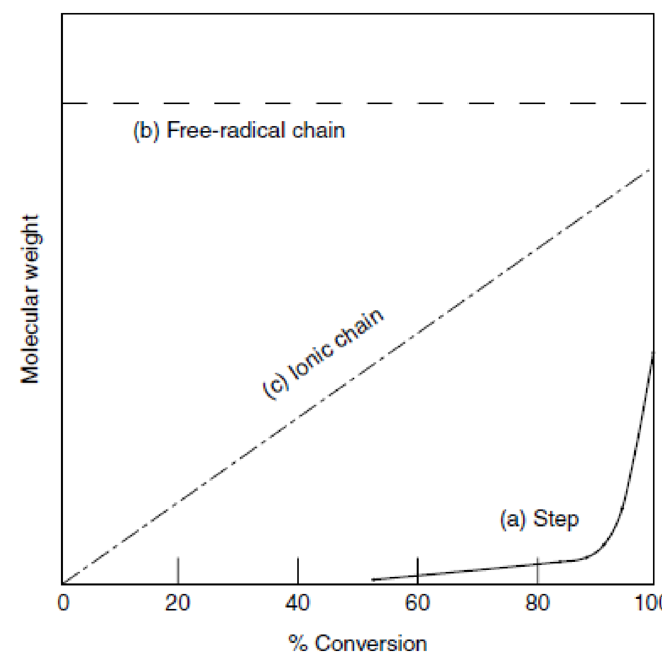
- by rxn of functional groups



- step-wise growth of chain

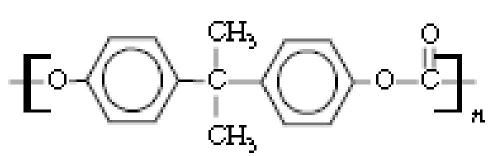
$$n - \text{mer} + m - \text{mer} \rightarrow (n + m) - \text{mer}$$

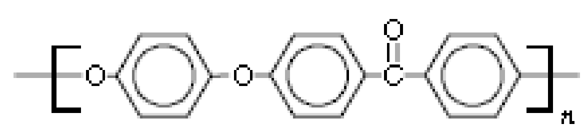
Fig 1.18 p25
mol wt vs conversion



- step polymers
  - polyester, polyamide, PU --- Table 1.2
  - PC, PEEK --- [engineering plastics] Table 1.3
  - higher performance (than chain polymers)
    - due to crystallizability
    - due to stiffer backbone, esp with aromatic

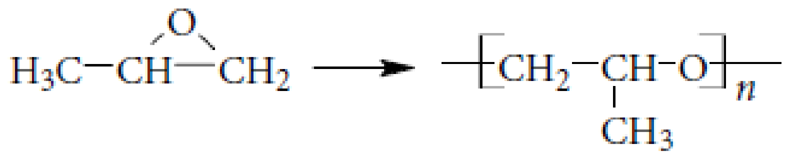
ester ($-\overset{\displaystyle O}{\overset{\|}{C}}-O-$), amide ($-\overset{\displaystyle O}{\overset{\|}{C}}-NH-$), imide ($-N\langle^{CO-}_{CO-}$), urethane ($-O-\overset{\displaystyle O}{\overset{\|}{C}}-NH-$), sulfide ($-S-$), ether ($-O-$), carbonate ($-O-\overset{\displaystyle O}{\overset{\|}{C}}-O-$), and sulfone ($-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-$) linkages.



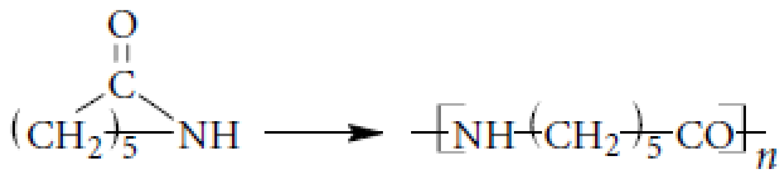


Ring-opening polym'n

- mostly chain polym'n



chain polymer

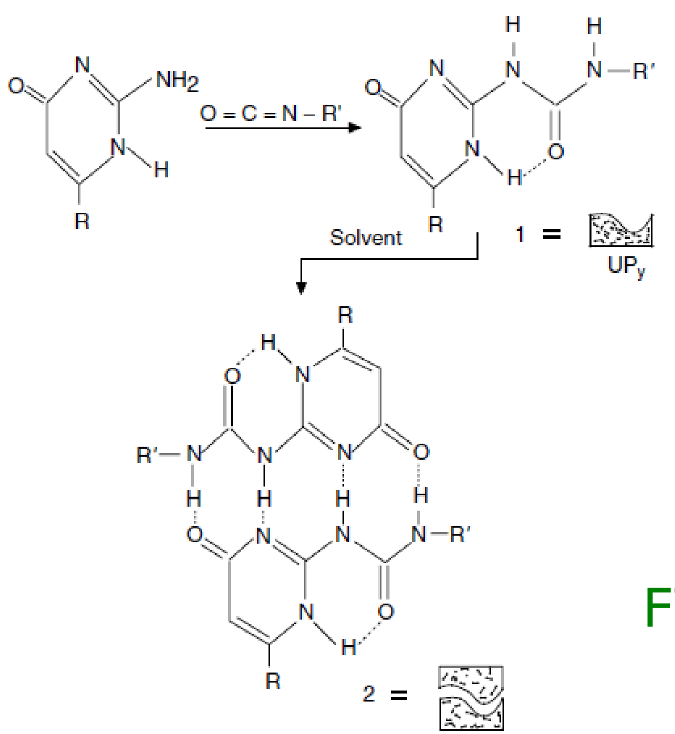


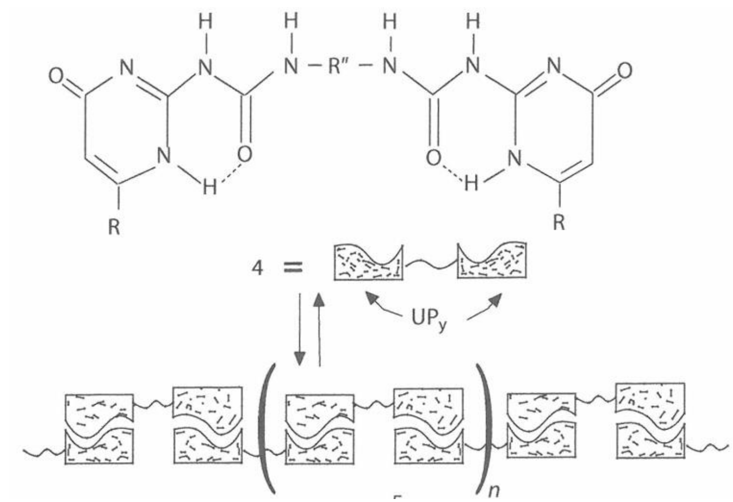
step polymer

- PPrO and PA6 are classified as condensation polymers, ----- p34
  - chain or addition polymer(ization)
  - step or condensation polymer(ization)
  - ignore

Supramolecular polym'n

- polym'n through secondary bonding
  - like (multiple) H-bonding
- stable yet reversible chain
  - high mechanical property and good processability





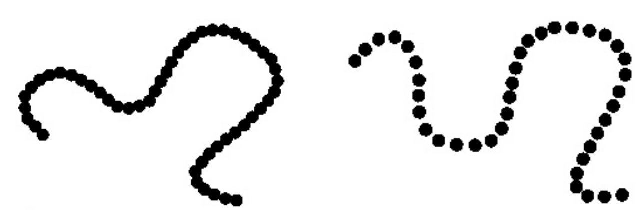


Fig 1.23,24

Copolymers

- homopolymer, copolymer, terpolymer
- types
  - random
  - alternating
  - block
  - graft
- morphology
  - 1-phase vs 2-phase
- property
  - average vs composite
    - SAN vs SBS

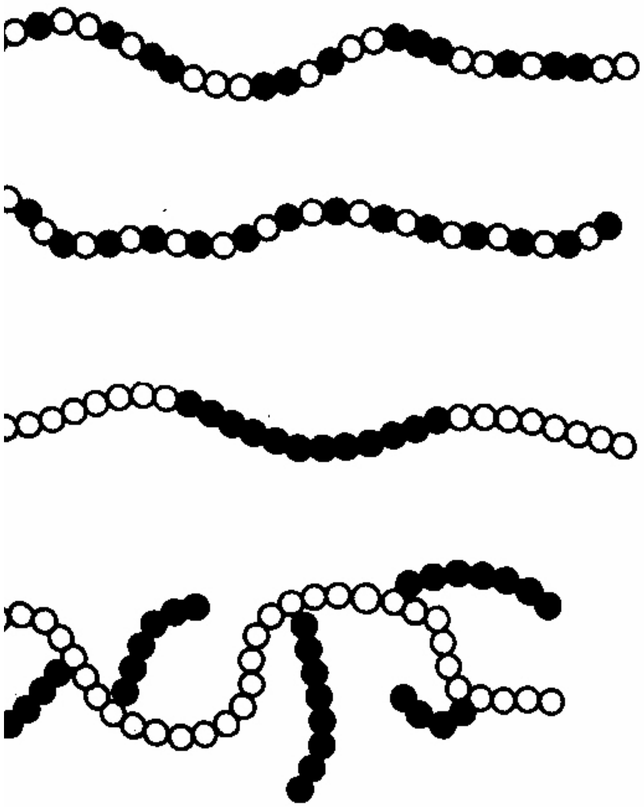


Fig 1.26