Polym’n processes

- factors to consider
  - mechanism [radical, ---]
  - state of monomer [gas, ---]
  - form of product [bead, ---]
  - solubility
  - viscosity
- during polym’n
  - heat evolves (slowly or fast)
  - viscosity up (very much)

- 4 methods of polym’n
  - bulk polym’n ~ monomer (+ initiator) only
    - polymer precipitates (like PVC) ~ precipitation polym’n
  - solution polym’n ~ monomer(s) (+ initiator) in solvent
    - interfacial polymerization (between organic/water phases)
  - suspension polym’n ~ M + I in non-solvent
  - emulsion polym’n ~ M and I in different phases
- step polymer by bulk or solution only
  - bulk more favored
  - low viscosity, low heat evolution

- bulk polym’n
  - simple and pure
  - problems at high conversion
    - heat, viscosity
    - autoacceleration
      [gel effect, Trommsdorf effect]
    - stop at low conversion
      and transfer to tower

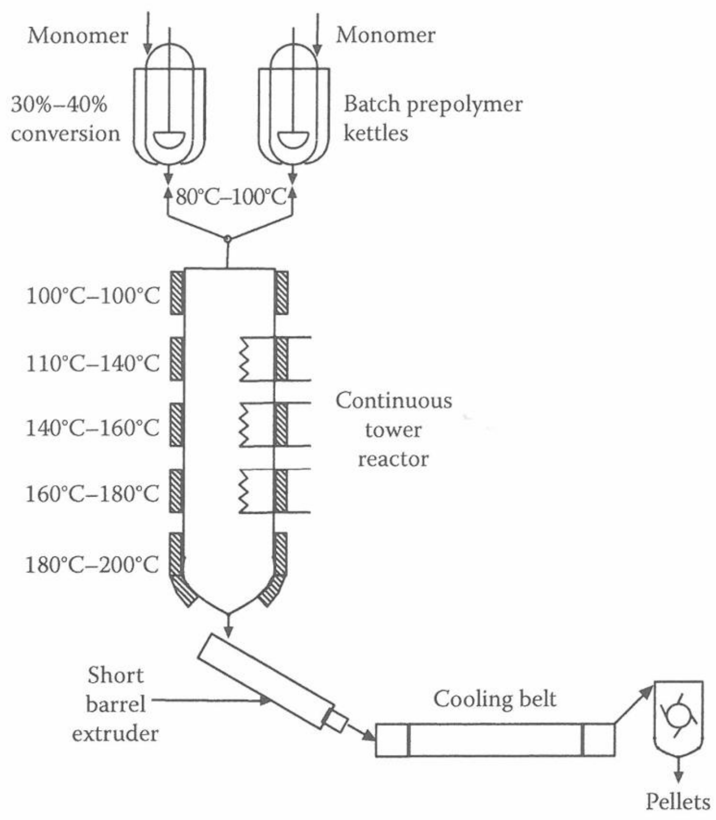


Fig 1.38
for PS

- solution polym’n
  - use of solvent that dissolve M, I, and polymer
    - no heat and autoacceleration problem
  - isolation of polymer needed
    - evaporation of solvent or precipitation in non-solvent
  - useful for polymers used as solution [paint, adhesive]
    - or for cutting low MM off

- suspension polym’n
  - M+I suspended in (heated) water to form droplets
    - with stirring → determine size (.1 – 5 mm)
    - with stabilizer (like PVA) and surfactant
  - bulk polym’n in droplet
    - no heat, viscosity problem
    - droplet → bead ~ ‘bead polym’n’
  - commonly used industrially
    - for many polymers esp for PVC
    - not for lower-T_g (than RT) polymers
  - What if monomer and/or polymer is water soluble?
    - inverse suspension polym’n, eg acrylamide [PAM]

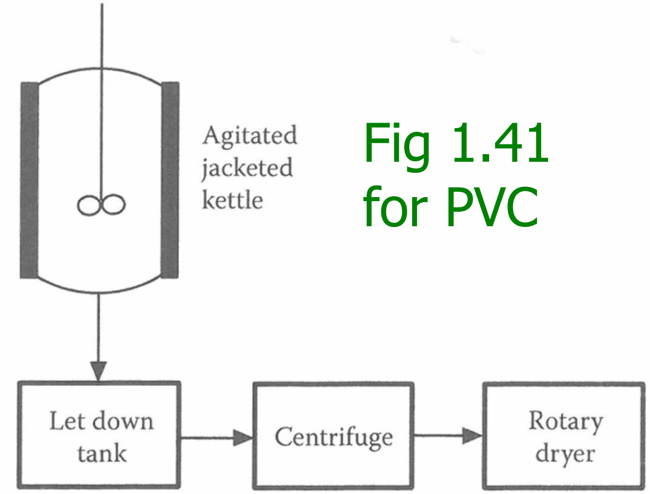
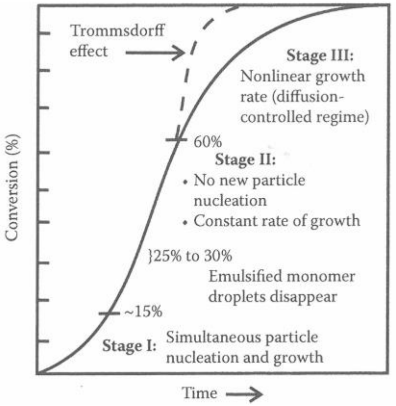


Fig 1.41
for PVC

- emulsion polym'n
  - emulsion = colloidal dispersion < few μm
  - monomer + initiator + emulsifier + water
    - water-insoluble M forms micelle (by emulsifier)
    - water-soluble I radical initiates/terminates polym'n (in micelle)
    - latex [polymer particles in water] formed

$$S_2O_8^{2-} \xrightarrow{50-60^{\circ}C} 2SO_4^{-\bullet}$$



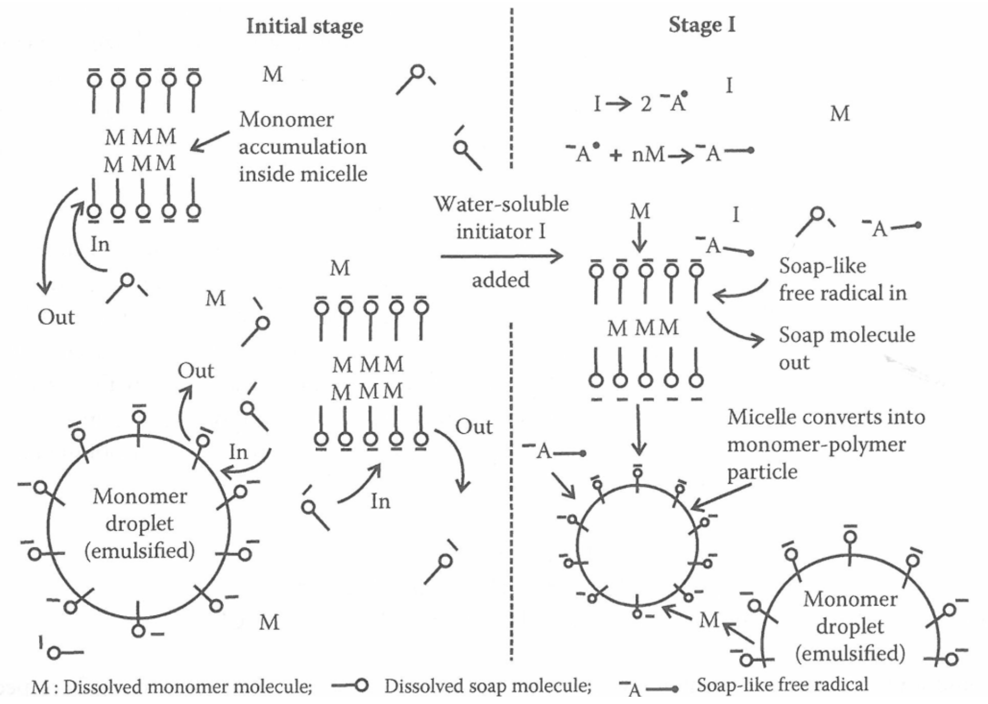


Fig 1.27,28

- emulsion polym’n (cont’d)
  - microemulsion [mini-emulsion]
    - particle size ~ 100 nm
    - with high shear + costabilizer
  - inverse emulsion
  - microgel
    = micron-size crosslinked polymer
    - temperature-sensitive microgel for drug delivery Chapt 5

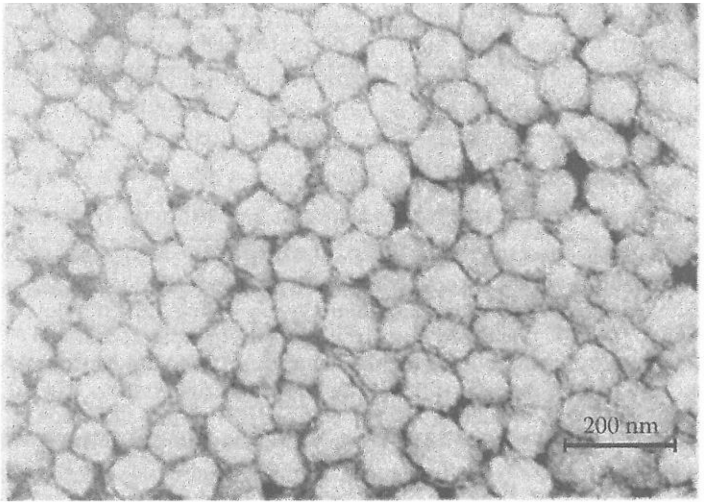
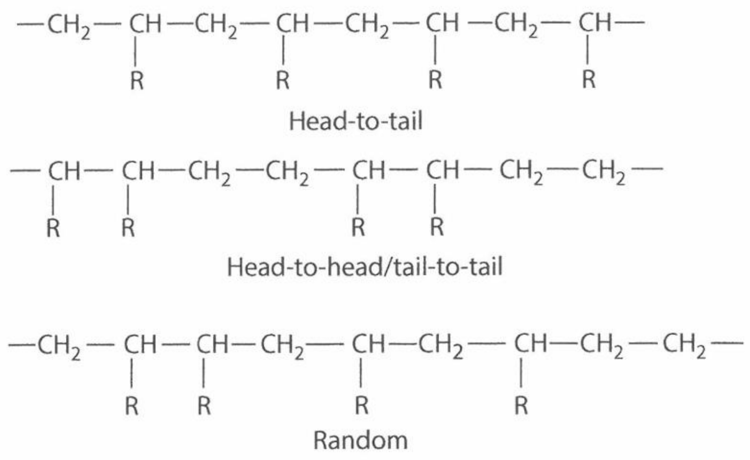


Fig 1.32

Configuration and conformation

- different configuration ~ isomer
    - different polymer
  - constitutional isomers
    - PVA [PVOH] and PEO
    - sequence ~ h-to-t dominant



$$-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-$$

Head-to-tail

$$-\underset{R}{CH}-\underset{R}{CH}-CH_2-CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2-CH_2-$$

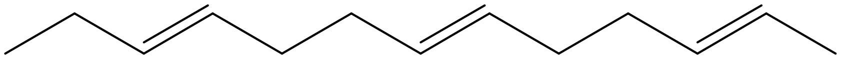
Head-to-head/tail-to-tail

$$-CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}-CH_2-CH_2-$$

Random

  - stereoisomers
    - geometric isomers
      - cis- and trans-1,4-PBD, -PIP

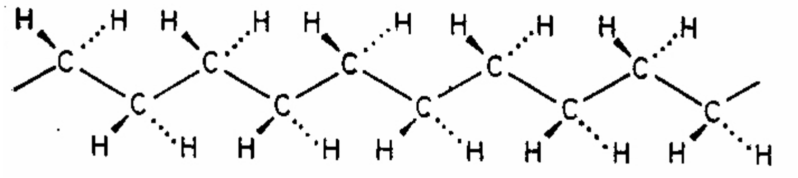
Cis-tactic



Trans-tactic

    - tacticity~ stereoregularity
  - different crystallizability and properties

- different conformation ~ conformer
  - the same polymer with different shape (by bond rotation)
  - conformational or configurational isomer? misnomer!
- with N bonds of length l_0



  - contour length
    - $r = N\, l_0$ or $0.8\, N\, l_0$ ($\theta = 110^o$)
  - (artificial) freely-jointed chain

$$\langle r^2 \rangle = N l_0^2$$

    - end-to-end distance, $r = N^{1/2}\, l_0$
  - (artificial) freely-rotating chain

$$\langle r^2 \rangle = \frac{1 - \cos\theta}{1 + \cos\theta} N l_0^2$$

    - $\theta = 110^o \rightarrow r = 2^{1/2}\, N^{1/2}\, l_0$
  - real chain with unperturbed dimension (amorphous)
    - $r = (CN)^{1/2}\, l_0$
    - radius of gyration, $s = (CN/6)^{1/2}\, l_0$

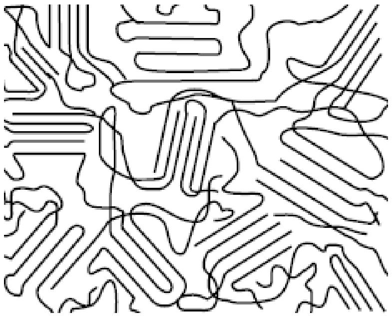
C = characteristic ratio (5-10)

Aggregation structure

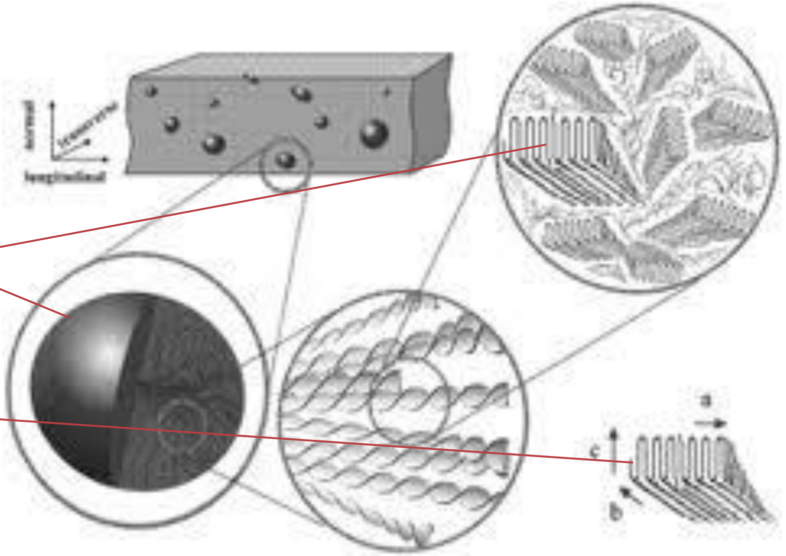
- Polymers in the solid state can be either
  - amorphous

  - (semi)crystalline
    - crystals in amorphous ~ crystallinity

Fig 1.47 p61

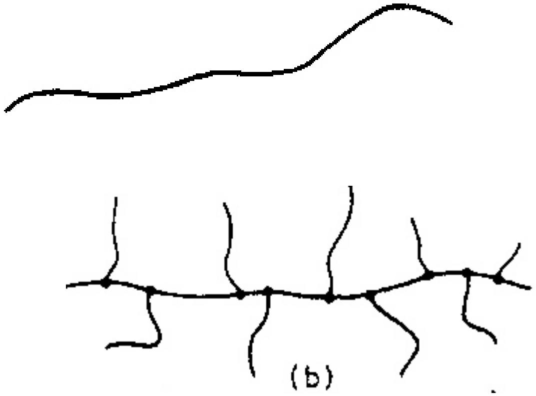


- semicrystalline from melt
  - spherulite [球晶]
    - composed of lamella
  - lamella [版晶]
    - composed of folded chain



Crystallinity

- vol or wt % of crystal
- High Xtallinity gives high thermomechanical properties [heat resistance, strength].
- Xtallinity depends on
  - chain regularity p60-61
    - linearity
      - step vs chain
      - linear vs branched
    - tacticity
  - rate of cooling
    - slow-cooling vs quenching



Amorphous state

- Polymers are in the amorphous state
  - at above T_m for (semi)crystalline polymers ~ melt
    - rheology
  - at all T range for amorphous polymers
    - viscoelasticity ~ time-dependent
- entanglement
  - entanglement mol wt, M_e (= $\rho RT/G_N{}^0$)
  - critical mol wt for entanglement, $M_c \approx 2\text{–}3\ M_e$

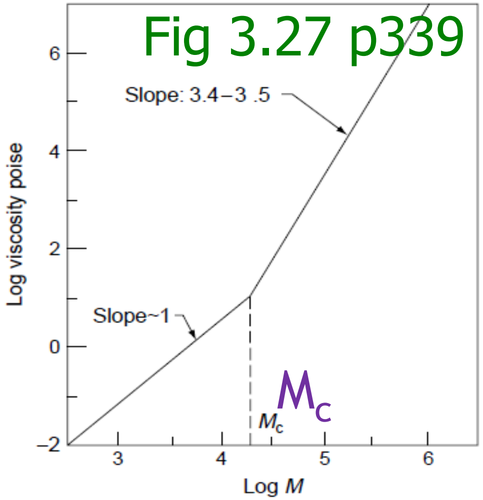
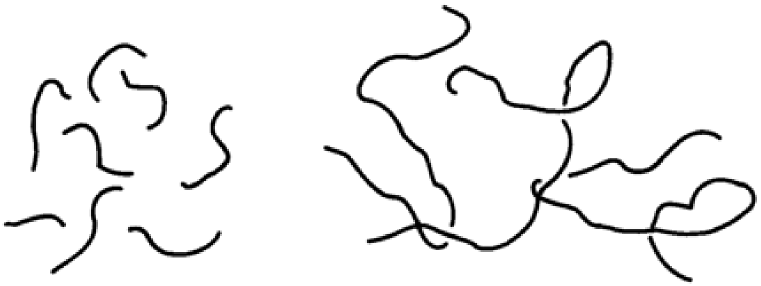


Fig 3.27 p339



p63

M_c at DP of 600?

partly yes/no

Structural shape & materials

- linear, branched, crosslinked
- polymer materials [products]
  - plastics [resins]
    - thermoplastic – thermoplastics
      - fusible, soluble
    - thermosetting – thermosets
      - infusible, non-soluble
  - fibers
    - (cold) drawing → orientation
  - rubbers [elastomers]
    - flexible chains
    - crosslinked ← vulcanization

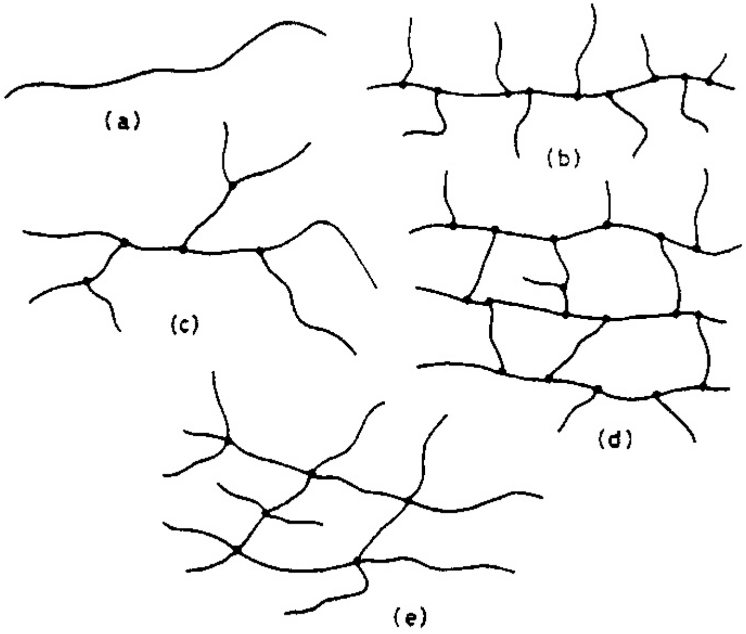
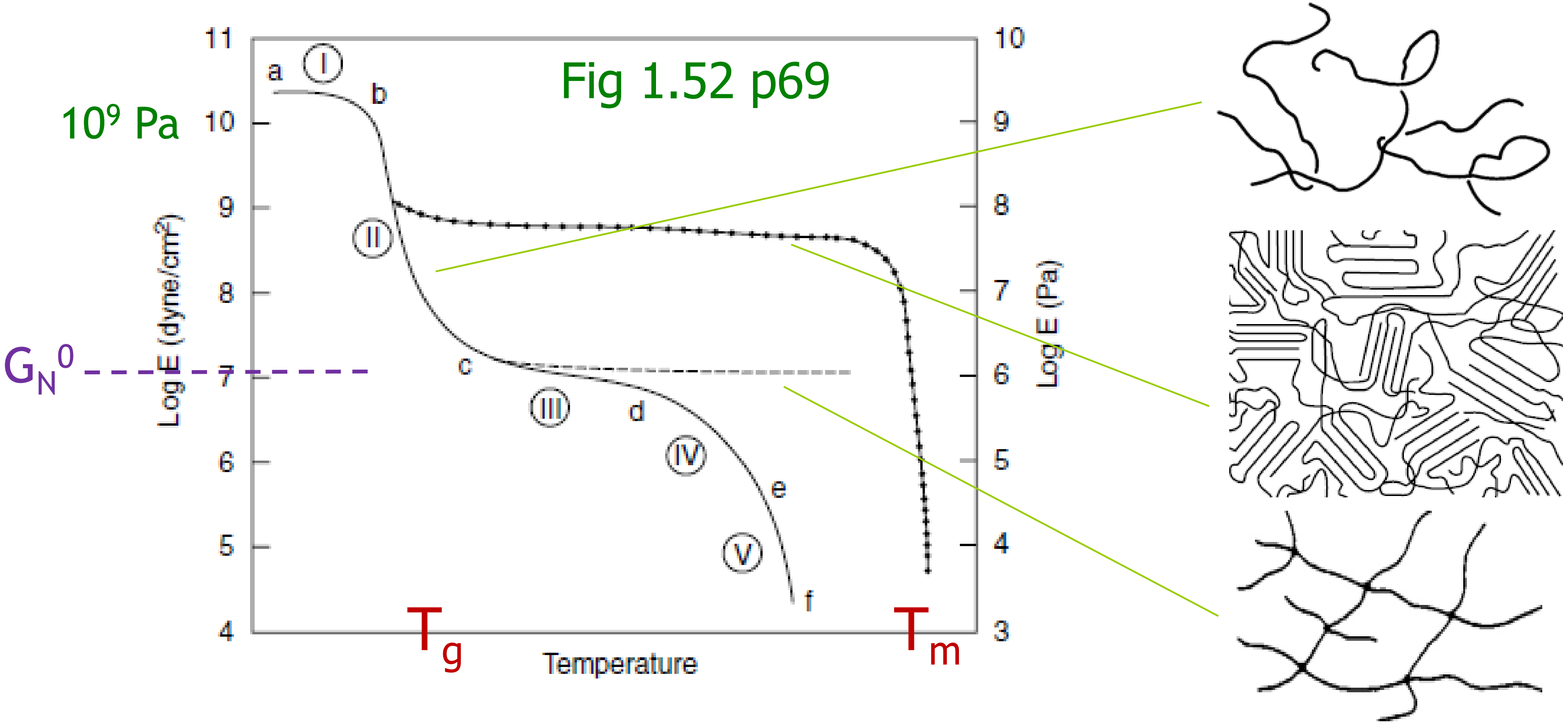
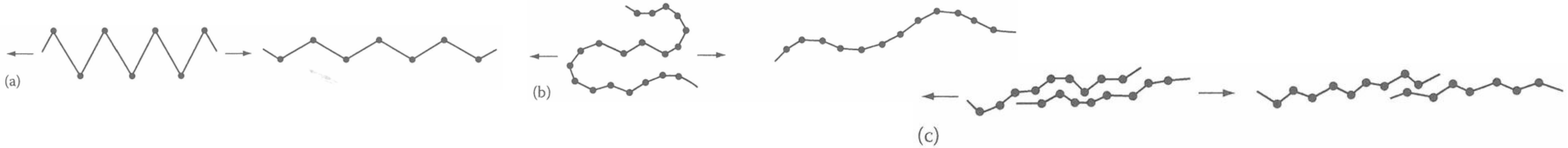


Fig 1.48

Regions of viscoelastic behavior



- glassy – T_g – rubbery plateau – rubbery flow – liquid flow
- local – part of chain – entanglement – disentangle - slip



Thermal transitions

- T_m [T_f]
  - melting temperature
    - for crystallites to melt [fuse]
  - melting transition is a 1st-order phase transition

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

  - T_m^0
    - equilibrium melting temp
    - T_m of perfect crystal
      - infinitely thick crystal
      - of infinitely long chain

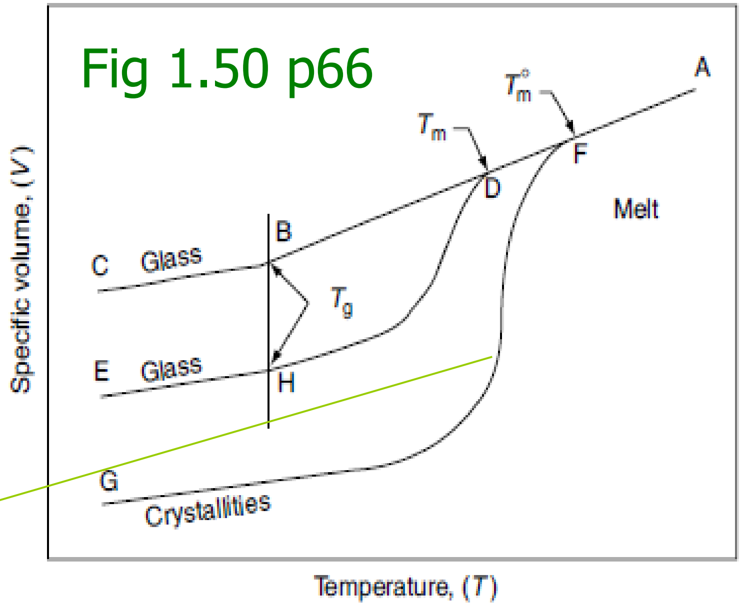
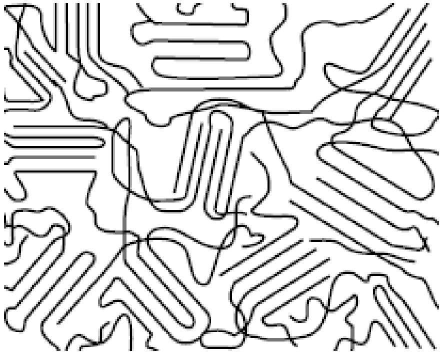


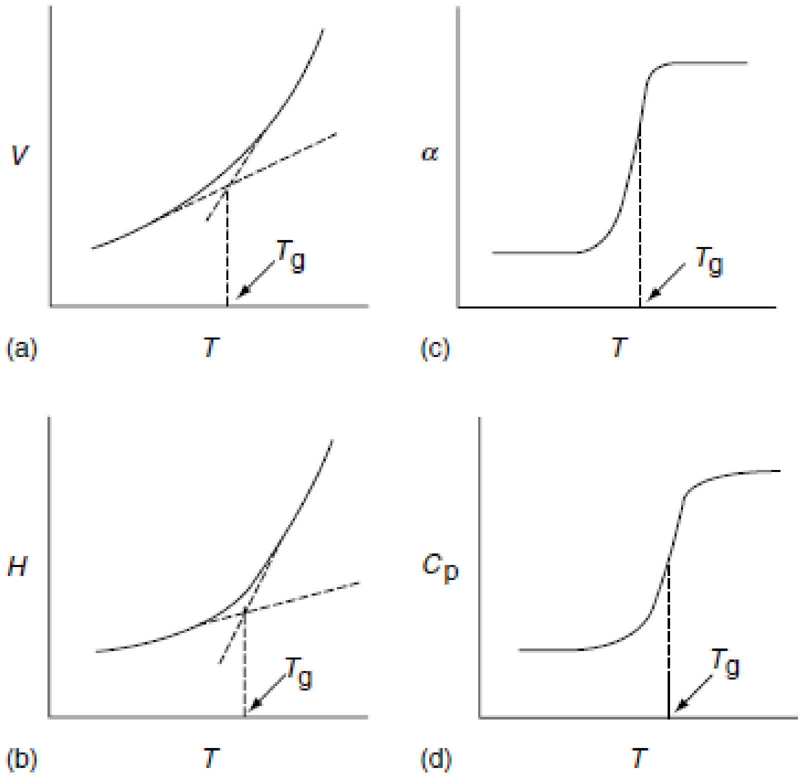
Fig 1.50 p66



- T_g
  - glass transition temperature
  - glass(-rubber) transition is a 2nd-order phase transition

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

    - actually, pseudo-2nd-order ← rate-dependent



$$\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P = H$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

Fig 1.51 p66

- T_m or T_g dictate use temperature range. Read p67-68

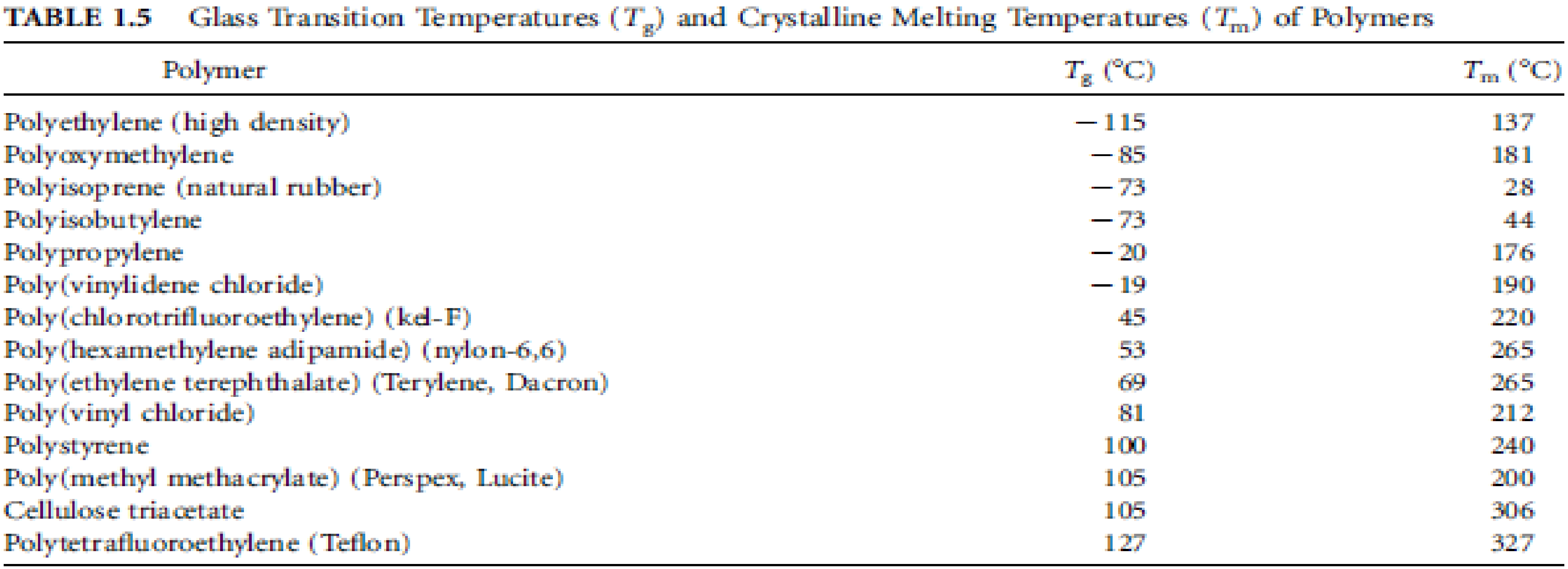


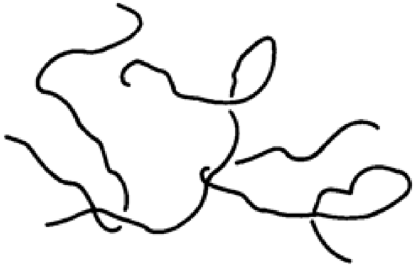
TABLE 1.5 Glass Transition Temperatures (T_g) and Crystalline Melting Temperatures (T_m) of Polymers

Polymer	T_g (°C)	T_m (°C)
Polyethylene (high density)	−115	137
Polyoxymethylene	−85	181
Polyisoprene (natural rubber)	−73	28
Polyisobutylene	−73	44
Polypropylene	−20	176
Poly(vinylidene chloride)	−19	190
Poly(chlorotrifluoroethylene) (kel-F)	45	220
Poly(hexamethylene adipamide) (nylon-6,6)	53	265
Poly(ethylene terephthalate) (Terylene, Dacron)	69	265
Poly(vinyl chloride)	81	212
Polystyrene	100	240
Poly(methyl methacrylate) (Perspex, Lucite)	105	200
Cellulose triacetate	105	306
Polytetrafluoroethylene (Teflon)	127	327

- glassy polymers ~ below T_g or HDT ($T_g \approx$ HDT) Chapt 3
  - heat deflection Temp [HDT]; Vicat softening Temp [VSP]
- semicrystalline polymers ~ below T_m or betw T_g and T_m
- elastomer or rubber ~ above T_g

Factors affecting T_g

- chain flexibility ~ intramolecular p70-71
  - backbone flexibility
    - effect of O, Si, Ph, ---
  - (substituent) steric effect
    - subs size ↑ → T_g ↑
  - configurational effect
    - cis < trans, syndio > iso
- intermolecular interaction
  - dispersion [VdW] force
    - subs size ↑ → T_g ↓
  - dipole interaction
    - main-chain and side-chain polarity
  - H-bonding



PE < PP < PS < PVN
PMA < PMMA
PE < PP > PB > C3 -- < C8 < C9
PE < PVC > PVDC
PA66 ≈ PET

Factors affecting T_m

p72-74

- symmetry
  - linear > side groups
  - cis < trans; ortho < para
- chain flexibility
  - stiffer > flexible
- intermolecular interactions
  - VdW, dipole, H-bonding
- tacticity
- branching
- mol wt

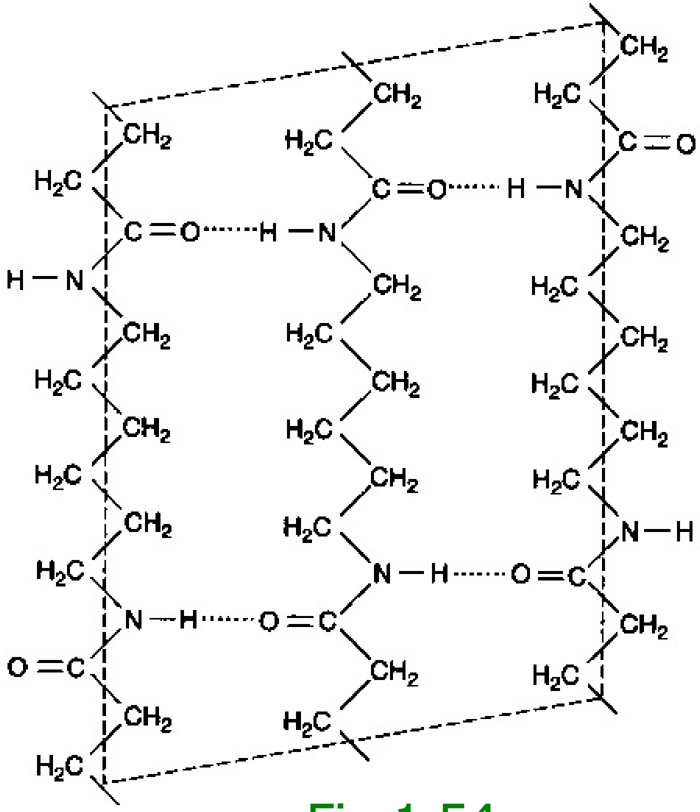


Fig 1.54

Thermodynamics of T_m

- $\Delta G_m = \Delta H_m - T\Delta S_m$
- $T_m^0 = \Delta H_m^0 / \Delta S_m^0 \leftarrow \Delta G_m = 0$
  - T_m^0 = equili melting temp
  - ΔH_m related to interchain interaction, CED
  - ΔS_m related to chain flexibility

Relation between T_g and T_m

- Both of T_g and T_m determined by
  - chain flexibility and
  - intermol interaction.
- Two-thirds rule
  - $T_g \approx 2/3\ T_m$ typically
    - PEster, nylon, ---
  - $T_g \approx 0.5\ T_m$ for linear polymers [symmetrical]
    - PE , POM , PVDF, ---
  - $T_g \approx 0.75\ T_m$ for vinyl polymers [asymmetrical]
    - PS, PVC, PMMA, ---
  - $T_g \approx 0.8\ T_m$ for unusual polymers
    - branched polymers, PC, PPO, ---

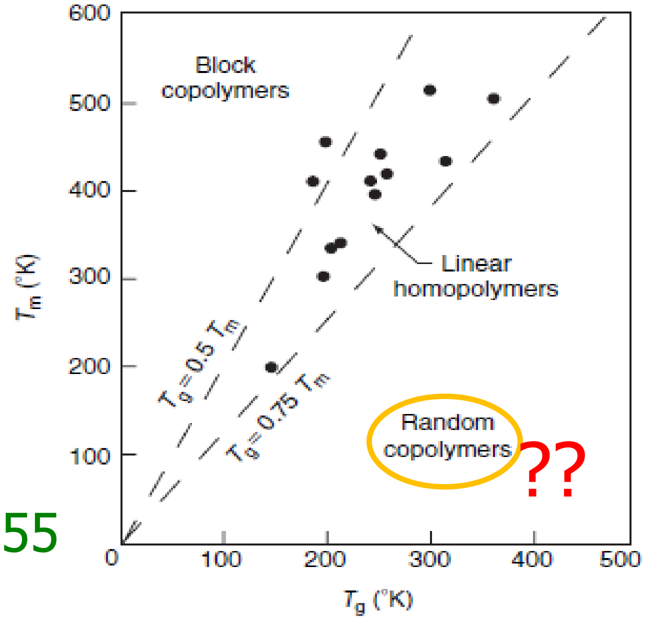


Fig 1.55

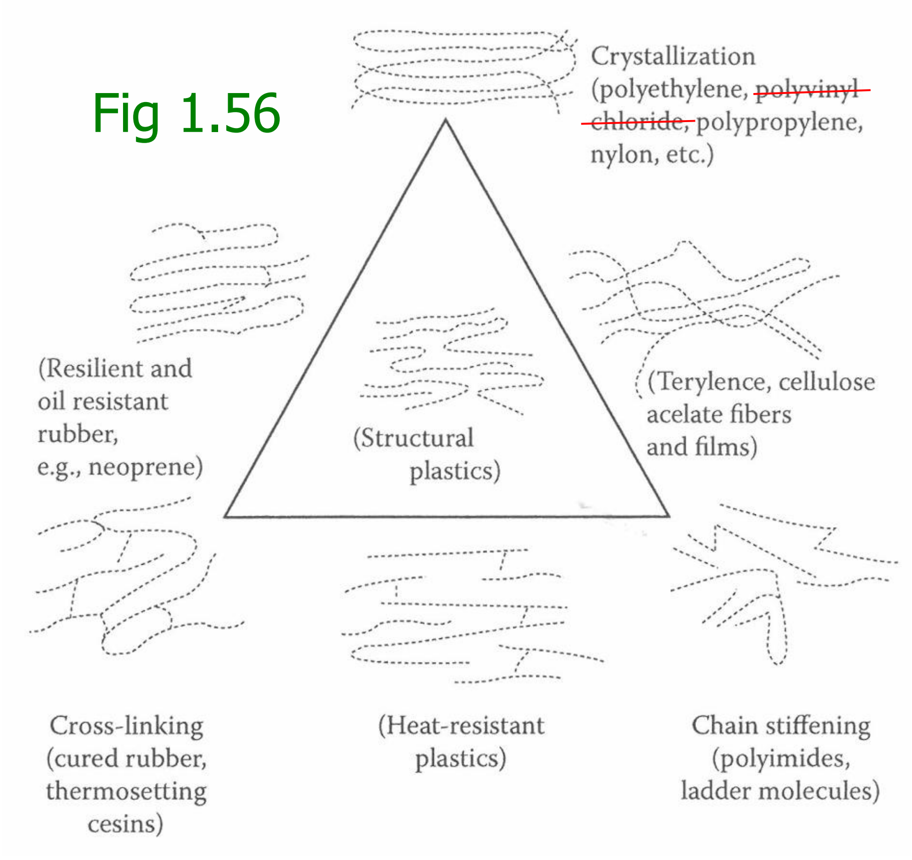
Improving performance

- high-performance structural polymers
  - high thermomechanical properties
    - heat resistance [HDT] and strength [TS]

cf> engineering plastics

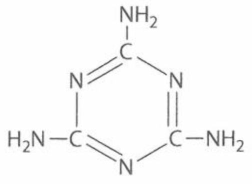
- for high(er) performance
  - high crystallinity
    - annealing
  - crosslinking
  - chain stiffening
    - substituents
    - rings in backbone
    - ladder

Fig 1.56



Crosslinking of polymers

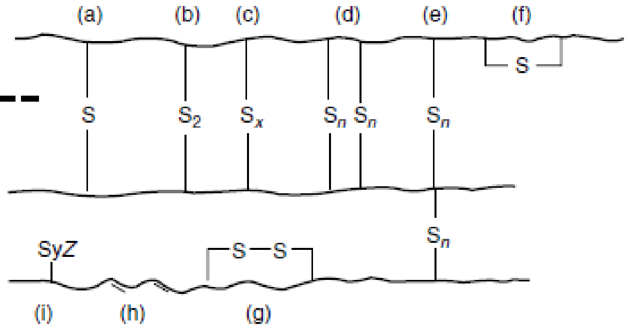
- network structure
  - rubbers, thermosets
  - What you see is one molecule.
  - not fusible, not soluble
  - formed by curing [setting, hardening] of prepolymers
- method 1 ~ reaction of (multi-)functional groups
  - for thermosets
  - phenolic and amino resins [PF, UF, MF]
  - epoxies, unsaturated PEsters, PU foams, alkyds ---
  - curing with or without heat, w/ or w/o hardener
  - many for composite matrix
  - Fig 1.57-63 and Chapt 4



Melamine

- method 2 ~ vulcanization
  - for elastomers
  - with peroxide ~ PE, polyolefins, silicones eqn (1.66-72)
    - stable but expensive
  - with sulfur ~ natural rubbers, SBR ---
    - cheap and common
    - with accelerators, activators Chapt 2
  - with oxide/amine ~ fluororubbers, acryl rubbers, --
    - eqn (1.73) and Chapt 4

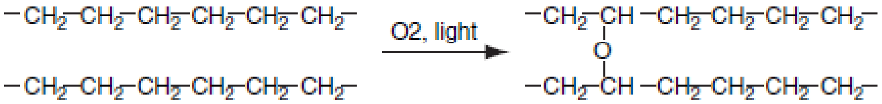
silicon
silicone = siloxane polymer



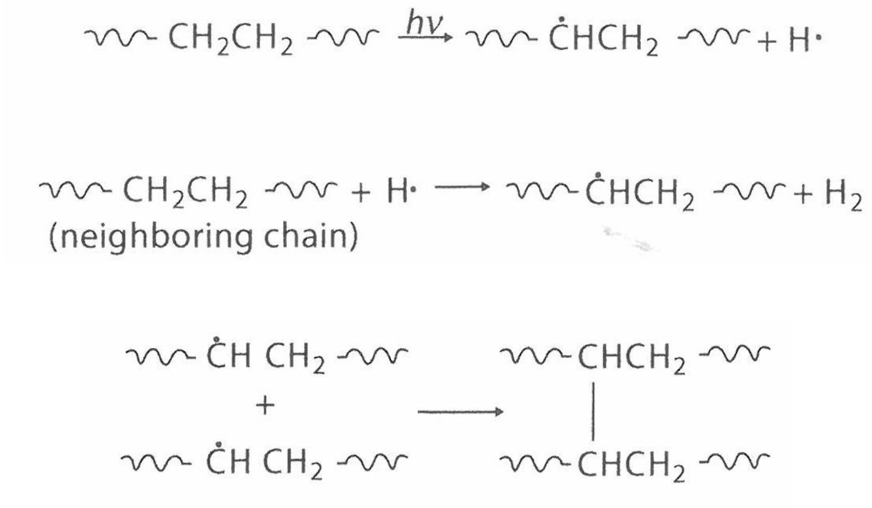
≠ aging (of glassy polymer)

<cf> oxidative Xlinking = aging (of rubber)

- undesirable
- prevented by antioxidant



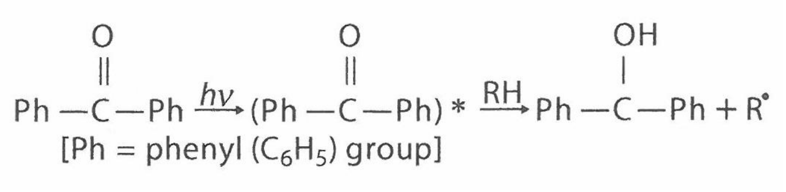
- method 3 ~ radiation
  - with (low-dose) ion beam
  - for PE and vinyl polymers
    - not for 1,1-disubstituted or PVC ~ degradation Table 1.6
  - mechanism similar to peroxide vulcanization
  - useful for coatings, adhesives, (packaging) films



eqn (1.74-76)

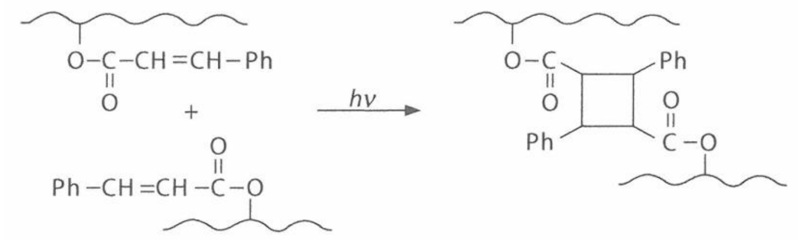
- method 4 ~ photochemical
    - with UV/vis
    - useful for photoresists, finishes, --
    - with external or internal photosensitizer

eqn (1.79-80)

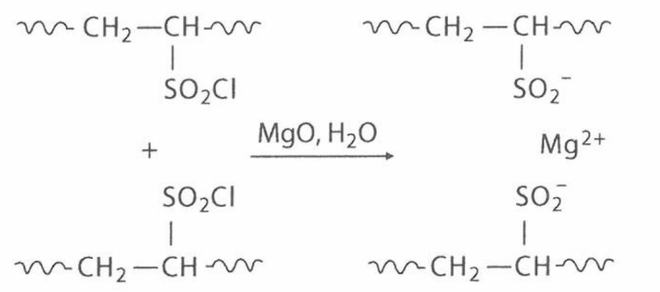


$$\mathrm{Ph{-}C({=}O){-}Ph} \xrightarrow{h\nu} \mathrm{(Ph{-}C({=}O){-}Ph)^*} \xrightarrow{RH} \mathrm{Ph{-}C(OH){-}Ph} + \mathrm{R^\bullet}$$

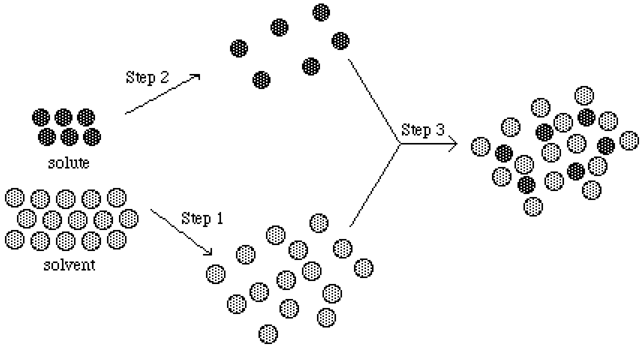
[Ph = phenyl (C_6H_5) group]



- method 5 ~ ionic
    - ionomers
    - thermally reversible Xlinks



Solubility of polymers



- $\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$ Eqn(1.87)
  - $\Delta S_{\mathrm{mix}} > 0$
    - $\Delta S_{\mathrm{m}}^{\mathrm{comb}} = -\mathbf{k}[N_1 \ln\phi_1 + N_2 \ln\phi_2]$
    - much smaller for polymer solutions
      - Flory-Huggins theory
  - $\Delta H_{\mathrm{mix}} \geq 0$
    - "like dissolves like"
    - $\Delta H_{\mathrm{mix}} = 0$ when solute is the same to solvent
    - if not, $\Delta H_{\mathrm{mix}} > 0$
    - $\Delta H_{\mathrm{mix}} < 0$ only when specific interaction like H-bonding exists
  - For solution, $\Delta H_{\mathrm{mix}} < T\ \Delta s_{\mathrm{mix}}$
    - ΔS_{mix} not much dep on type and MW (> M_{th}) of polymers

Solubility parameter

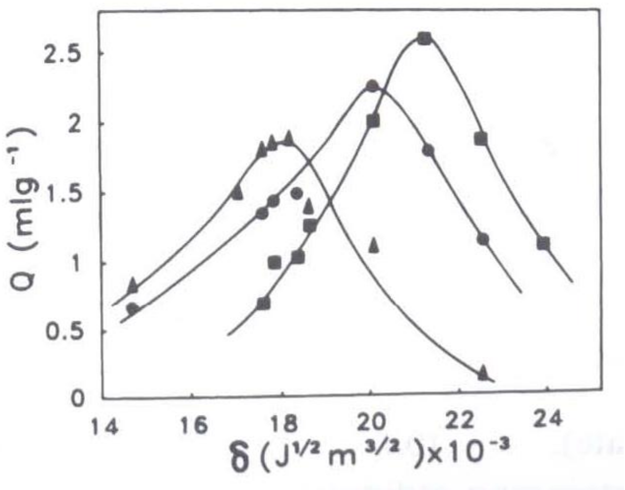
- $\Delta H_{\text{mix}} = V_{\text{mix}} \phi_1 \phi_2 (\delta_1 - \delta_2)^2$ Eqn(1.86), by Hildebrand
  - $\delta = (\Delta E/V)^{1/2} = [(\Delta H_{\text{vap}} - RT)/V]^{1/2}$
    - $\Delta E/V$ = cohesive energy density [CED]
    - δ = solubility parameter [MPa$^{1/2}$] = [(1/2)(cal/cm^3)$^{1/2}$]
- δ of solvents Table 1.8
  δ of polymers Table 1.9 (RT, amorphous)
- $\Delta\delta < 1$ (cal/cm^3)$^{1/2}$ for solution of polymer/solvent
  - $\Delta\delta < 10$ for solvent/solvent

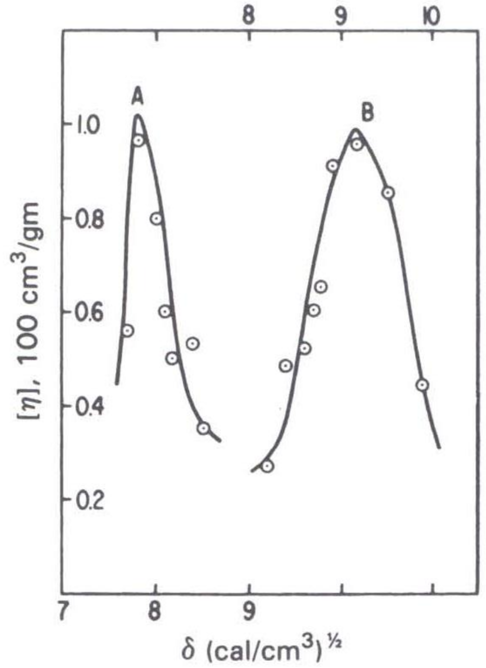
smaller ΔS_{mix}

- semicrystalline polymers are not soluble
  - due to positive ΔH_{fusion}
  - for solution, high Temp and/or specific interaction

δ of C_6H_6 = 9.2
δ of PP = 9.2

- Determination of δ
  - from ΔH_{vap} data ~ for low mol wt, not for polymers
  - experimentally with solvent of known δ
    - swelling
    - viscosity





- δ from group contribution
  - $$\delta = \frac{\rho}{M}\sum F$$ Eqn(1.88)
    - F ~ molar attraction constant Table 1.7; Do Example 6
- solubility map
  - $\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$ Eqn(1.90)
  - $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$
  - constructing map with
    - δ_d, δ_p, δ_h ~ 3-D, Hansen Table1.10
    - f_d, f_p, f_h ~ triangle Eqn(1.94)
    - δ_v [= $(\delta_d^2 + \delta_p^2]^{½}$], δ_h ~ 2-D