

Chapter 3



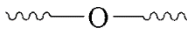

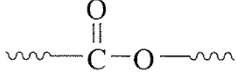
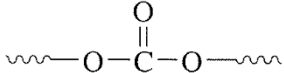
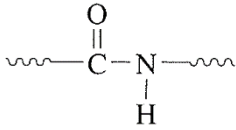
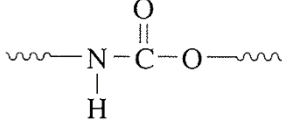
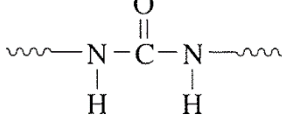
Step Polymerization

Introduction

Ch 3 Sl 2

- step polymers are;
 - grouped by linking structure
 - heteroatoms in main chain
← reaction of functional groups
 - molar mass range of $1\text{E}4 - 1\text{E}5$
 - more often, 15000 – 30000
 - chain polymers ~ one order higher
 - considering
 - property
 - processability
 - prepared by
 - polycondensation
 - polyaddition

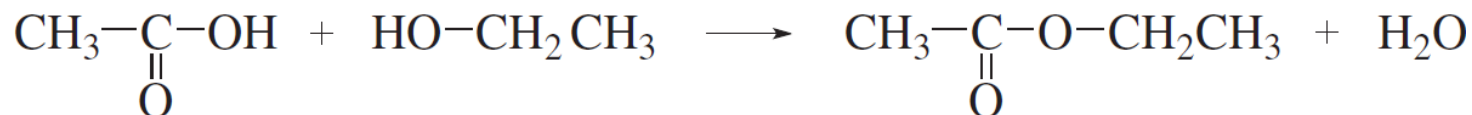
Table 3.1

Class of Polymer	Structure of Linking Group
Polyether	
Polysulphide	
Polyester	
Polycarbonate	
Polyamide	
Polyurethane	
Polyurea	

Linear step polym'n

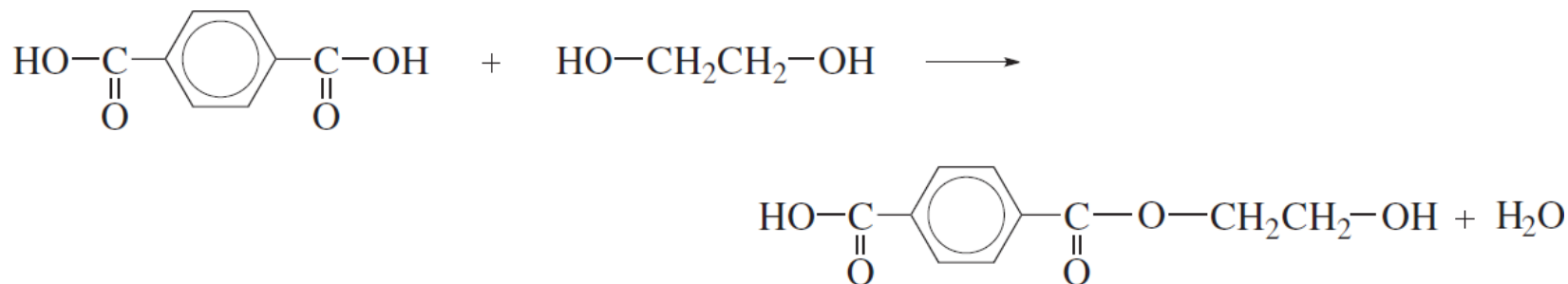
Ch 3 Sl 3

- monofunctional monomers ($f=1$) \rightarrow no polym'n



- useful for MM control, when needed

- difunctional monomers ($f=2$) \rightarrow linear polym'n



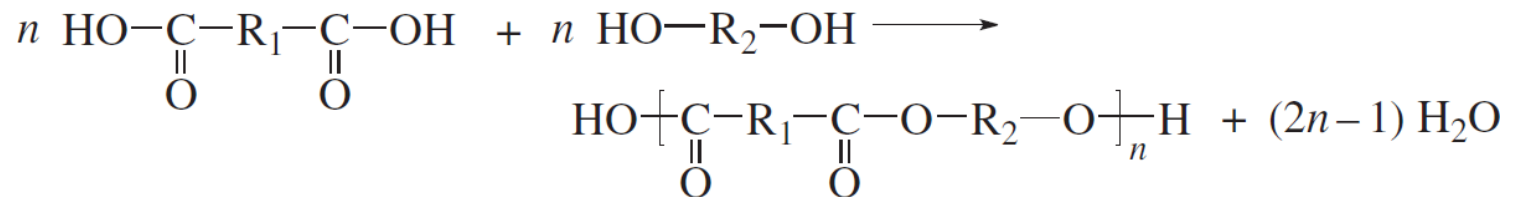
- $f > 2 \rightarrow$ non-linear polym'n **Section 3.3**

Polycondensation polymers

Ch 3 Sl 4

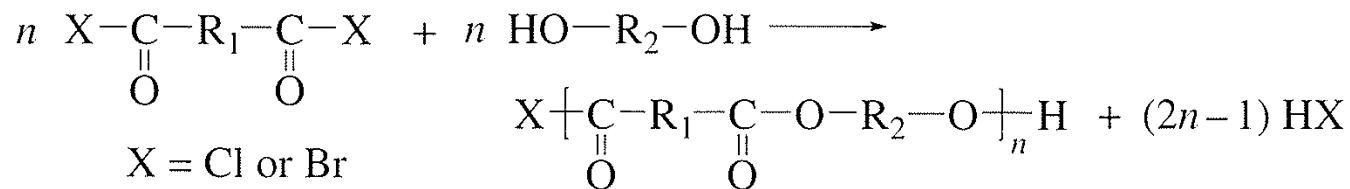
□ polyesters

□ $RA_2 + RB_2$ step polym'n [diacid + diol]



- at high Temp with catalyst (under reduced pressure)
- for high conversion and MM

■ diacid halide (faster) or diester can be used instead of diacid

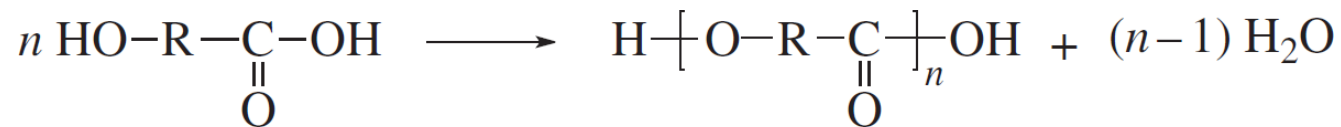


Polycondensation polymers

Ch 3 Sl 5

- polyesters (cont'd)

- ARB step polym'n [self-polycondensation]

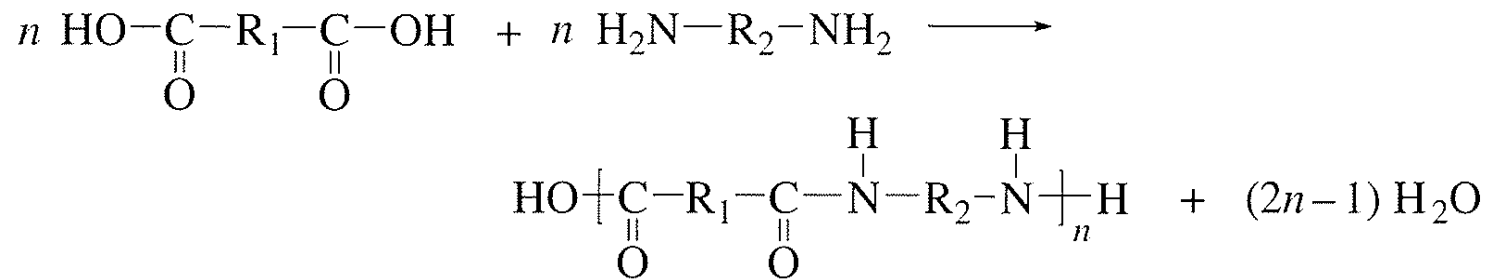


- stoichiometric balance kept automatically
- HO-R-COX is not available. ~ not stable

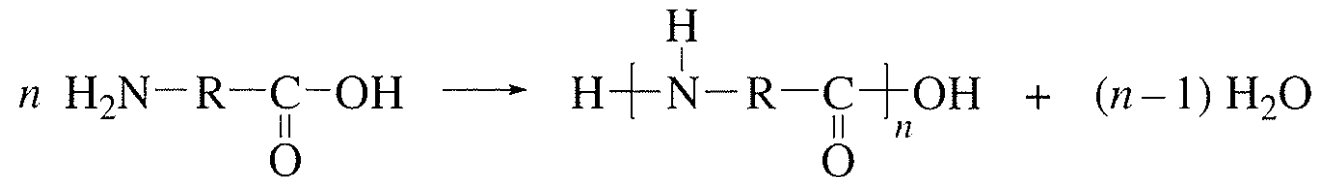
□ polyamides

□ synthesis analogous to polyester

- $RA_2 + RB_2$ [diacid (or diacid halide) + diamine]



- ARB with amino acid



□ polyamides (cont'd)

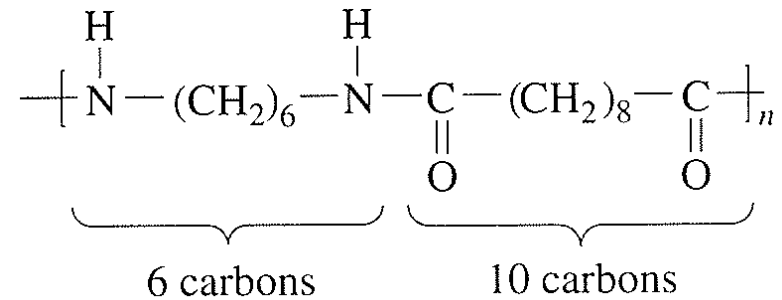
□ nylon = aliphatic polyamide

■ nylon xy

- x = number of C in amine
- y = number of C in acid

■ nylon x

- x = number of C in repeat unit
- from ARB step or (more frequently) ring-opening polym'n



nylon 610; nylon 6 10;
 nylon 6.10; nylon 6,10;
 nylon 6-10

Table 7.1 p170

➤ even-odd effect Figure 17.37 p442

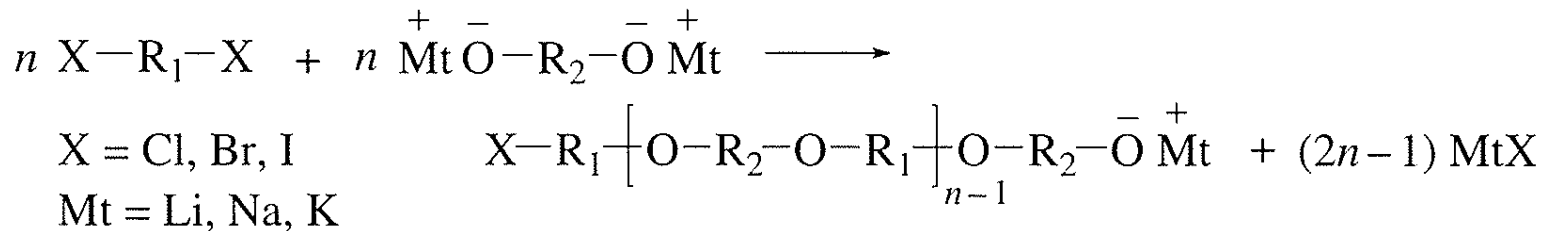
□ polyethers

□ polycondensation ~ not popular

■ RA₂ of diol



■ RA₂+RB₂ [dihalide + dialkoxide]



□ ring-opening polym'n of cyclic ether ~ more popular

Table 7.1 p170

□ engineering plastics (EP)

□ high thermal and mechanical properties

- withstand high temperature and load
- for engineering applications, replacing metals
- high-performance polymers [고성능]

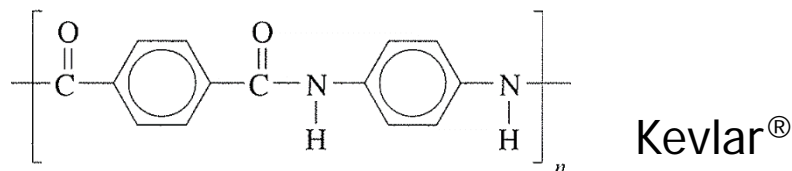
<cf> functional polymers [기능성]

<cf> commodity or general-purpose plastics ← chain polym'n

□ structure? contain (aromatic) rings Table 3.2 p25

□ 5 EPs ~ polyamides, polyesters, PC, polyacetal, mPPO

- PAs ~ aliphatic and aromatic
 - aramid = aromatic polyamide (fiber)

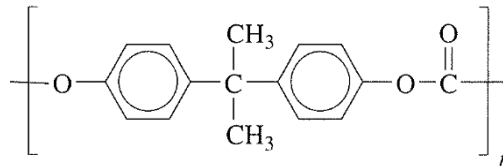


5 EPs (cont'd)

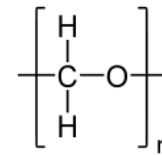
- polyesters ~ partially or fully aromatic

- PET, PBT, PEN, Vectra(n), ---

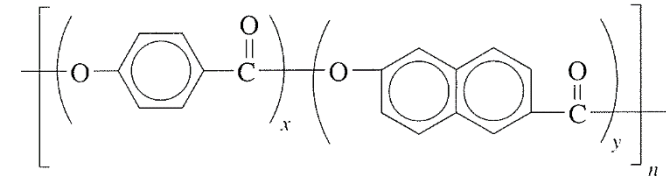
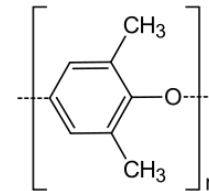
- polycarbonate



- polyacetal (POM)



- modified PPO ~ PPO blended with PS

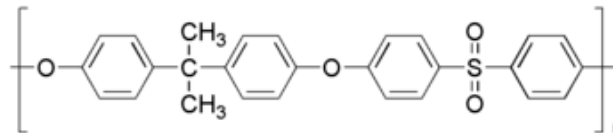


Vectran® LCP



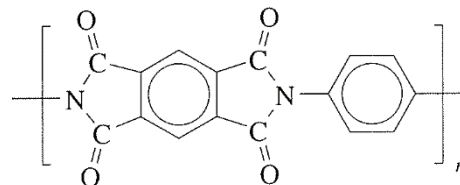
super EPs

- polysulfone (PSF)

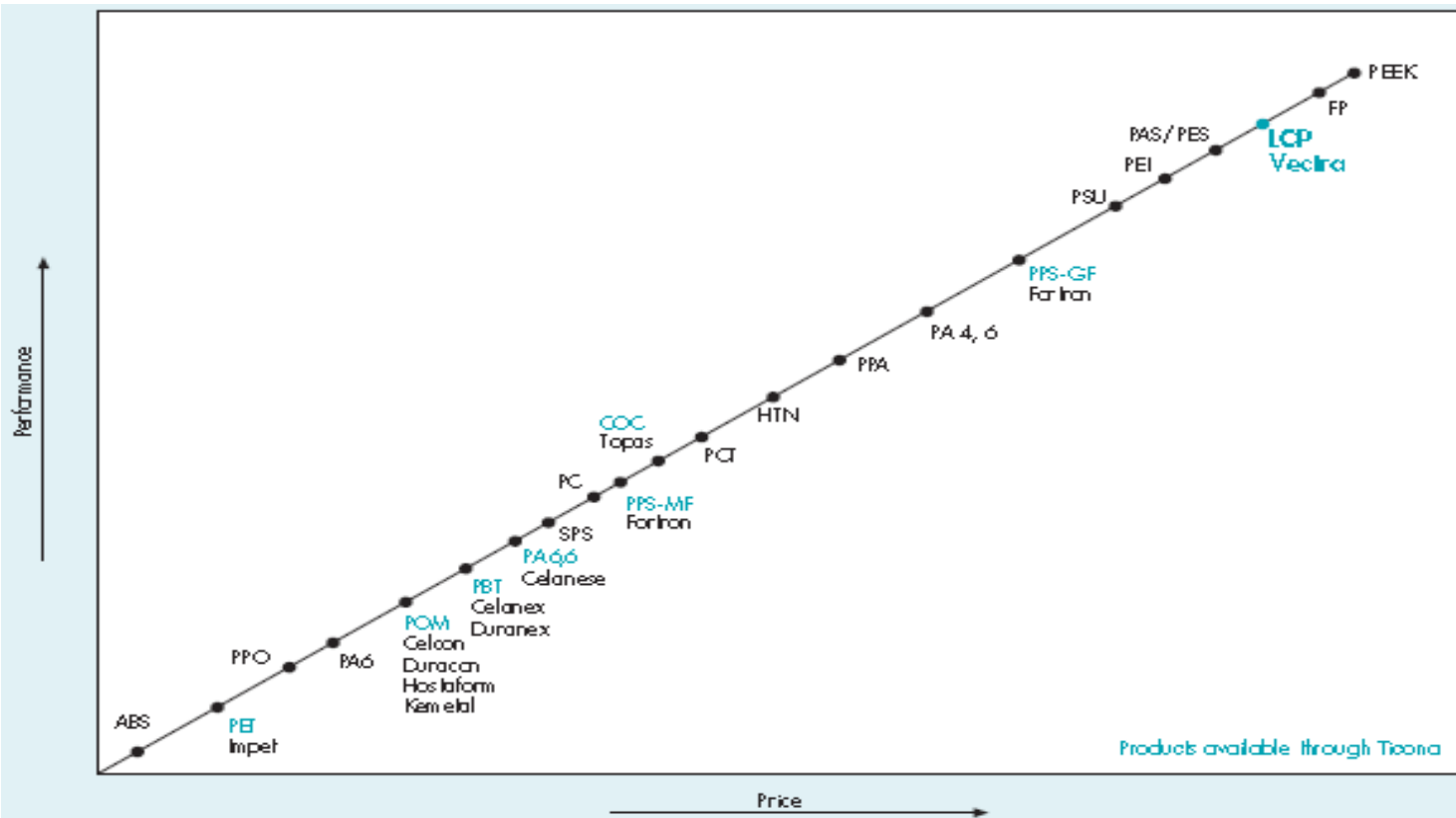


- polyimides (PI)

- PES, PEEK, ---



Kapton®



* High Performance Plastics Acronyms

ABS = acrylonitrile-butadiene-styrene
 COC = cyclic olefin copolymer
 FP = fluoropolymers
 PA6 = polyamide 6 (nylon)
 PA4,6 = polyamide 4,6 (nylon)
 PBT = polybutylene terephthalate
 PEEK = polyether ether ketone
 PES = polyether sulfone
 POM = polyoxymethylene (polyacetal)
 PPS-MF = polyphenylene sulfide (mineral filled)
 PPA = polyphthalamide
 SPS = syndiotactic polystyrene

HTN = high temperature polyamide (nylon)
 LCP = liquid crystal polymer
 PA6,6 = polyamide 6,6 (nylon)
 PAS = polyarylate
 PCT = polycyclohexylenedimethylene terephthalate
 PEI = polyether imide
 PET = polyethylene terephthalate
 PPO = modified polyphenylene oxide
 PPS-GF = polyphenylene sulfide (glass filled)
 PSU = polysulfone
 PC = polycarbonate

□ conducting [conductive] polymers

□ structural characteristic?

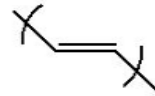
□ some CP prepared by polycondensation (pp24-27)

- Wittig, Heck, or McMurry coupling for PPV

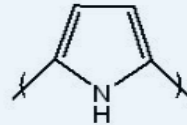
□ some by chain polym'n (Section 8.3 pp194-197)

- more popular

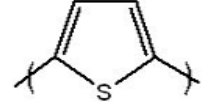
poly(acetylene)
PA



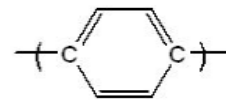
poly(pyrrole)
PPy



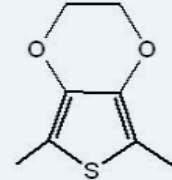
poly(thiophene)
PT



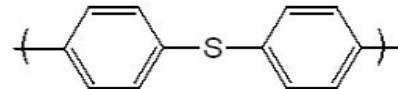
poly(para-phenylene)
PPP



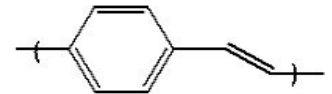
poly(3,4-ethylenedioxythiophene)
PEDOT



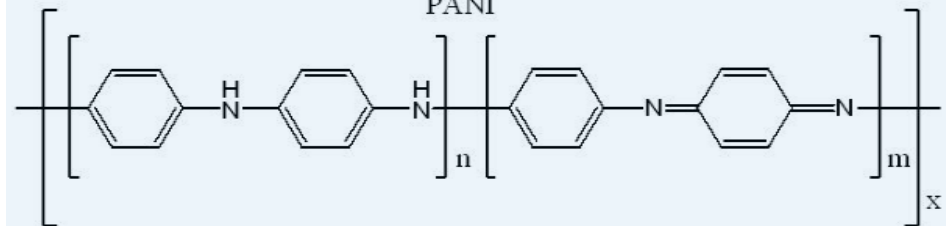
poly(phenylene sulfide)
PPS



poly(para-phenylene vinylene)
PPV

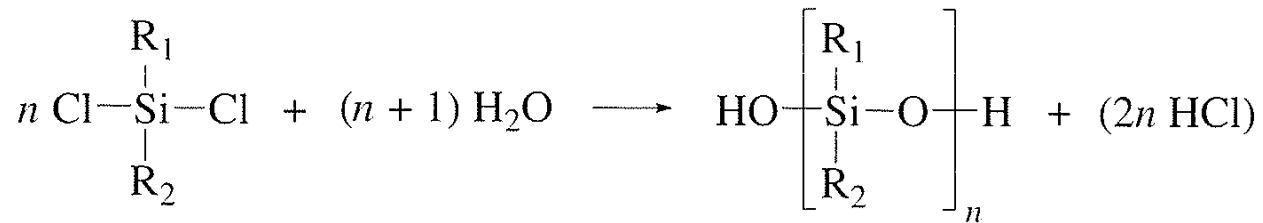


polyaniline
PANI



□ polysiloxanes

□ = siloxanes? (p27) → polymerized siloxanes (better)



□ silicones = silicon-containing polymers

■ silicone ≠ silicon ≠ polysilicon

□ PDMS ~ most popular

■ silicone oil, rubber, resin

■ depending on MM and/or crosslinking

■ higher MM silicones by ring-opening polym'n (Ch 7)

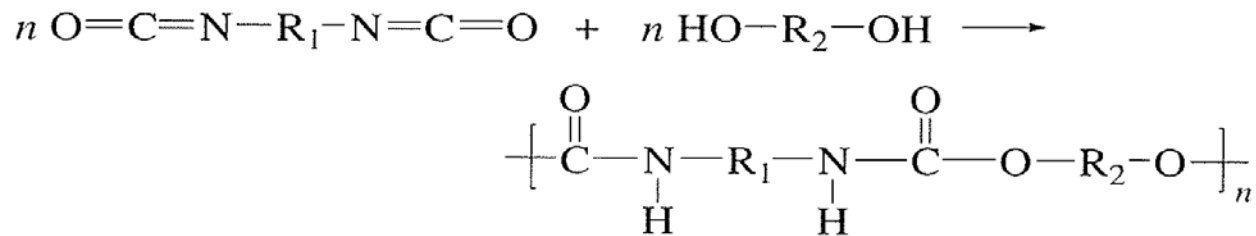
Polyaddition polymers

Ch 3 Sl 14

❖ no small group released → not condensation, but addition

□ polyurethanes (PU)

□ $RA_2 + RB_2$ [diisocyanate + diol]



□ wide range of monomers **p29**

■ aromatic or aliphatic diisocyanate

■ small to polymeric diol ~ give rigid to rubbery PU

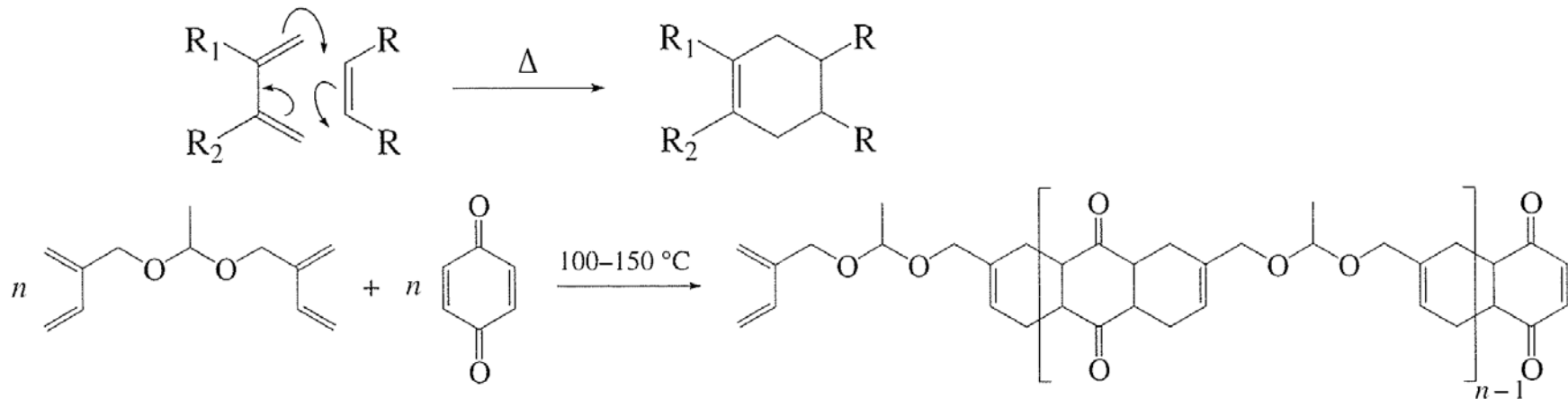
□ segmented copolymers ~ thermoplastic PU [TPU] **Section 9.4.1**

□ polyureas



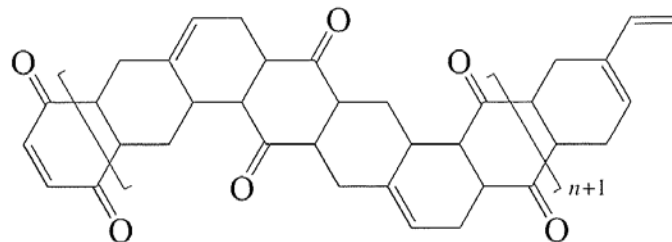
□ Diels-Alder polymers

□ cycloaddition of diene and dienophile

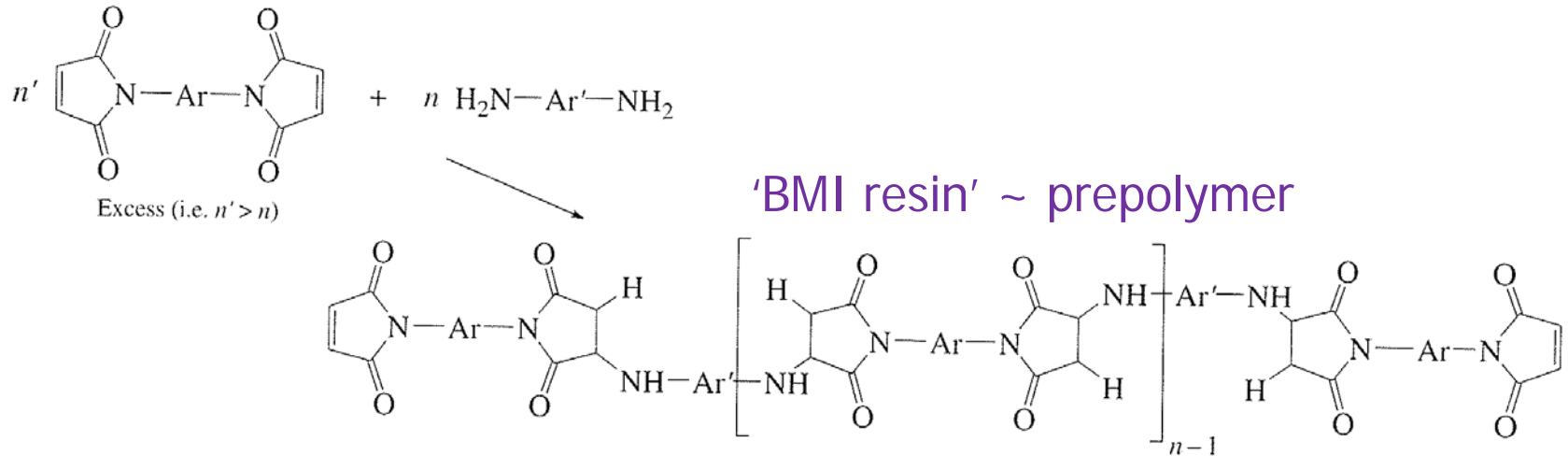


□ may give ladder polymers

- high heat resistance [耐熱性] and thermal stability [熱安定性]



□ bismaleimide (BMI) resins



□ further reaction [crosslinking] using (bis)maleimide group

- C=C or multifunctional amine

□ composite matrix or high-Temp adhesive ~ better epoxy

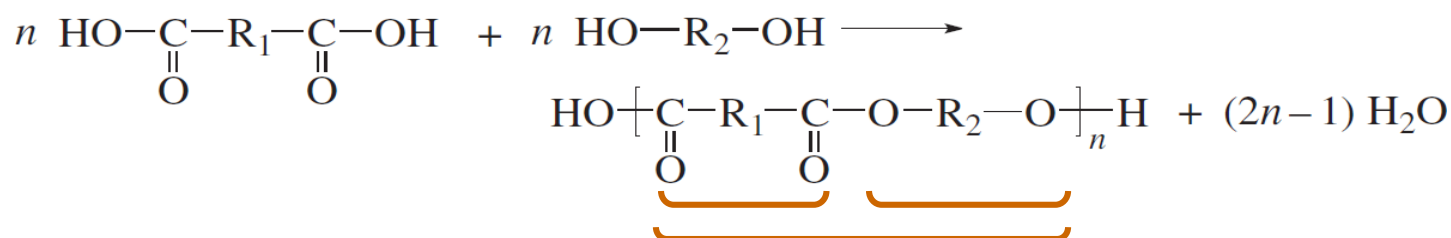
- composite ~ polymer + filler [carbon, ceramics, ---]
- polymer blend ~ polymer + polymer

Theories for step polym'n

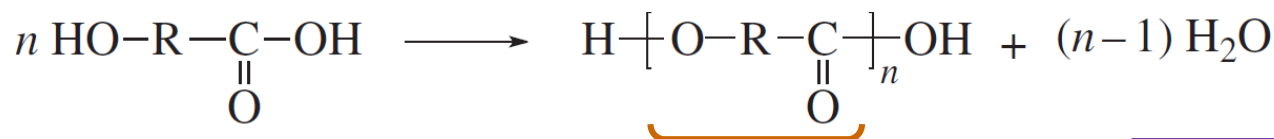
Ch 3 Sl 17

- ❑ assumption: principle of equal reactivity of ft'nal grp
- ❑ (number avg) deg of polym'n, x_n
- ❑ based on number of monomer units, not repeat units

- in $RA_2 + RB_2$, monomer unit \neq repeat unit



- in ARB , monomer unit = repeat unit



❑ $M_n = x_n M_0$

end group? ignore

- $M_0 = (\text{mean}) \text{ MM of monomer unit} = [\text{MM of repeat unit}] / 2$

Carothers theory for MM

Ch 3 Sl 18

Carothers theory for stoichiometric balance (# A = # B)

□ $x_n = N_0/N$

- N_0 = initial # of molecules
- N = present # of molecules

□ extent of reaction [conversion] , p

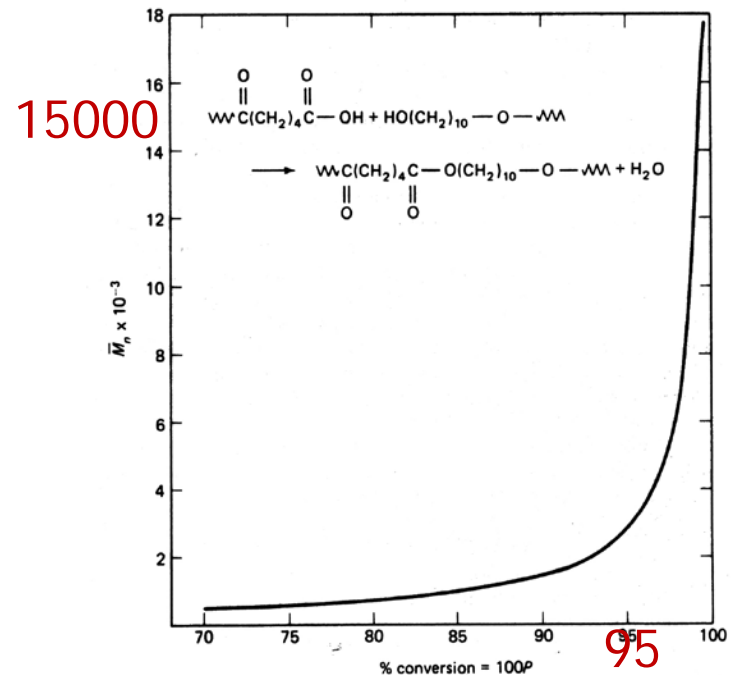
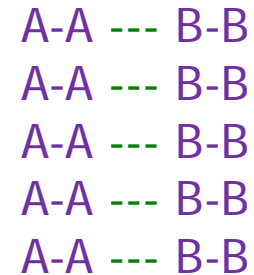
- p = # ft'nal group reacted/initial #

$$= (N_0 - N)/N_0$$

■ $N = N_0 (1 - p) \rightarrow$

$$\bar{x}_n = \frac{1}{1 - p}$$

□ For high x (MM), high p is critical.



❑ Carothers theory for imbalance

❑ reactant ratio, $r = N_A/N_B$

- $N_A = \# \text{ of ft'nal group A} = N_B r \text{ (} r \leq 1, \text{ defined)}$
- $N_0 = (N_A + N_B)/2 = N_B(1+r)/2$
- $N = [\{N_A - pN_A\} + \{N_B - pN_A\}] / 2 = \frac{rN_B(1-p) + N_B(1-rp)}{2}$

❑ $x_n = N_0/N \rightarrow \boxed{\bar{x}_n = \frac{1+r}{1+r-2rp}}$

- $r = 1 \rightarrow x_n = 1/(1-p)$
- $p = 1 \rightarrow x_n = (1+r)/(1-r)$

❑ For high MM, r and p close to 1 necessary.

- $r = 1 \leftarrow$ high purity monomer and accurate feed


Table 3.3 p31

When $p = r = .99$,
 $x = 67$

- ❑ controlling MM (not too high) by
 - ❑ stopping reaction early ~ not practical
 - ❑ imbalanced monomer feed
 - slight excess of one monomer
 - lowering r
 - chain end still reactive
 - ❑ addition of monofunctional monomer
 - $RA_2 + RB_2 + RB$ or $ARB + RB$
 - methanol in polyester synthesis
 - lowering r

$$r = \frac{N_A}{N_B + 2N_{RB}}$$

- chain end inactive



1 RB as effective as 1 RB_2

Statistical theory for MM

Ch 3 SI 21

- developed by Flory

- probability of finding a x-mer, chain with x monomer units

$$P(x) = p^{x-1}(1 - p)$$

- number of x-mers

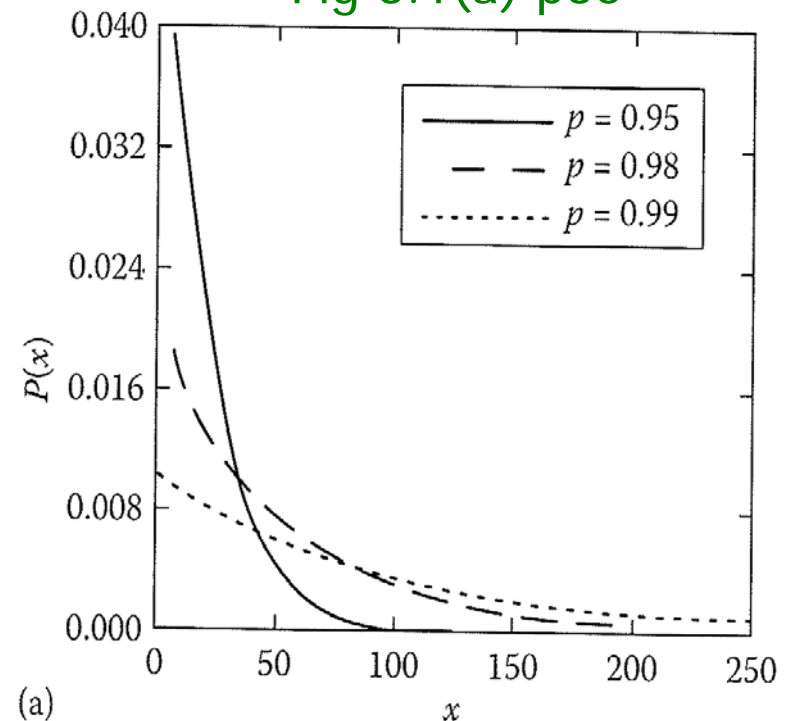
$$N_x = N P(x) = N_0 (1 - p)^2 p^{x-1}$$

$$N = N_0 (1 - p)$$

- $P(x)$ vs x

- number [mole] fraction
- Monomer is of the largest number.
- as p up, $P(x)$ gets broader

Fig 3.1(a) p35



□ weight fraction of x-mer

$$w_x = N_x M_x / N_0 M_0 = N_x x M_0 / N_0 M_0 = x N_x / N_0$$

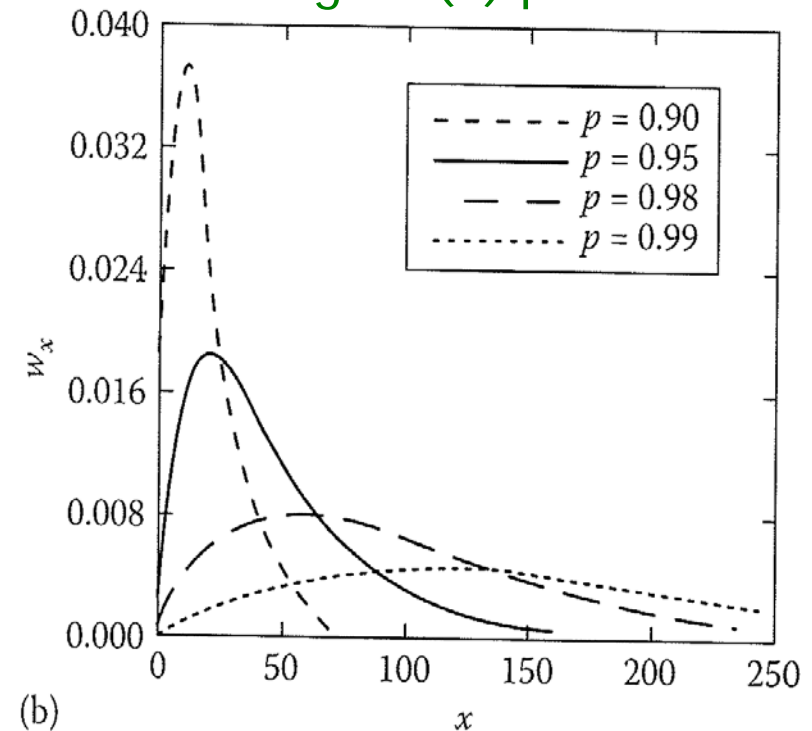
$$= x (1 - p)^2 p^{x-1}$$

$$N_x = N_0 (1 - p)^2 p^{x-1}$$

□ w_x VS x

- MM distribution curve usually presented
- As p up;
 - Max moves to higher x [MM].
 - Distribution gets broader.

Fig 3.1(b) p35



□ M_n vs M_w

$$\begin{aligned} \square M_n &= \sum P(x)M_x = \sum (1-p)p^{x-1} xM_0 = M_0(1-p) \underbrace{\sum x p^{x-1}}_{\sum_{x=1}^{\infty} xp^{(x-1)} = (1-p)^{-2}} \\ &= M_0 / (1-p) \end{aligned}$$

$x_n = 1/(1-p)$

$$\begin{aligned} \square M_w &= \sum w(x)M_x = \sum x(1-p)^2 p^{x-1} xM_0 = M_0(1-p)^2 \underbrace{\sum x^2 p^{x-1}}_{\sum_{x=1}^{\infty} x^2 p^{(x-1)} = (1+p)(1-p)^{-3}} \\ &= M_0 (1+p)/(1-p) \end{aligned}$$

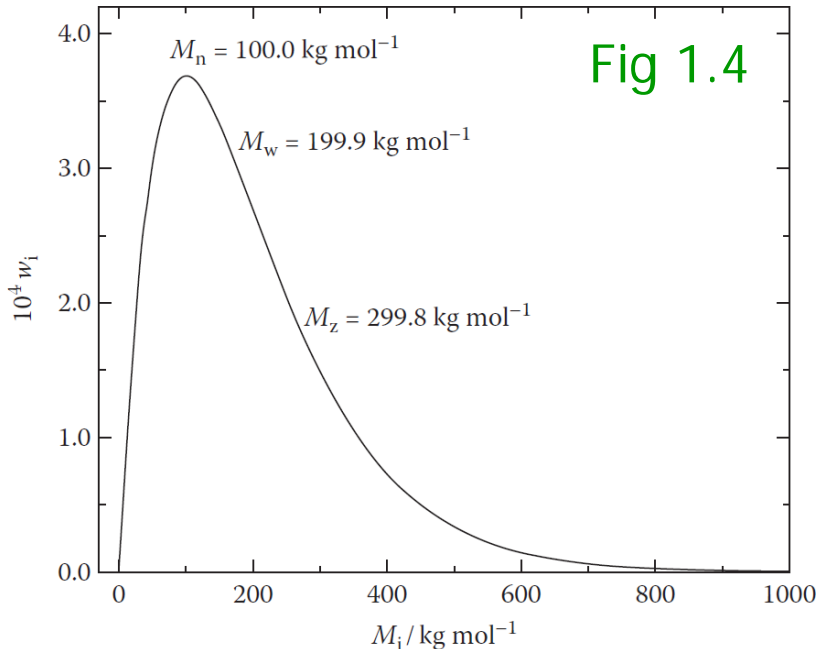
□ PDI or D,
 $\frac{\bar{M}_w}{\bar{M}_n} = 1 + p$

- 'most probable [Flory(-Schultz)] distribution'
- When $p \rightarrow 1$, PDI $\rightarrow 2$

❑ MM distribution

- ❑ Flory distribution $\sim M_n/M_w/M_z = 1/2/3$ (when $p \approx 1$)
- ❑ theoretically $PDI < 2$; in practice $PDI > 2$

❑ distribution curve and avg MM



max at M_n ?

$$w_x = x (1 - p)^2 p^{x-1}$$

$$dw_x/dx = 0 \rightarrow$$

$$x = -1 / \ln p \approx 1/(1 - p) = x_n$$

Kinetics of step polym'n

Ch 3 Sl 25



□ equal reactivity \rightarrow all k 's are equal indep of size

□ rate of **external-catalyzed** polym'n

□ $-d[A]/dt = -d[B]/dt = k'[A][B][\text{cat}] = k[A][B]$

$$k'[\text{cat}] = k$$

↙ $[A] = [B] = c$

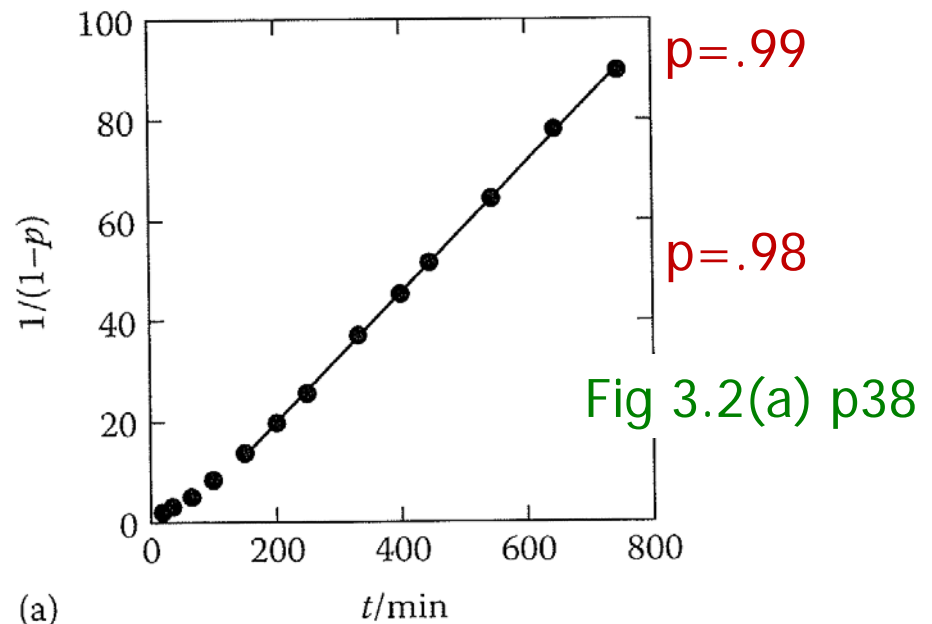
□ $-dc/dt = kc^2$

□ $\int (-1/c^2) dc = \int k dt$

□ $(1/c) - (1/c_0) = kt$

↙ $c = c_0 (1-p)$

□ $1/(1-p) = c_0 kt + 1$



□ rate of self-catalyzed polym'n

- A is catalyst awa ftnal group (eg -COOH in polyesterification)

□ $-d[A]/dt = k''[A][B][A]$

↙ $[A] = [B] = c$

□ $-dc/dt = k''c^3$

□ $(1/c^2) - (1/c_0^2) = 2k''t$

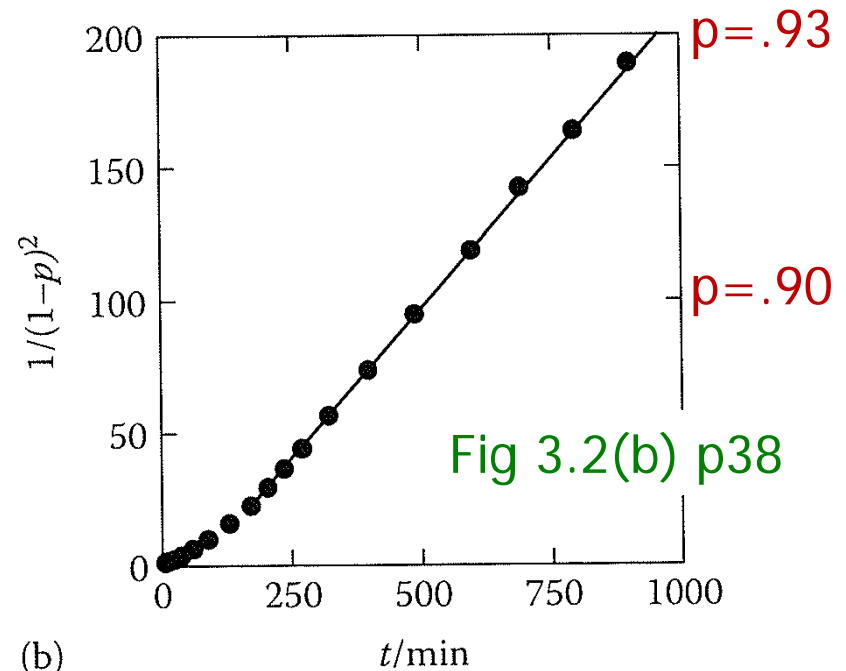
↙ $c = c_0(1-p)$

□ $1/(1-p)^2 = 2c_0^2k''t + 1$

□ very slow ~ impractical

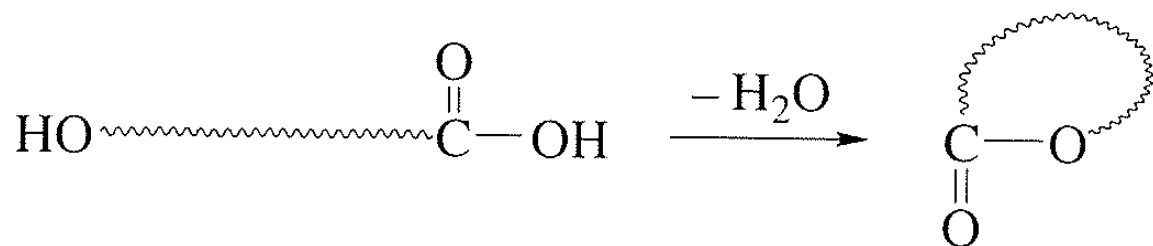
□ Actually, equilibrium rxn

- Equilibrium consideration requires removal of eliminate products!



Ring formation (cyclization)

Ch 3 Sl 27



- ❑ Cyclization favored for 5, 6, 7-membered rings.
- ❑ Cyclization interferes the growth \rightarrow lower MM
- ❑ intramolecular vs intermolecular rxn
 - ❑ unimolecular vs bimolecular rxn
 - ❑ inter favored at high conc'n \rightarrow bulk process preferred

Step polym'n processes

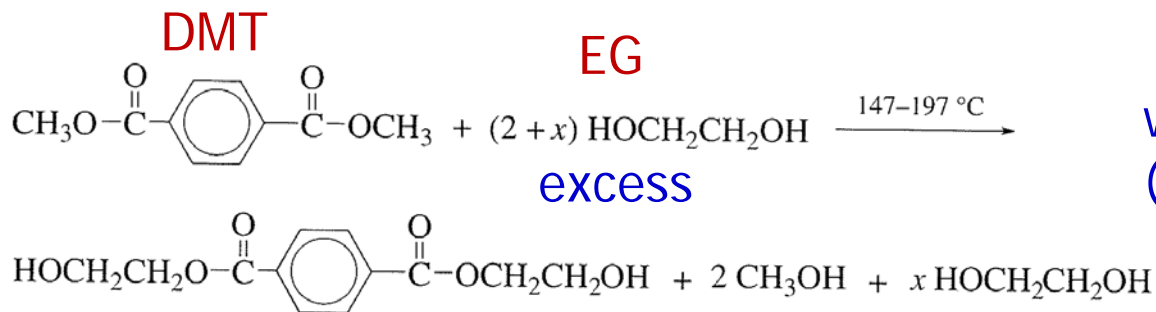
Ch 3 Sl 28

- ❑ For high MM
 - ❑ high conversion ($p \rightarrow 1$)
 - long reaction time, high Temp
 - use of catalyst
 - shifting equilibrium by removing small molecule like water
 - may need high vacuum
 - ❑ stoichiometric balance ($r \rightarrow 1$)
 - use of high purity monomer
 - self-polycondensation, ARB
 - multi-stage polym'n
 - ❑ avoiding cyclization
 - bulk, no solvent

Polyethylene terephthalate (PET)

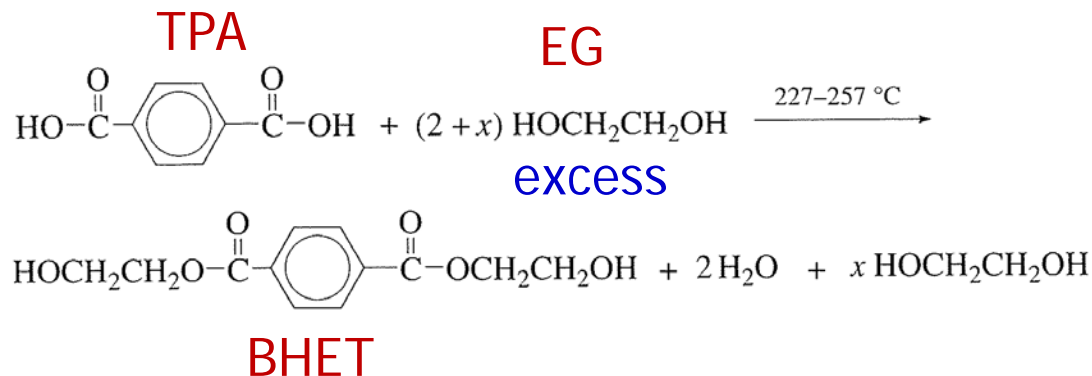
Ch 3 Sl 29

- ❑ direct esterification of TPA and EG not popular
 - ← difficulty in stoichiometry control at high Temp
- ❑ (two-stage) transesterification preferred
 - ❑ 1st stage



was popular
(easy to get DMT)

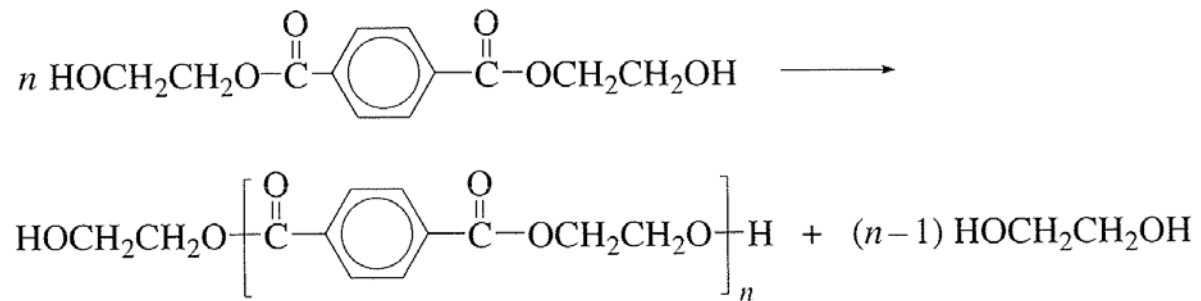
or



is popular
(faster, no need
MeOH recovery)

□ 2nd stage

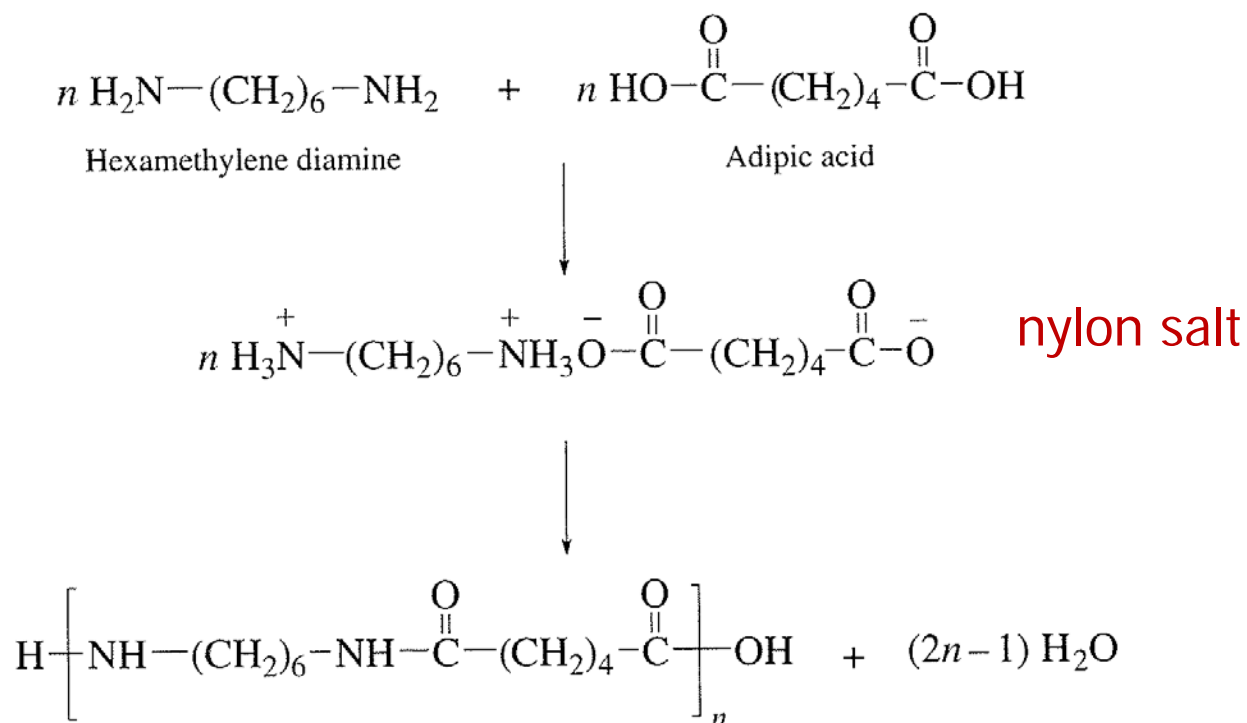
- at higher Temp
- EG pumped out under high vac



□ automatic stoichiometry

Nylon 66

- ❑ melt polym'n of 'nylon salt'
 - separated by recrystallization
 - stoichiometry kept

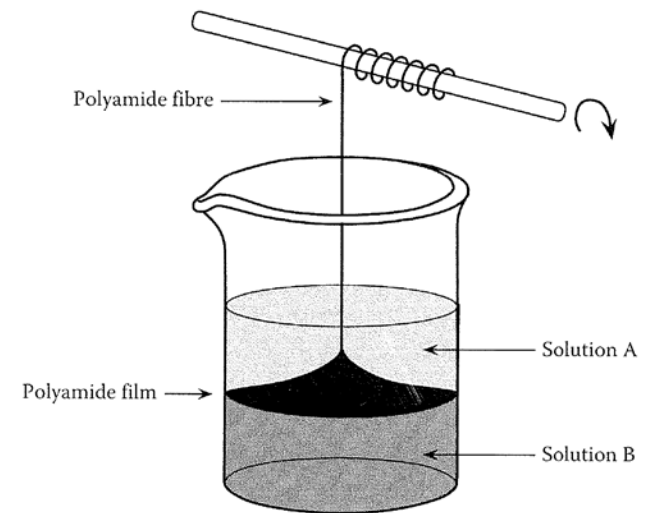
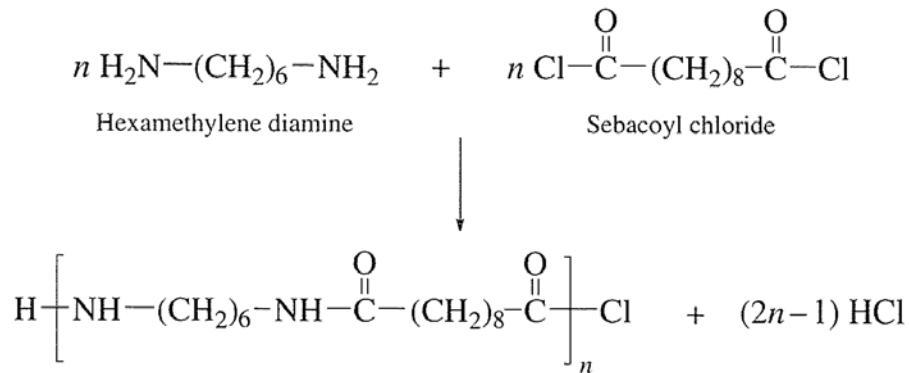


Interfacial polym'n

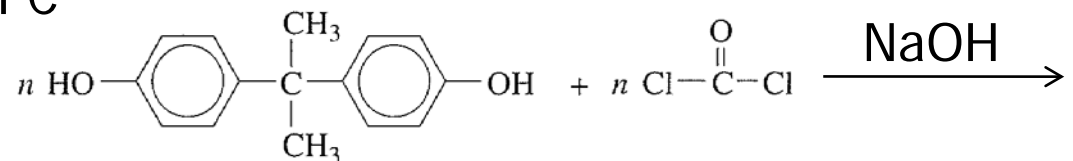
Ch 3 Sl 32

polycondensation at aqueous/organic interface

- Reaction must be fast.
 - use of diacid halide rather than diacid
 - Schotten-Baumann reaction



- High MM achieved ← stoichiometry kept
- typically with vigorous agitation
 - commercial process for PC



Polymerization processes

Ch 3 Sl 33

- ❑ 4 types
 - ❑ bulk polym'n ~ monomer (+ initiator) only
 - ❑ solution polym'n ~ monomer(s) (+ initiator) in solvent
 - polymer precipitates ~ precipitation polym'n
 - ❑ suspension polym'n ~ monomer + initiator in non-solvent
 - ❑ emulsion polym'n ~ monomer and initiator in different phase
- ❑ only bulk and solution processes for step polym'n
 - ❑ bulk more favored
 - low viscosity
 - low heat evolution

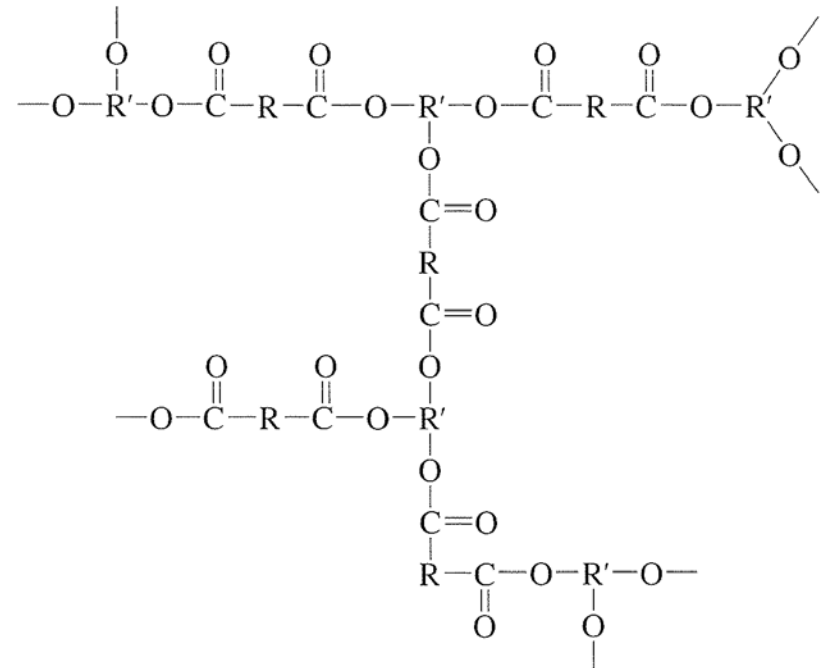
Non-linear step polym'n

Ch 3 Sl 34

□ monomer with $f > 2 \rightarrow$ branching \rightarrow crosslinking

□ $\text{HOOC-R-COOH} + \text{R}'(\text{OH})_3 \rightarrow$

- $\text{RA}_2 + \text{RB}_f$
- $\text{RA}_2 + \text{RB}_2 + \text{RB}_f \sim$ general
- $\text{ARB} + \text{RA}_2 + \text{RB}_f$
- $\text{ARB} + \text{RB}_f \rightarrow$ branching only
- $\text{ARB}_f \rightarrow$ HBP



□ gelation \sim network formation

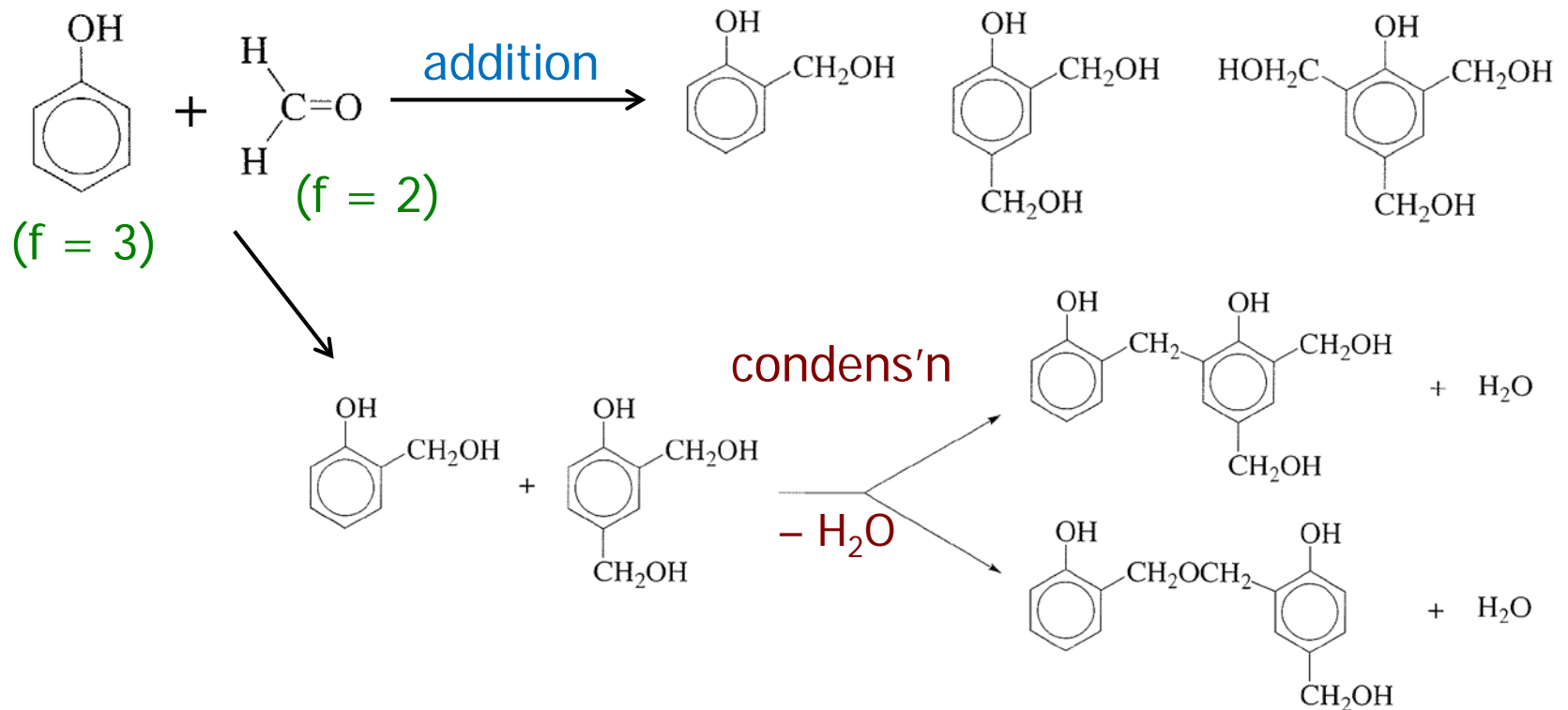
□ gel point \sim at which the first network molecule is formed

Network polymers

Ch 3 Sl 35

- p42 'Network polymers are termed resin.' ~ wrong
 - network polymers = crosslinked polymers
 - resin [樹脂] = thermoplastic resin + thermosetting resin

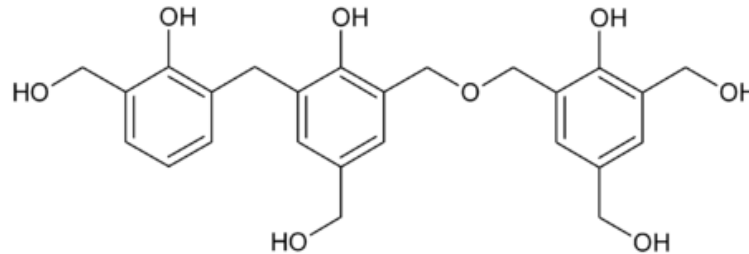
□ phenol-formaldehyde resin [phenolic resin]



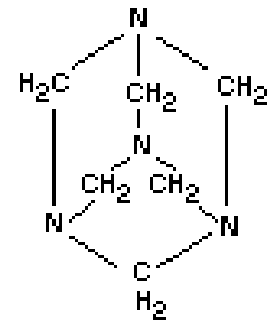
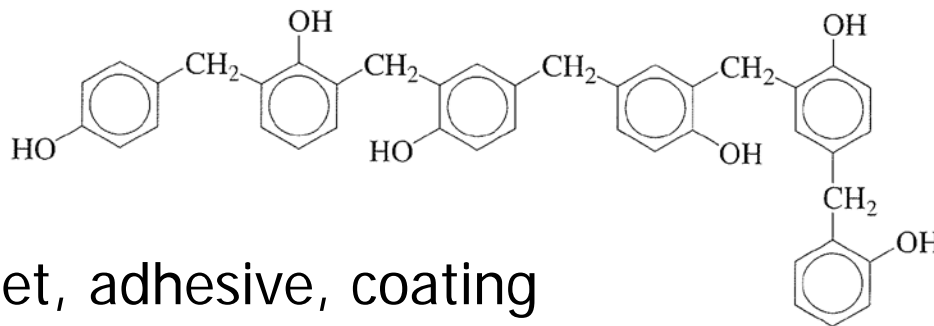
□ phenol-formaldehyde resin (cont'd)

□ prepolymers

- resole [resol] ~ aldehyde xs → more addition → polyalcohol → cured by heat



- novolac [novolak] ~ phenol xs → more condens'n → polyphenol → cured by hardener like 'hexa' (HMTA)

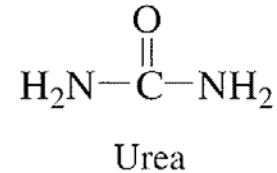


□ thermoset, adhesive, coating

□ amino resins = UF resin + MF resin

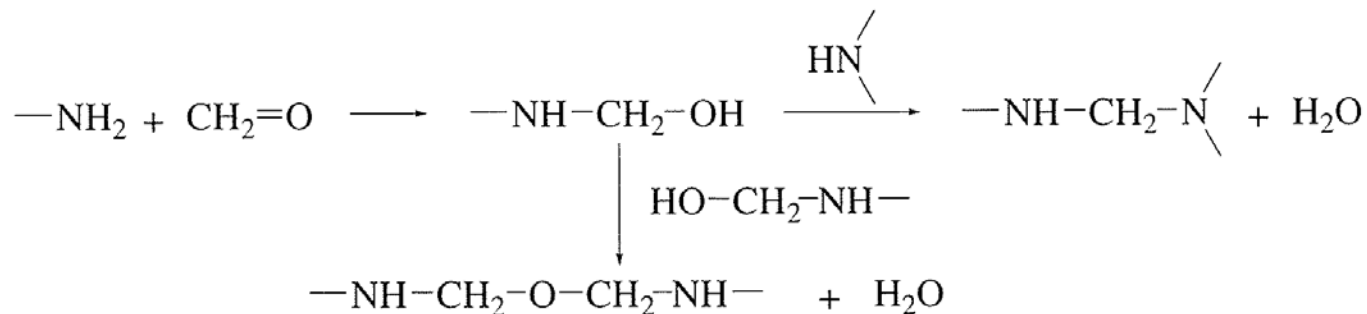
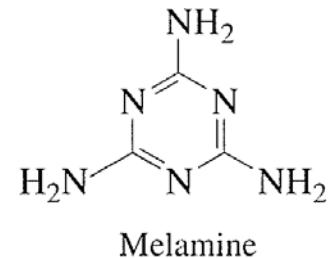
□ urea-formaldehyde resin

- urea ~ $f = 4$
- $U + F \rightarrow$ prepolymer \rightarrow hardening
- molding, laminating, adhesive

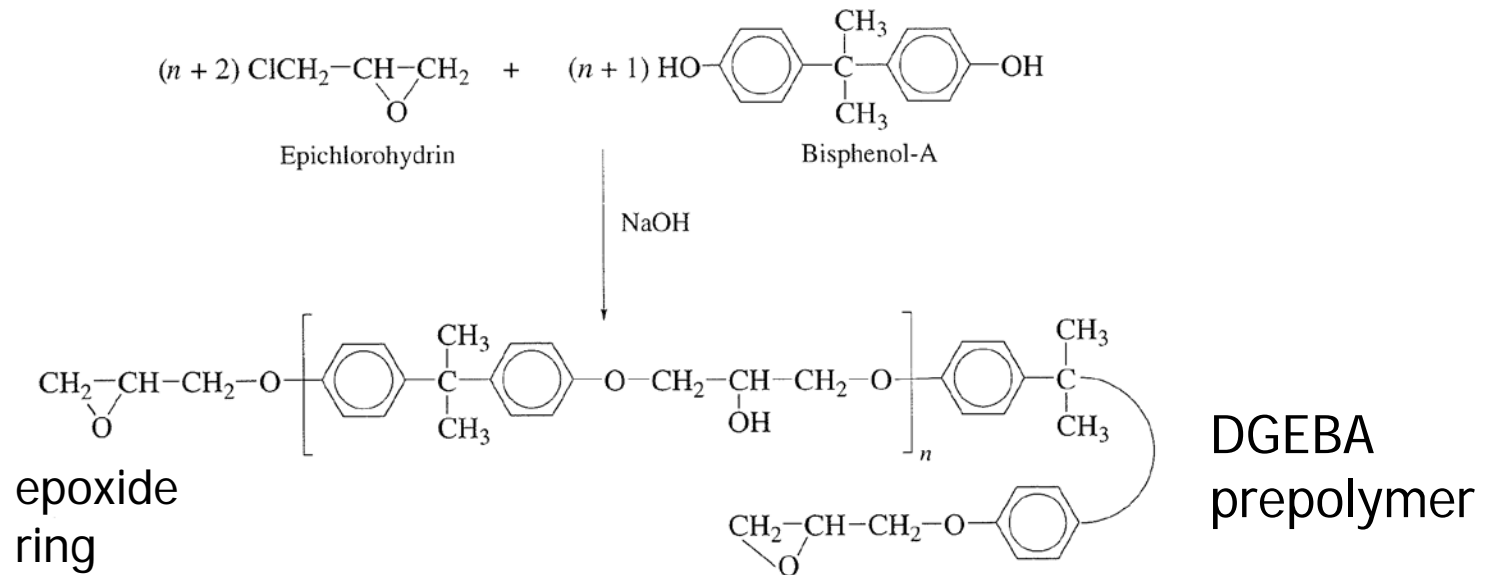


□ melamine-formaldehyde resin

- melamine ~ $f = 6$
- reaction, application similar to PF and UF
- utensil, table-top Formica®



□ epoxy resins = epoxy



□ cured by hardener

- amine curing (f of DGEBA = 2)
 - tertiary amine
 - multifunctional amine pp44-45

curing = crosslinking
hardener = curing agent

□ epoxies (cont'd)



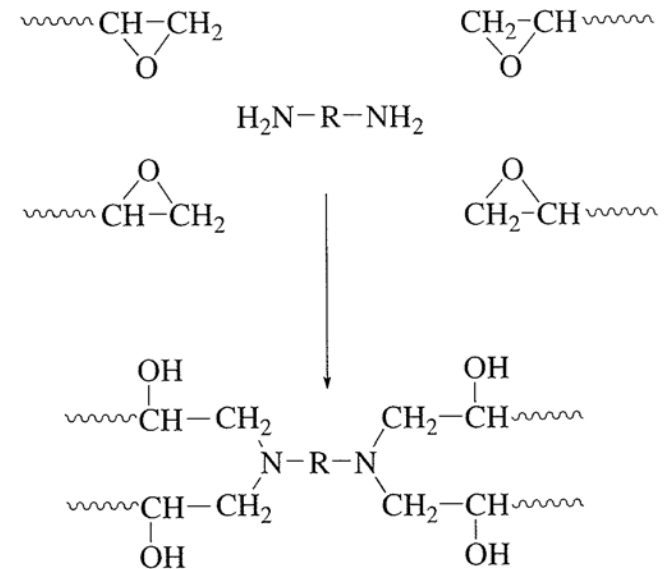
Diethylenetriamine (DETA), $f = 5$

- anhydride curing (f of DGEBA > 2)



$f = 2$

catalyzing rxn of -OH



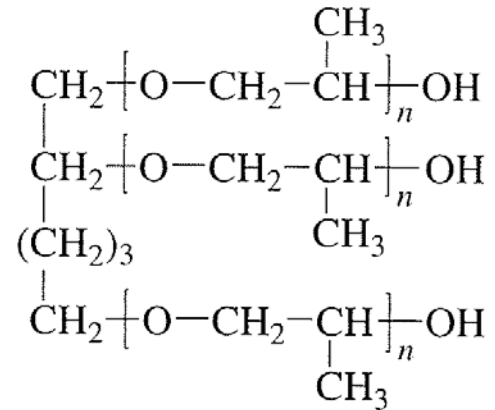
□ variety of property and application

- dep on structure of prepolymer and hardener
- (high-performance) composite matrix, adhesive, coating
- electronics part, insulator (PCB)

□ network PU's

□ diisocyanate + polyol

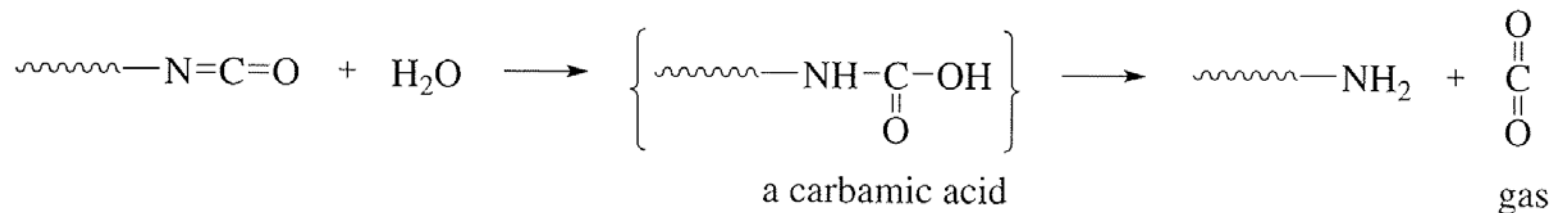
- polyether polyol
- polyester polyol



□ property dep on length of polyol

- rigid (MM < 1000) to flexible (MM > 2000)

□ elastomer, foam (sponge)



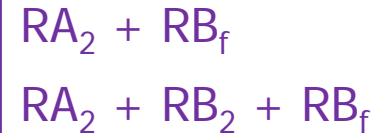
Carothers theory of gelation

Ch 3 Sl 41

□ gelation [crosslinking] at $x_n = \infty$

□ avg functionality, f_{av}

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$



□ extent of reaction, p

$$p = \frac{2(N_0 - N)}{N_0 f_{av}} = \frac{2}{f_{av}} \left(1 - \frac{1}{\bar{x}_n} \right)$$

$$x_n = N_0/N$$

□ gel point, p_c

$$p_c = \frac{2}{f_{av}}$$

□ $f_{av} \uparrow \rightarrow p_c \downarrow$ Table 3.4 p47

□ valid only for stoichiometric balance ($r = N_A/N_B = 1$)

■ like 3 mol of diacid + 2 mol of glycerine

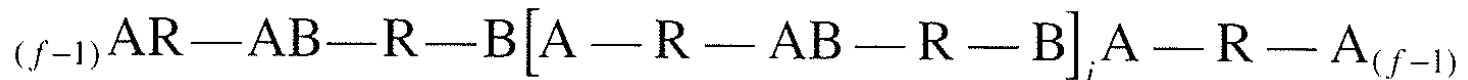
■ $f_{av} = 12/5 = 2.4 \rightarrow p_c = .83$

■ for non-stoichiometric system, See Odian pp106-108

Statistical theory of gelation

Ch 3 Sl 42

- developed by Flory
- For $RA_2 + RB_2 + RA_f$
 - crosslinking when there exist chain segment like



- branching coeff, α
 - probability of a chain branching point (from A_f) meets another chain from branching (A_f)
 - probability of having the above chain segment
- gelation when $\alpha \geq 1/(f-1)$
 - For $f = 3$, gelation when $\alpha \geq 1/2$.
 - When $\alpha < 1/(f-1)$, only branching occur.

□ probability of the chain segment

$$= p_A [p_B(1-\gamma)p_A]^i p_B \gamma$$

$$\gamma = N_A \text{ in } A_f / \text{total } N_A$$



$$\alpha = p_A p_B \gamma \sum_{i=0}^{\infty} [p_A p_B (1-\gamma)]^i = p_A p_B \gamma [1 - p_A p_B (1-\gamma)]^{-1}$$

$$\sum_{i=0}^{\infty} x^i = \frac{1}{(1-x)} \quad \text{for } x < 1$$

□ gel point, $\alpha_c = \frac{1}{(f-1)}$

$$r = N_B/N_A = p_B/p_A; r \leq 1$$

$$(p_A p_B)_c = \frac{1}{1 + \gamma(f-2)}$$

$$(p_A)_c = [r + r\gamma(f-2)]^{-1/2}$$

$$(p_B)_c = r^{1/2} [1 + \gamma(f-2)]^{-1/2}$$

Comparison of theories

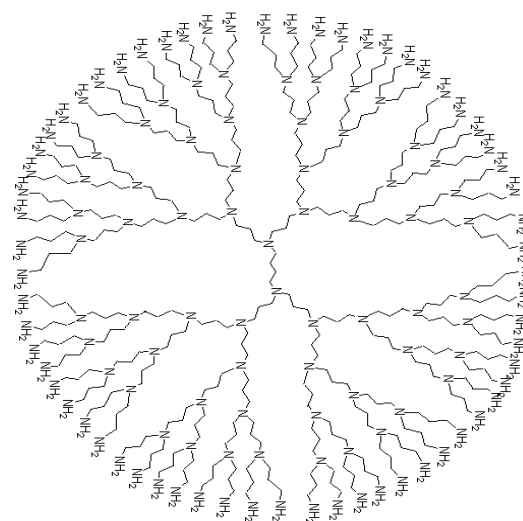
Ch 3 Sl 44

- ❑ 3 mol of diacid + 2 mol of glycerine
 - ❑ by Carothers $\sim p_c = 2 / 2.4 = .833$
 - ❑ by statistical $\sim p_c = 2^{-1/2} = .707$
 - $r = 1, \gamma = 1, f = 3$
 - ❑ experimental (with a few acids), $p_c = .765$
- ❑ Carothers theory overestimates p_c .
 - ❑ Molecules larger than average present, which gel earlier.
- ❑ Statistical theory underestimates p_c .
 - ❑ Cyclization wastes reactants.
 - ❑ Reactivity of functional groups in A_f not the same.

Dendrimers

Ch 3 Sl 45

- ❑ dendritic polymer with regular structure
 - ❑ highly branched to form sphere
 - ❑ monodisperse MM and symmetric
 - ❑ internal void and dense surface
- ❑ property-applications
 - ❑ compact, no entanglement
→ low viscosity → rheology modifier
 - ❑ internal void → holds catalyst, drug
 - ❑ high conc'n of surface group
→ attaching sensor, drug, gene



□ synthesis

□ # of branching unit N_{br}

$$N_{br} = \sum_{x=1}^g f_{core} (f_{br} - 1)^{x-1} \quad x \sim \text{generation}$$

- increases rapidly with generation

□ starburst limit

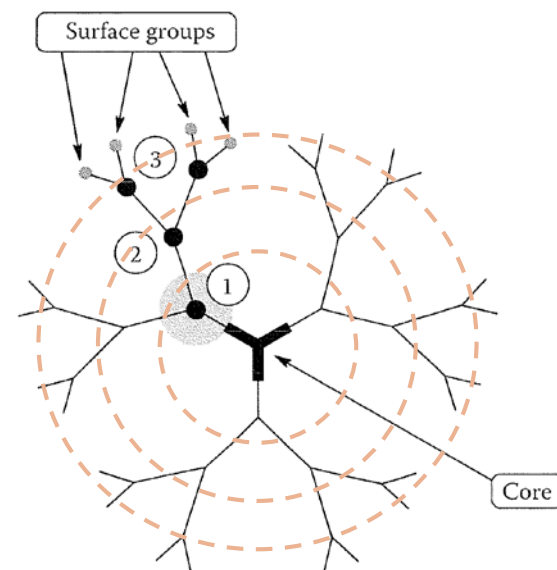
- crowding at surface \rightarrow imperfect surface, broken symmetry
- 10th generation when $f_{br} = 3$; 5G for tetrafunctional

□ methods \sim multi-step \leftarrow multi-generation

- divergent, convergent, mixed, double exponential

□ reactions

- must be fast and clean



❑ divergent approach

- G by G from core
- repeated coupling – activating [deprotecting]

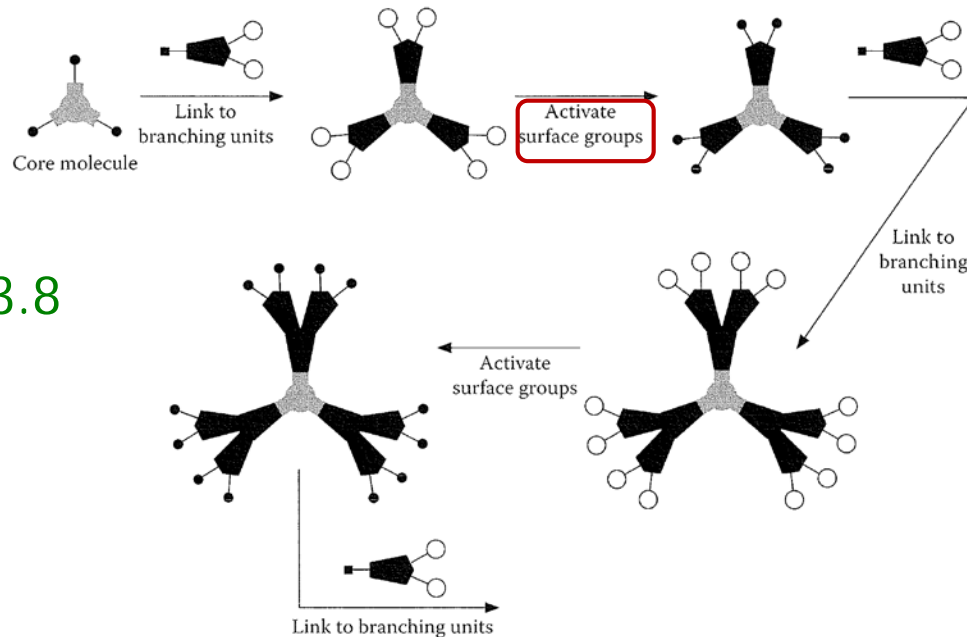


Fig 3.8

eg, p52

□ convergent approach

- wedges [dendrons] connected to core
- coupling – activating also
- starburst limit also
- possible to prepare chemically-asymmetric dendrimer

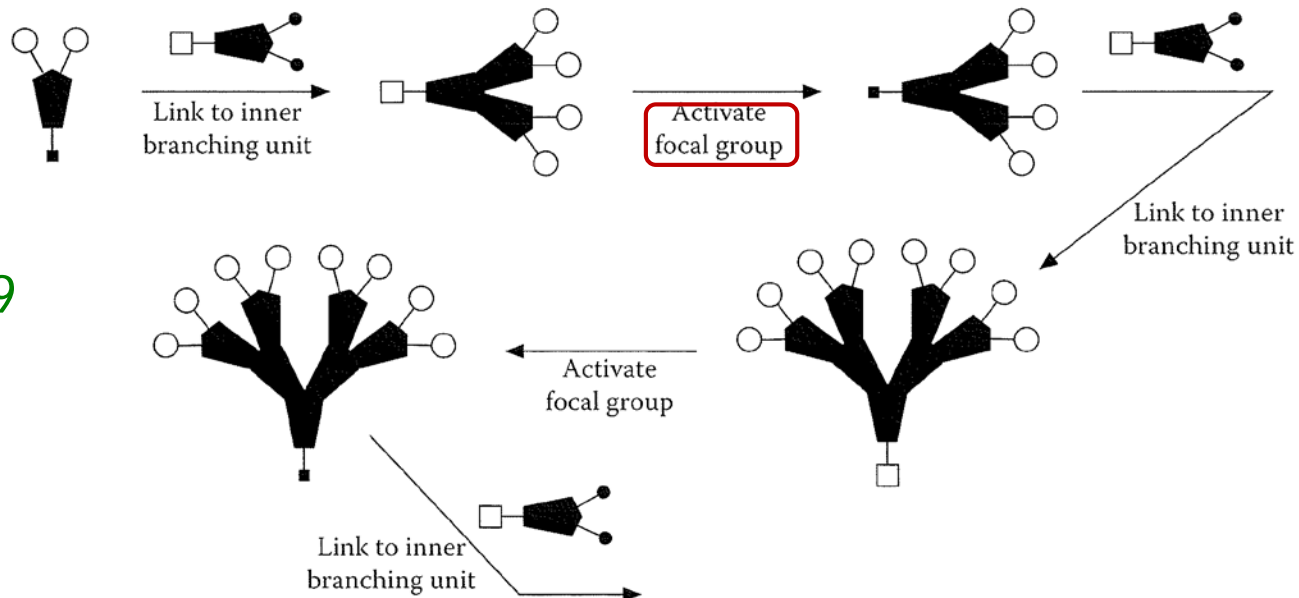


Fig 3.9

- ❑ divergent and convergent mixed
 - wedges linked to 3-4 G dendrimer from divergent
- ❑ double exponential approach
 - coupling – activating surface and focal group

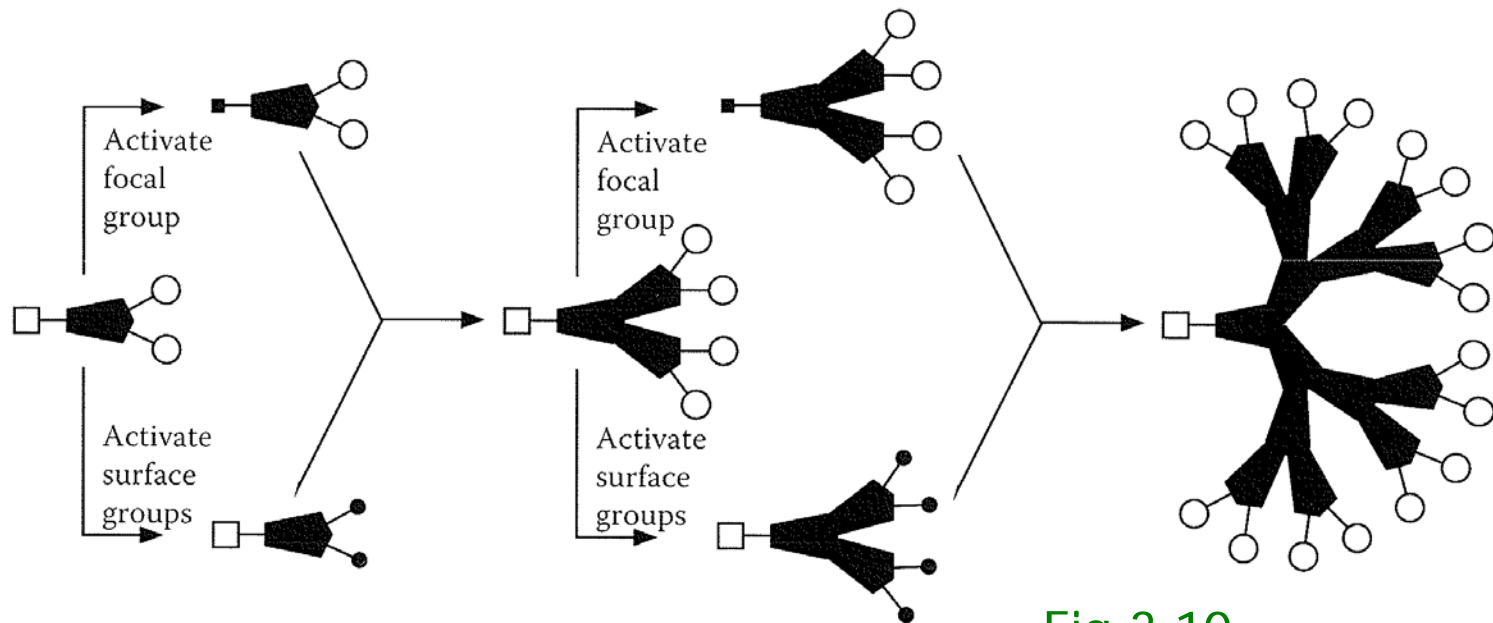
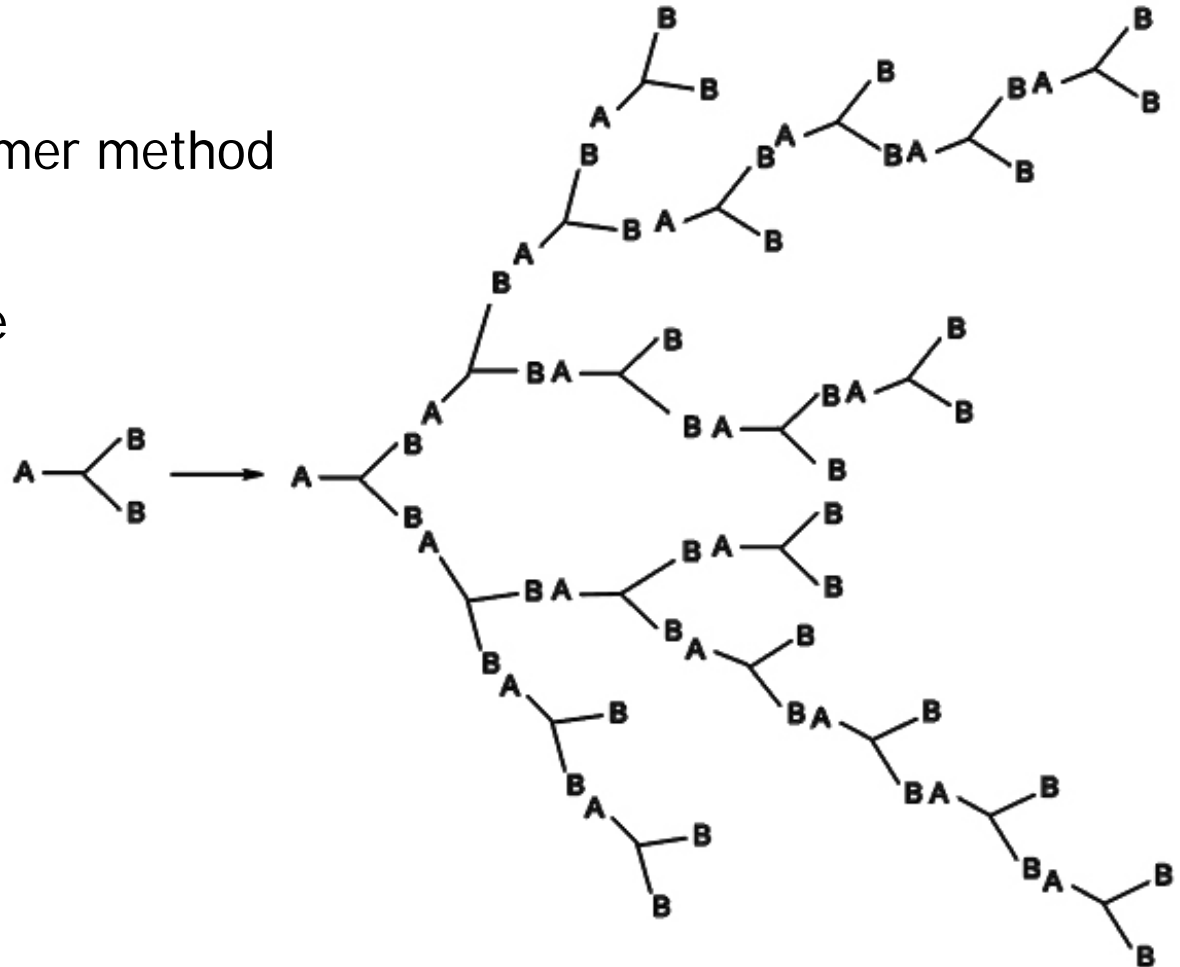


Fig 3.10

Hyperbranched polymers (HBP)

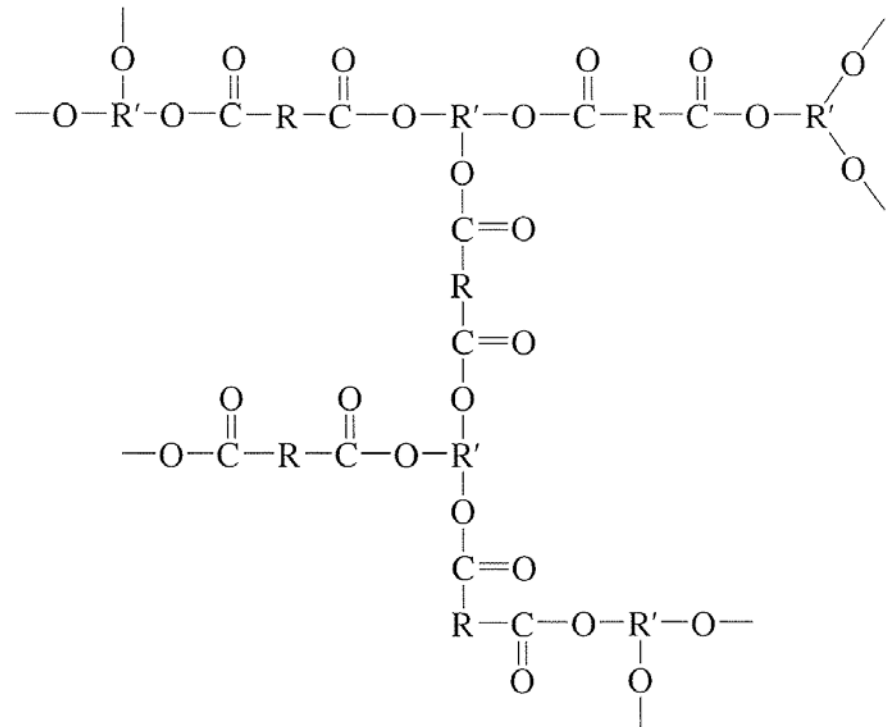
Ch 3 Sl 50

- ❑ dendritic polymer with **irregular** structure
- ❑ 'one-pot' synthesis
 - ❑ ARB_x monomer
 - AB_x or single monomer method
 - $x \geq 2$
 - no gelation possible



□ $RA_2 + RB_f$

- A2B3 or double monomer method
- $f > 2$
- can crosslink
- stop before gel point



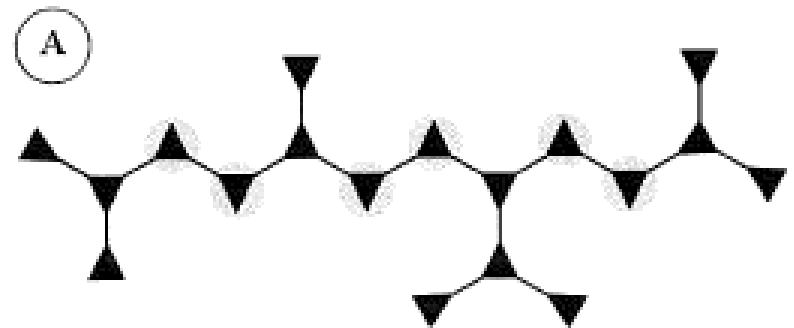
□ structure

- distribution of MM and branching
- branching factor [(average) degree of branching]

$$\text{branching factor} = \frac{N_{\text{fbr}} + N_{\text{term}}}{N_{\text{total}}}$$

$$\blacksquare N_{\text{total}} = N_{\text{fbr}} + N_{\text{term}} + N_{\text{linear}}$$

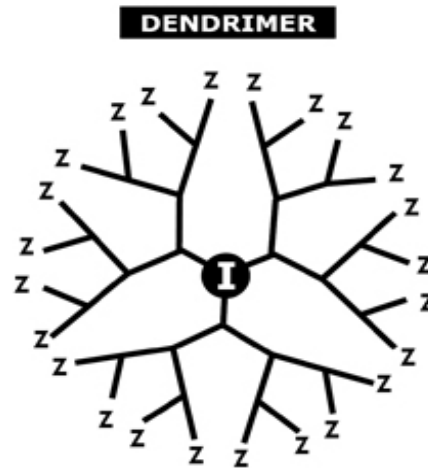
Fig 3.11 p56



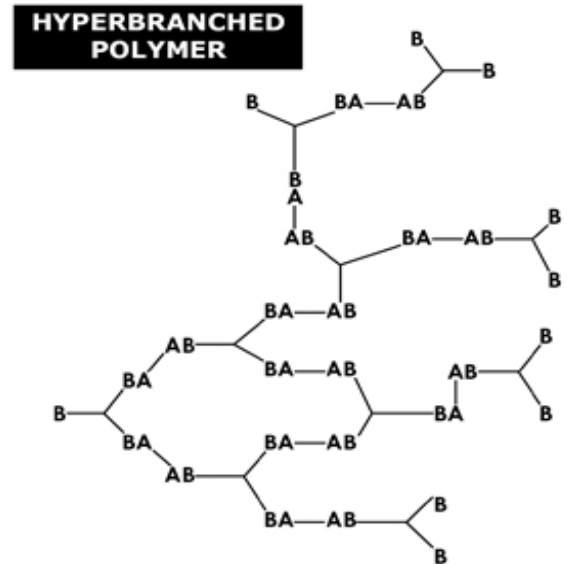
$$\text{Branching factor} = 12/18 = 0.67$$

- max 0.5 for AB_2 , 0.8 for A_2B_3 HBP

- ❑ property-application
 - ❑ irregular but close to spherical
 - irregular inner voids ~ carrier
 - low viscosity ~ rheology modifier
 - ❑ dense surface with functional B



- Well-defined core (I)
- Maximum branching
- Isomolecularity
- Large-number of end-groups (Z)
- Almost spherical shape
- Intramolecular cargo space



- No core
- High degree of branching
- Polymolecularity
- Large number of end-groups (B)
- Distribution of globular shapes
- Less well-defined intramolecular cargo space