Chapter 16

Amorphous State

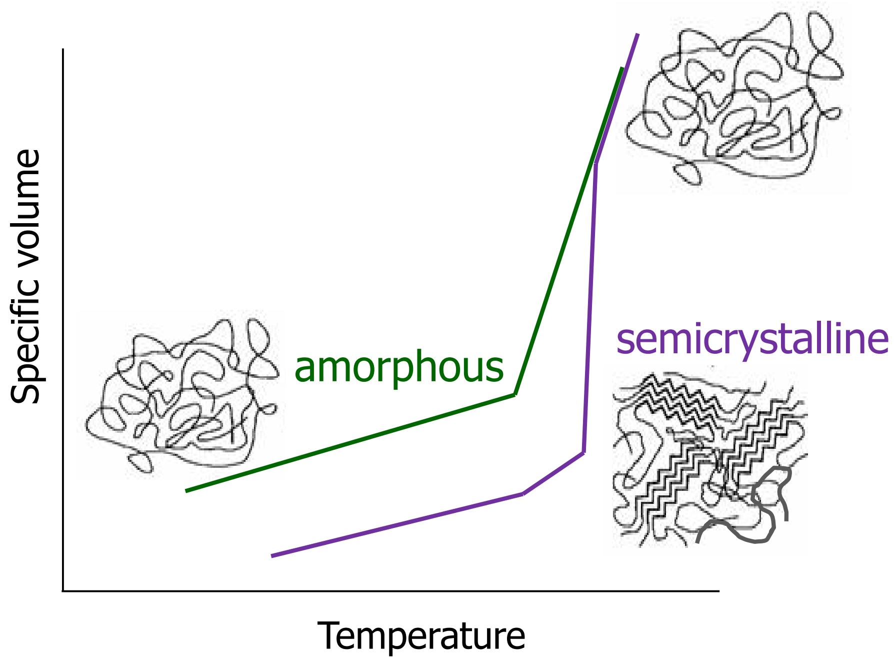
Structure in amorphous state

Glass transition

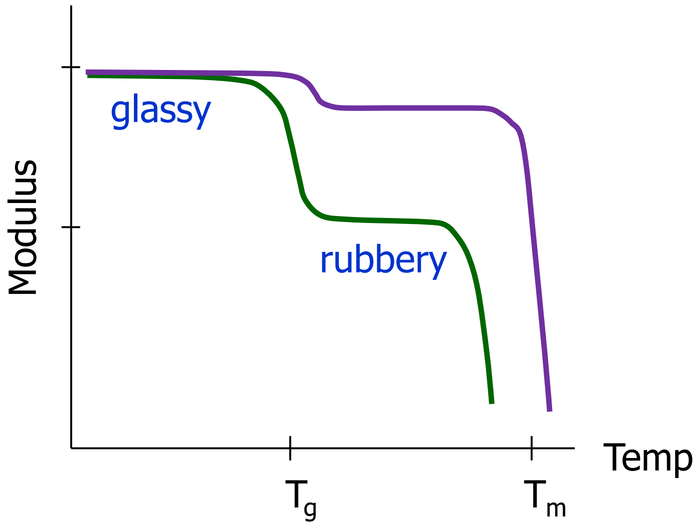
Macromolecular dynamics

Solid-state structure of polymers

- Polymers upon cooling from melt



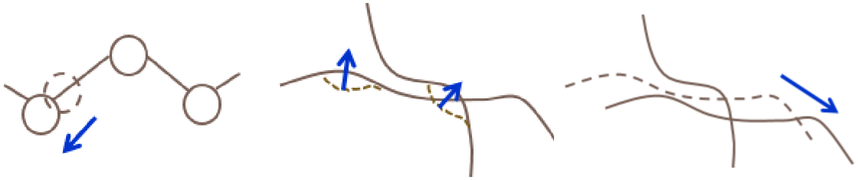
upon heating from solid



glass(-rubber) transition
- only for amorphous polymers or regions

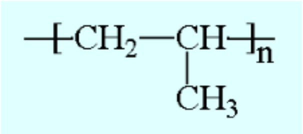
melting
(of crystal)

- amorphous or semicrystalline
- depending on
  - regularity of chain
  - rate of formation [cooling rate]

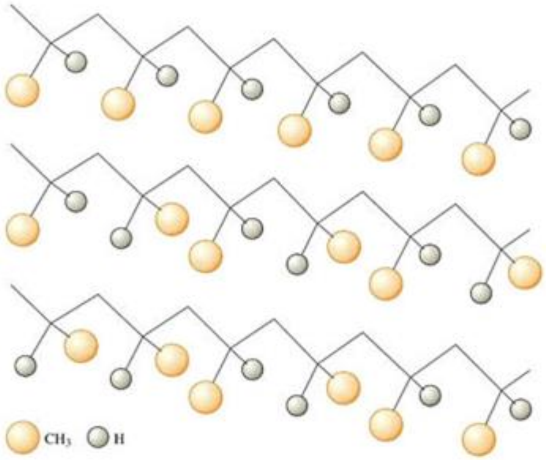


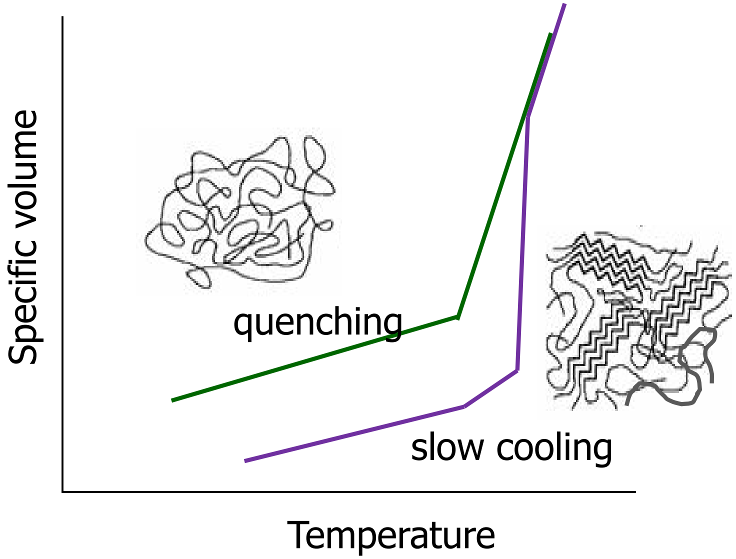
Chain regularity and cooling rate

- regular chain → crystallizable
  - stereoregular [isotactic or syndiotactic] vinyl polymers
    - iPP, sPS, ---
  - main-chain polymers (w/ no pendant group)
    - PE, polyester, nylon, ---
  - semicrystalline when slow-cooled; amorphous upon quenching

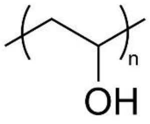


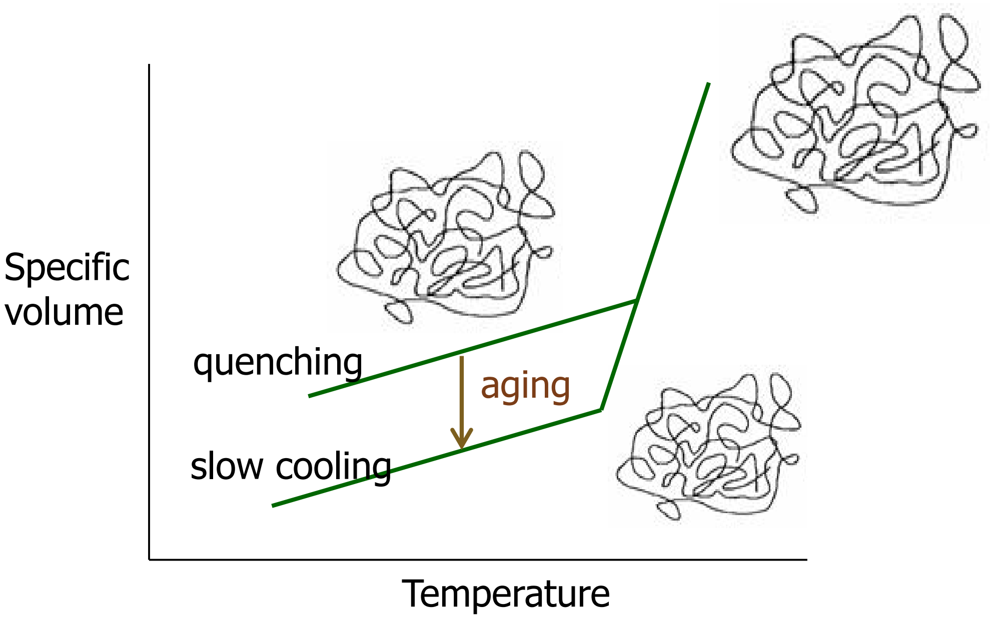
$-\!\!\left[CH_2-\underset{CH_3}{\underset{|}{CH}} \right]\!\!-_n$





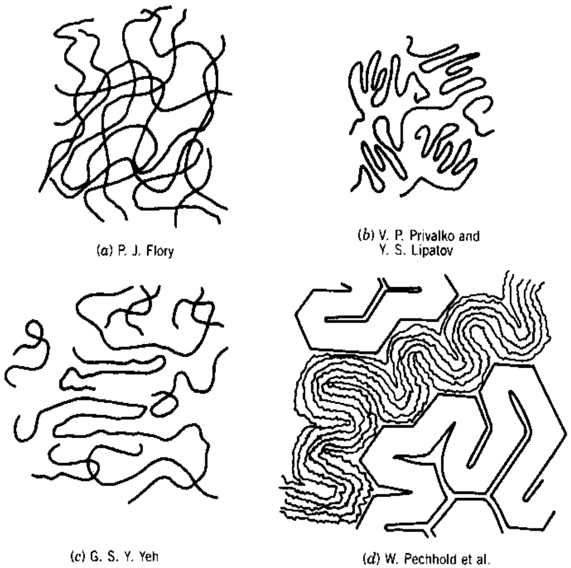
- irregular chain → not crystallizable
  - atactic vinyl polymers
  - (massively) branched polymers
  - amorphous upon quenching;
    aged amorphous upon slow-cooling
  - semicrystalline when side group is (very) small (like PVA) or crystallizable itself (>C8 or mesogenic)





Structure in amorphous polymers

- ❑ morphology of amorphous state?
  = order in disordered state?
  = Is it completely disordered?
  - ❑ arguing partial ordering
    - ■ electron diffraction, WAXS, (SEM ~ artifact)
  - ❑ arguing no ordering over 1 nm
    - ■ birefringence, WAXS, Raman, NMR, etc
  - ➢ natural parallelization ~ ‘spaghetti’
  - ➢ Order should be local, incomplete, and in a very short range, if any.
- ❑ chain dimension in amorphous state
  - ❑ can be determined by SANS
  - ❑ same to that determined in theta condition [unperturbed state]

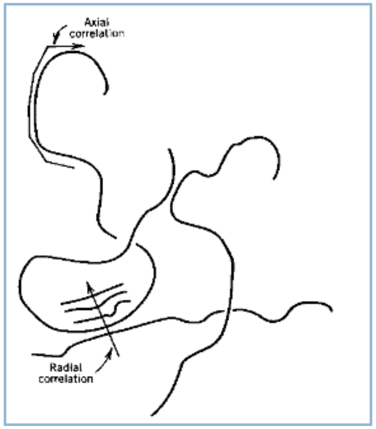


(a) P. J. Flory

(b) V. P. Privalko and Y. S. Lipatov

(c) G. S. Y. Yeh

(d) W. Pechhold et al.



Glass transition 1: Thermodynamics

- phase transition (by Ernfest)
  - 1st-order transition
    - 1st derivatives of free energy G is discontinuous

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

    - step change in V, H, S
    - melting, boiling, polymorphism, ---
  - 2nd-order transition
    - 2nd derivative of free energy is discontinuous
    - step change in α, κ, C_p

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial V}{\partial T}\right)_P = \alpha V \qquad \left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = -\kappa V$$

$$-\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{\partial S}{\partial T}\right) = \frac{C_p}{T} \qquad \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$$

    - glass-rubber, normal-superconducting, ---

Fig 16.3

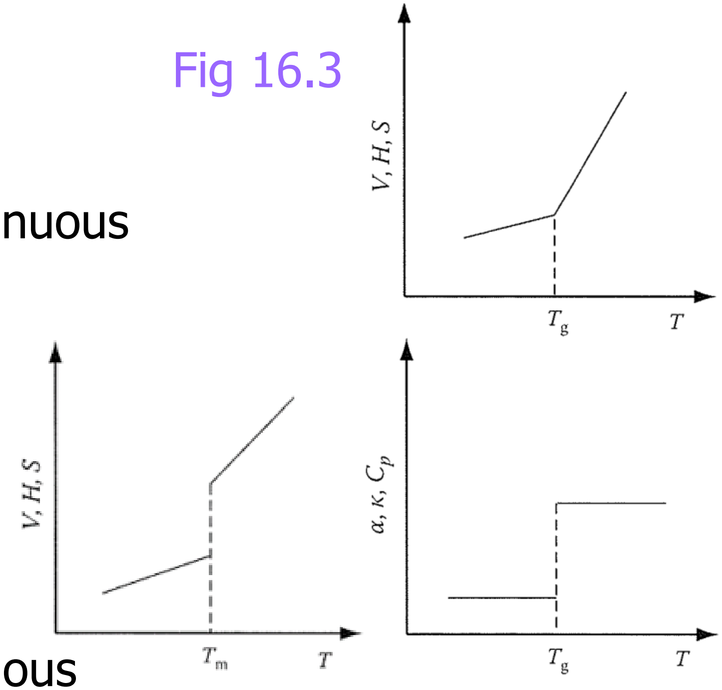
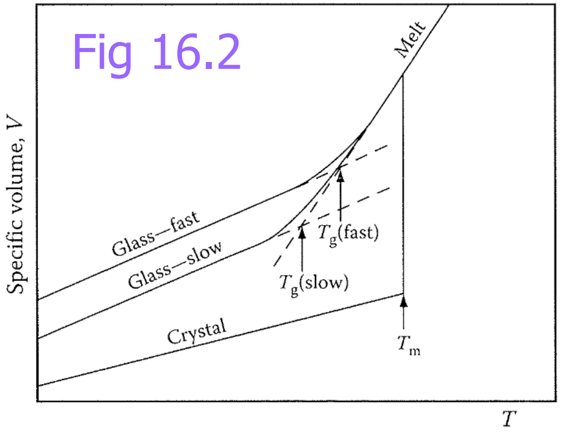
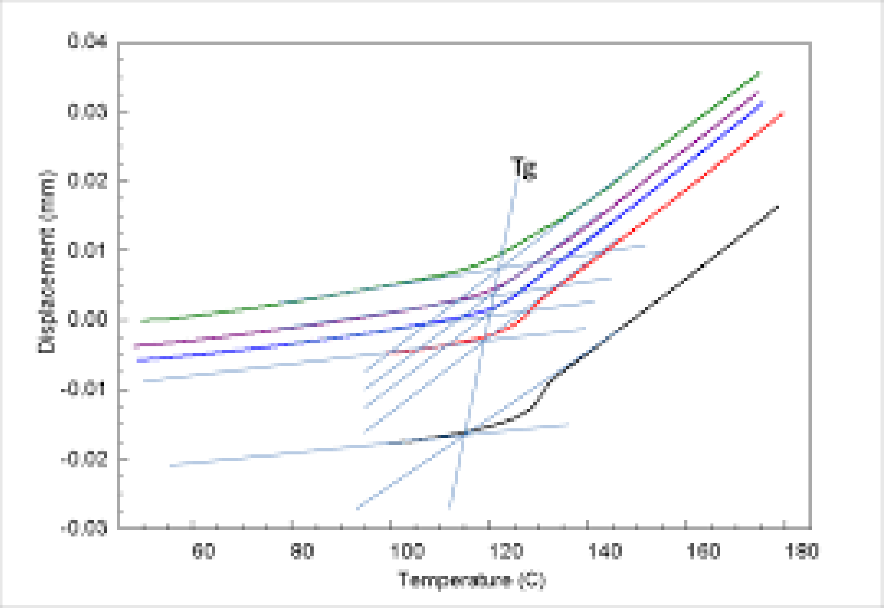


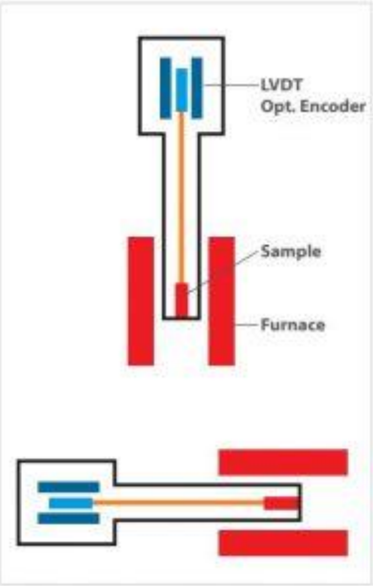
Fig 16.2

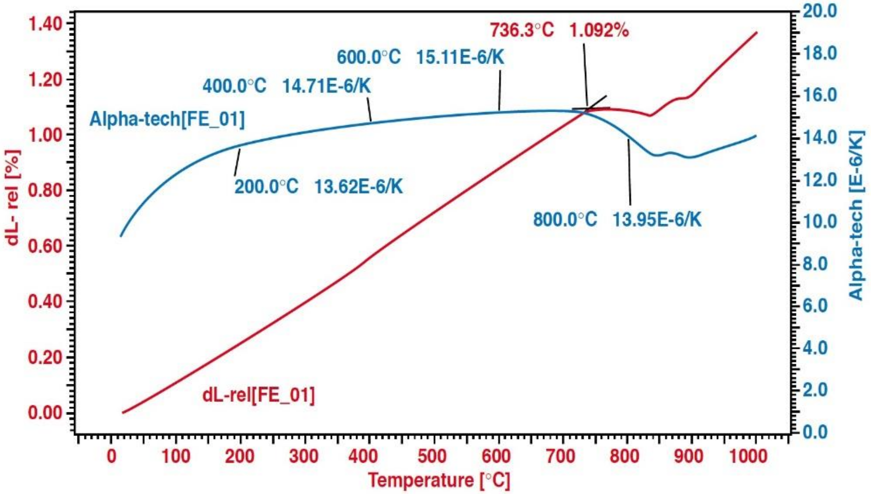


Determination of T_g

- dilatometry
  - change in volume (or α)
    - $\Delta V \leftarrow \Delta L$ if isotropic
  - dilatometer or thermomechanical analyzer [TMA]







- thermal analysis
  - change in heat (or C_p)
  - differential scanning calorimeter [DSC]
    - power-compensation type ~ ΔE
    - heat-flux type ~ ΔT
      - differential thermal analyzer [DTA], actually

Fig 17.33

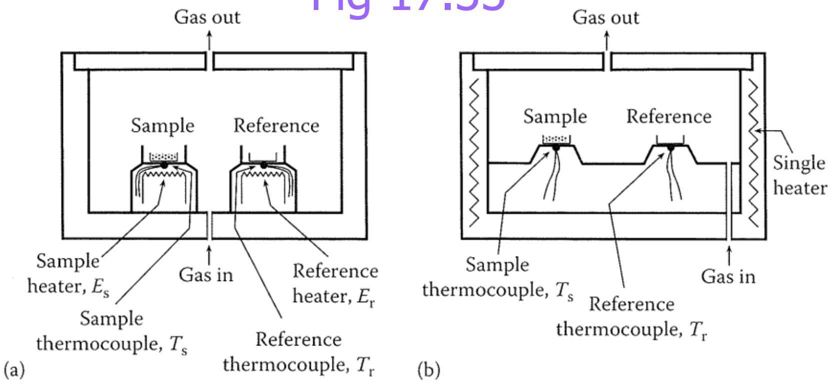
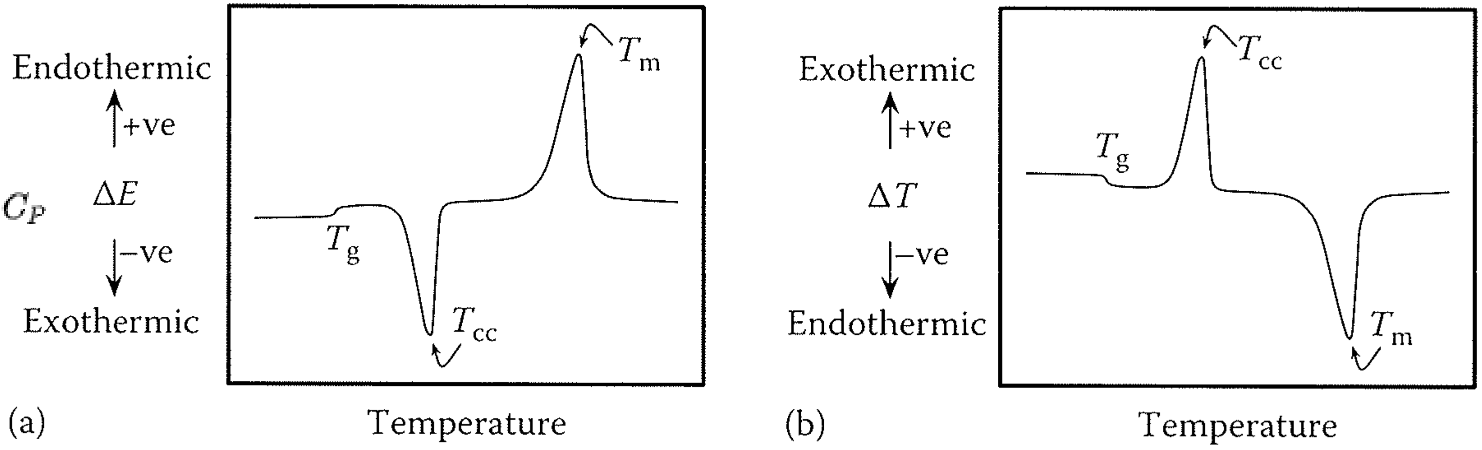


Fig 17.34

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



- mechanical analysis
  - mechanical damping [δ]
  - dynamic mechanical (thermal) analyzer [DM(T)A]

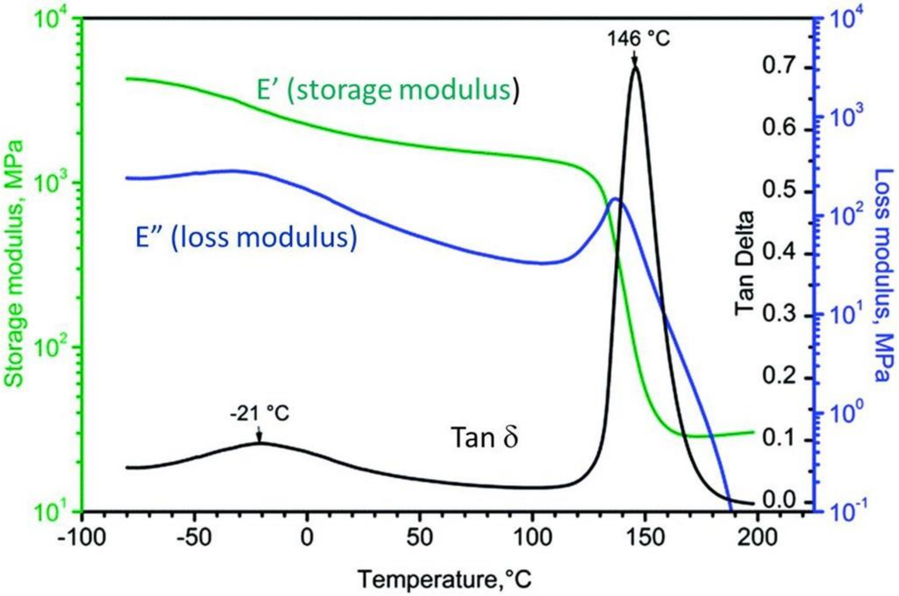
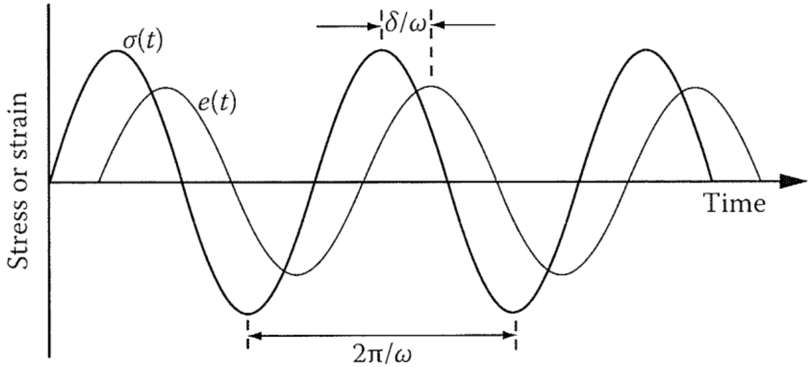
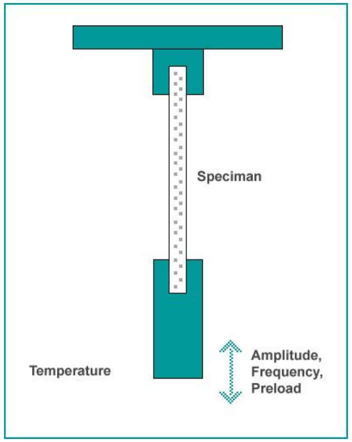
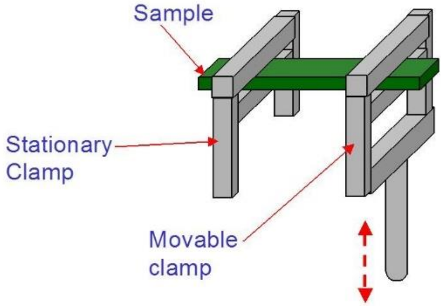


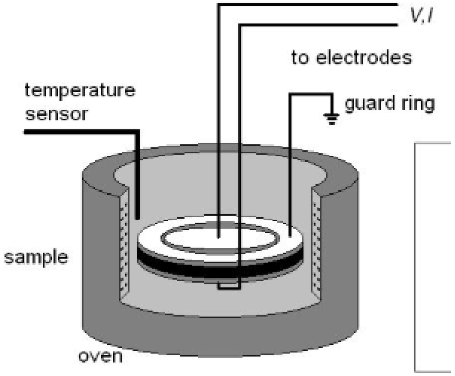
Fig 20.6

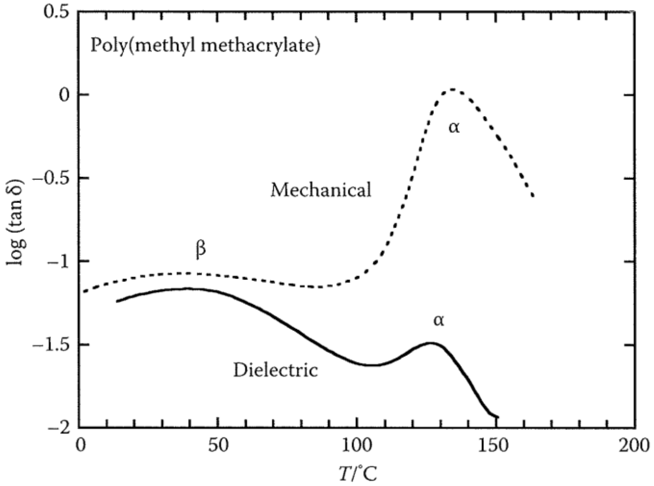




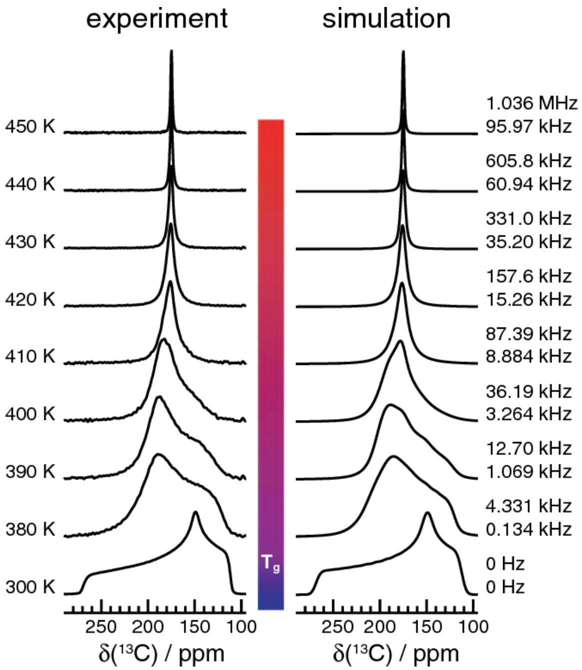


- dielectric analysis
  - electrical damping [δ]
  - dielectric thermal analyzer [DE(T)A]





- NMR
  - relaxation time [τ]



Glass transition 2: Kinetic theory

- T_g is rate-dependent.
  - cooling rate ~ dilatometry
  - dT/dt ~ DSC
  - frequency ~ DMA
- Glass transition is a pseudo-2nd-order phase transition.

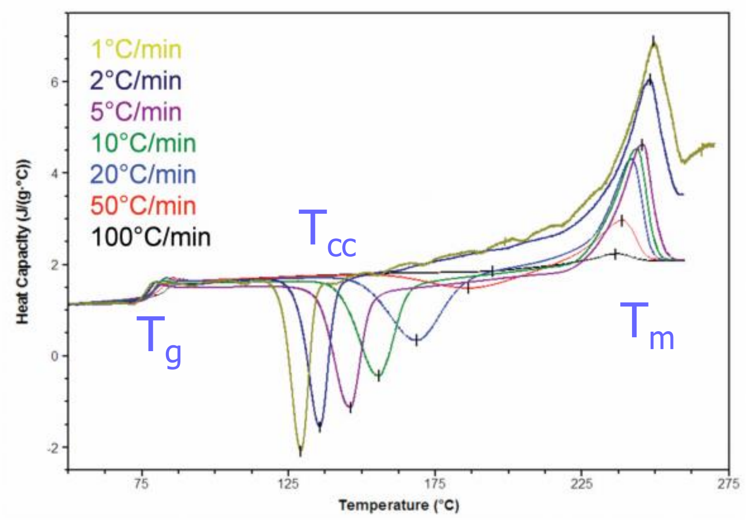
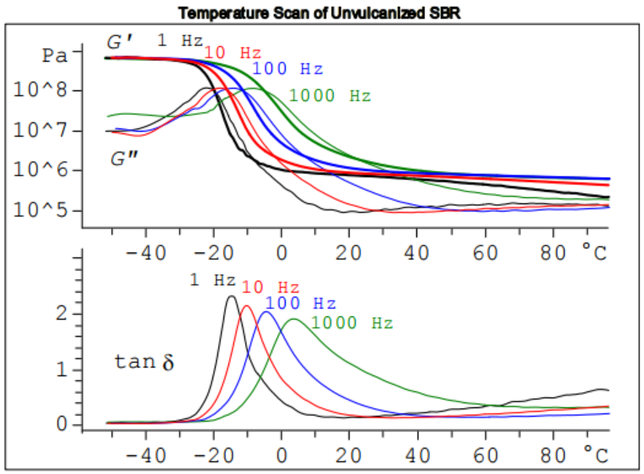


Figure 7: DSC thermal curves of PET at various scan rates, showing the glass transition, crystallisation and melting events.

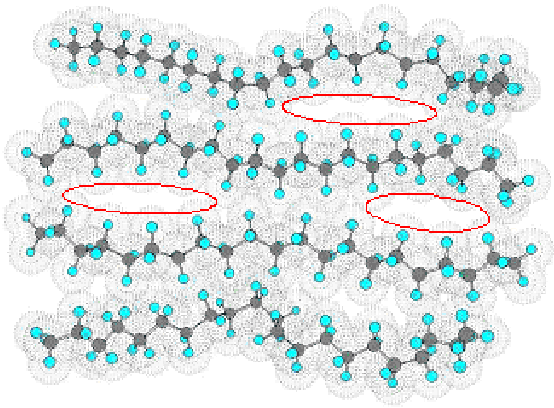


- Glass transition when $t = \tau$.
  - Deborah number $De = \tau/t$
    - τ = material [relaxation] time; t = experimental [observation] time
    - $De > 1$ for (elastic) solid; $De < 1$ for (viscous) liquid
  - Every material is viscoelastic.
    - Deborah said “The mountains flowed before the Lord ....”
  - T_g when $De = 1$
  - exp’t rate $\uparrow \rightarrow t \downarrow \rightarrow De \uparrow \rightarrow T_g \uparrow$

- glass? glassy?
  - glassy vs rubbery
  - glassy vs semicrystalline
  - glassy polymer vs (semi)crystalline polymer

Glass transition 3: Free volume theory

- free volume
  - empty volume? expansion volume? fluctuation (sweep) volume?
  - Free volume is not a real physical volume.
    - Free volume is volume for molecular motion.



- Free volume expands at above T_g.
  - free volume $V_f = V_f^* + (T - T_g)\left(\frac{\partial V}{\partial T}\right)$
  - free vol fraction $f_V = f_g + \left(T - T_g\right)\alpha_f$
- Glassy state is an iso-free-volume state.
  - f_g is universal (2.5%?). Chapt 20

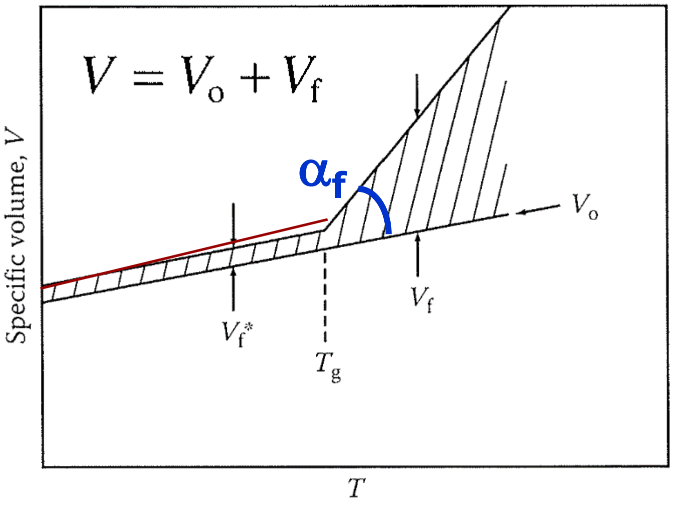


Fig 16.4

Factors controlling T_g

- (repeat unit) chemical structure
  - chain stiffness (intramolecular steric hindrance)
    - aromatic > aliphatic
    - substitutent, branching > linear
      - # and size ↑ → T_g ↑

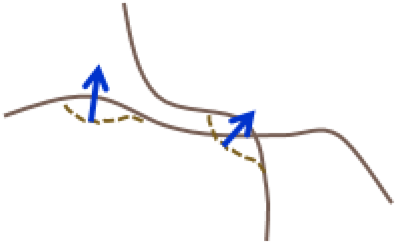


Table16.1

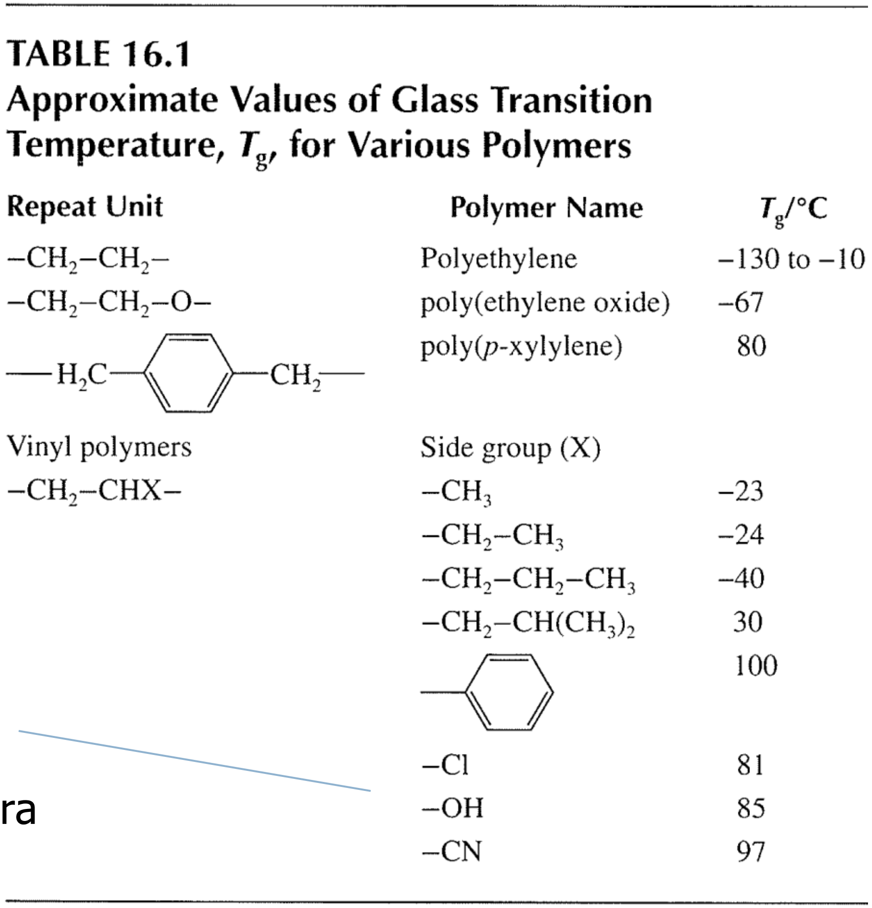
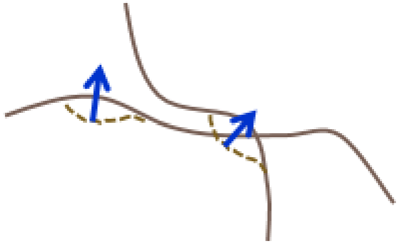


TABLE 16.1
Approximate Values of Glass Transition Temperature, T_g, for Various Polymers

Repeat Unit	Polymer Name	T_g/°C
$-CH_2-CH_2-$	Polyethylene	−130 to −10
$-CH_2-CH_2-O-$	poly(ethylene oxide)	−67
	poly(*p*-xylylene)	80
Vinyl polymers	Side group (X)	
$-CH_2-CHX-$	$-CH_3$	−23
	$-CH_2-CH_3$	−24
	$-CH_2-CH_2-CH_3$	−40
	$-CH_2-CH(CH_3)_2$	30
		100
	$-Cl$	81
	$-OH$	85
	$-CN$	97

p389
polar groups restrict rotation
more than non-polar subs?
<u>Not</u> really. inter rather than intra



- chemical structure (cont'd)
  - intermolecular interactions [2ndary bondings]
    - London dispersion forces [VdW forces]
      - subs size ↑ → distance ↑ → forces ↓ → T_g ↓
      - compete with stiffening effect: PE < PP > PB > C3 -- < C8 < C9
    - dipole-dipole interactions
      - subs dipole moment ↑ → T_g ↑: PE < PVC
    - H-bonding
      - polyamides, polyurethanes
  - intra- and intermolecular factors
    - $T_g = \frac{2\delta^2}{mR} + C_1$
      - δ ~ solubility parameter
      - m ~ mobility of single chain

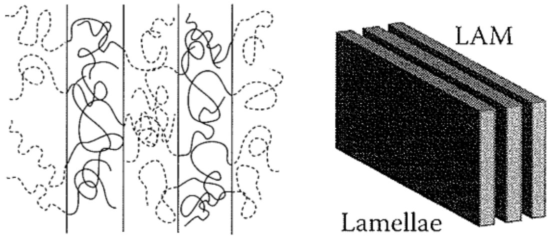
- copolymers and blends
  - block or graft copolymers and immiscible blends
    - 2 phase → 2 T_g
  - random copolymers and miscible blends
    - 1 phase → 1 T_g
    - rule of mixture ~ upper bound

$$T_g^{cop} = T_g^{A} w_A + T_g^{B} w_B$$

    - lower bound ~ better fit to exp't

$$\frac{1}{T_g^{cop}} = \frac{w_A}{T_g^{A}} + \frac{w_B}{T_g^{B}}$$

    - from free volume? p390 <u>not</u> necessary.



Chapt 18

A–A–A–A–A–A–A–A–A–A–B–B–B–B–B–B–B–B–B–B

∼B–B–B–A–B–B–A–B–A–A∼

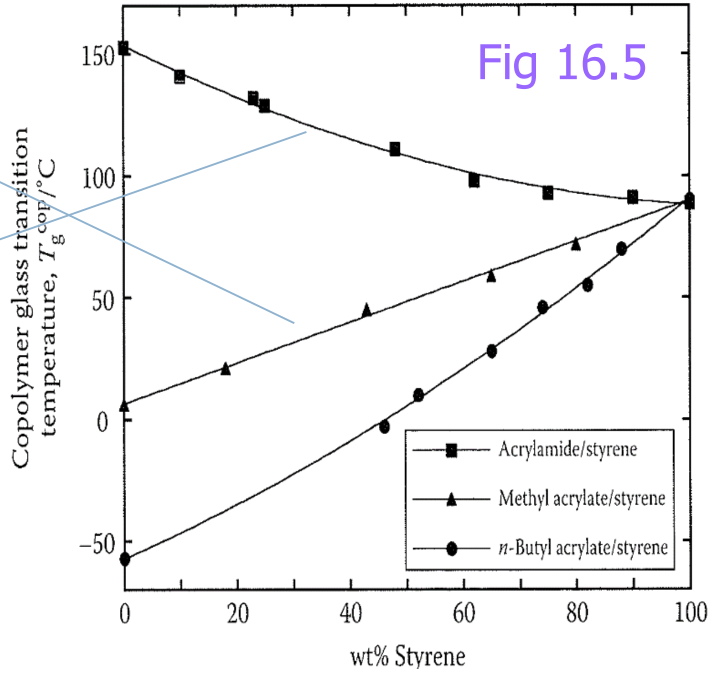
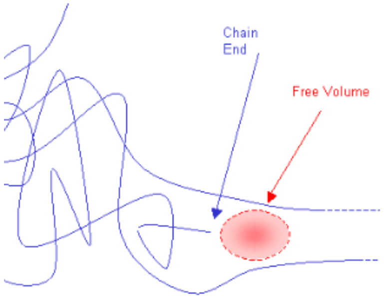
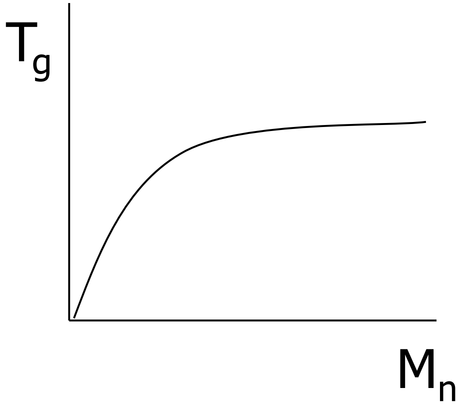


Fig 16.5

- molar mass
  - $T_g^\infty = T_g + \frac{K}{M}$
    - MM ↑ → # of chain ends ↓ → free vol ↓ → T_g ↑
    - M = M_n
    - asymptotic
    - from free volume, $K = 2\rho \mathbf{N}_A \theta / \alpha_f$
      - not that quantitative ~ ignore
- branching
  - small # of branches lowers T_g
    - introduce free volume
  - larger # of branches → higher T_g
    - stiffen chain like substituents





$$T_g = T_g^\infty - \frac{\rho y \mathbf{N}_A \theta}{\alpha_f \bar{M}_n}$$

y chain ends, y-2 branches

ignore also

- crosslinking
  - crosslinking density ↑ → free vol ↓ → T_g ↑

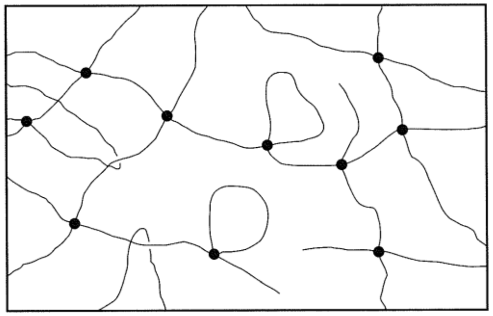


Fig 21.1

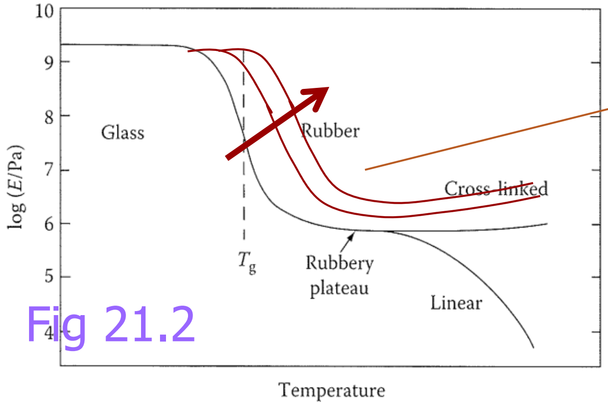


Fig 21.2

effect very much exaggerated

- film thickness
  - more mobility
    in the surface area
  - effect only in
    (very) thin films

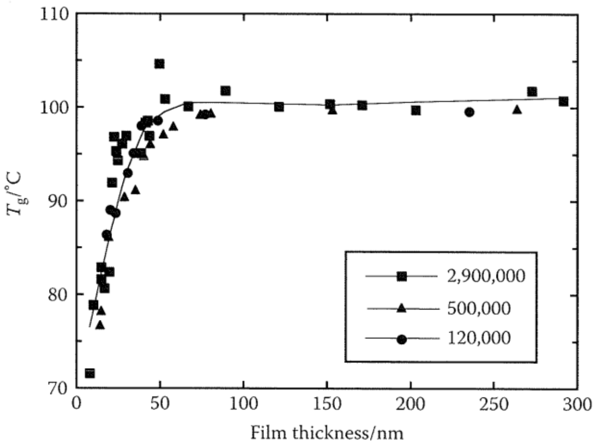
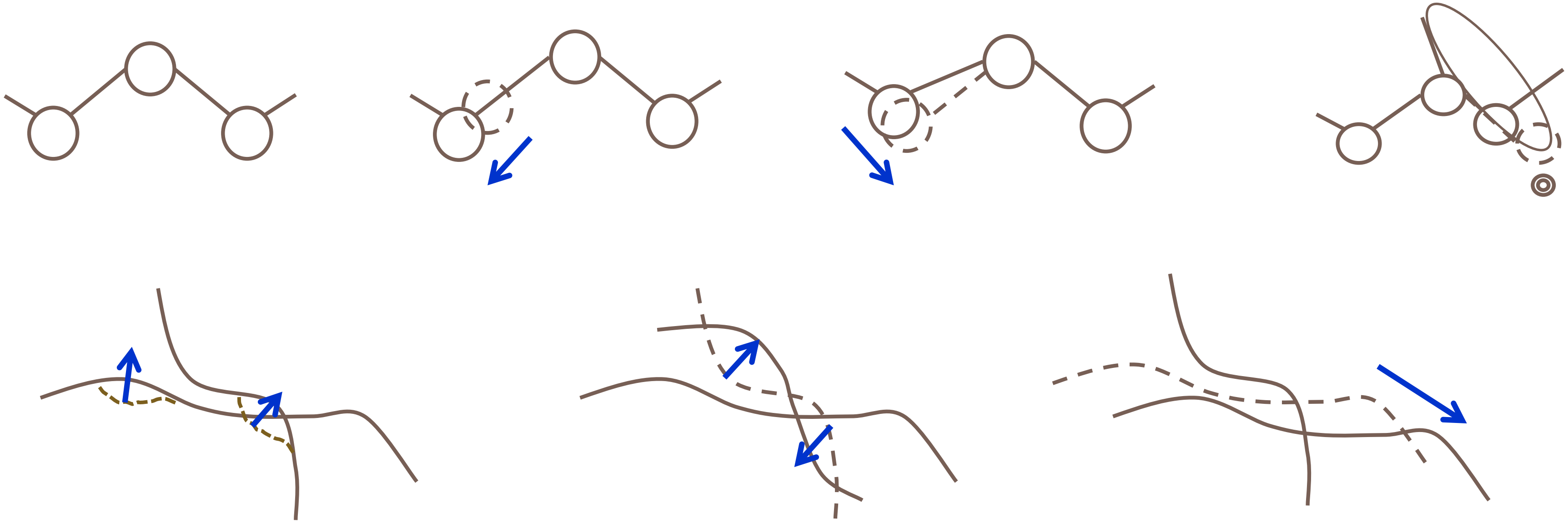


Fig 16.6

Macromolecular dynamics

- motions of polymers
  - deformation of bond length and angle ~ local ~ *elastic*
  - change in conformation ~ segmental ~ *viscoelastic*
  - translation ~ whole chain ~ *viscous*



Models for dynamics

- Rouse(-Bueche-Zimm) theory
  - ‘bead-and-spring’
  - models single chain in dilute solution
  - describes mechanical behavior like creep
  - describes melt viscosity for low MM (before entanglement) only → $\eta \propto M$

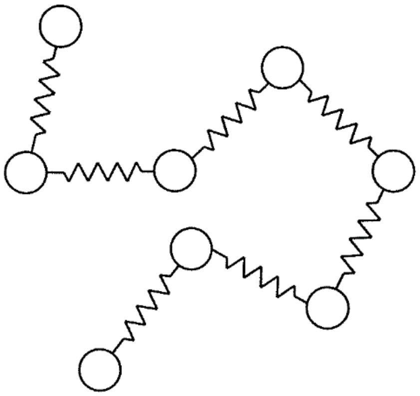
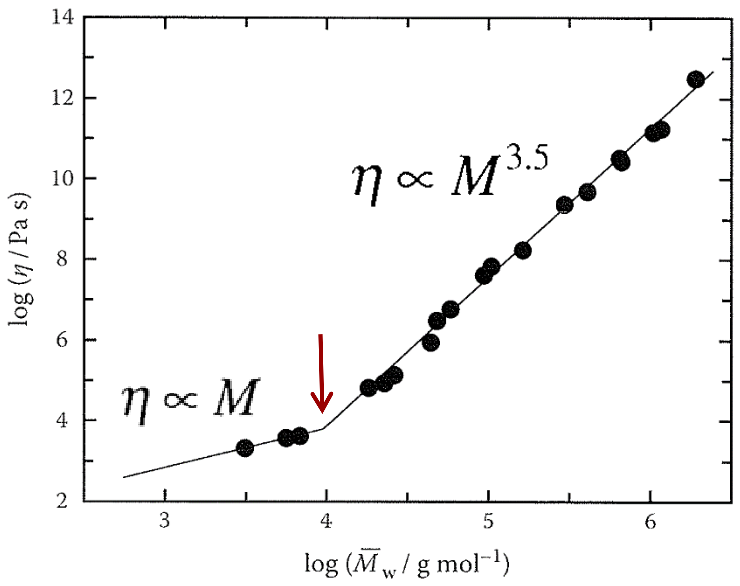
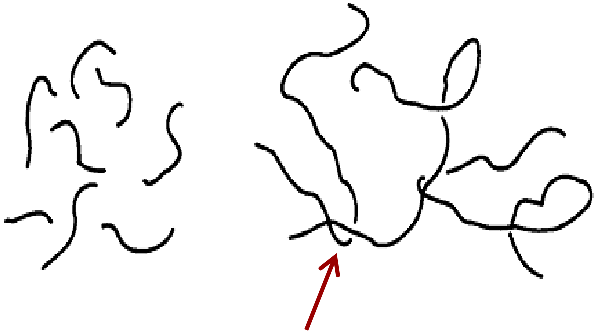


Fig 16.7

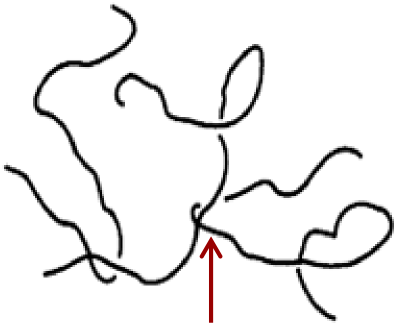




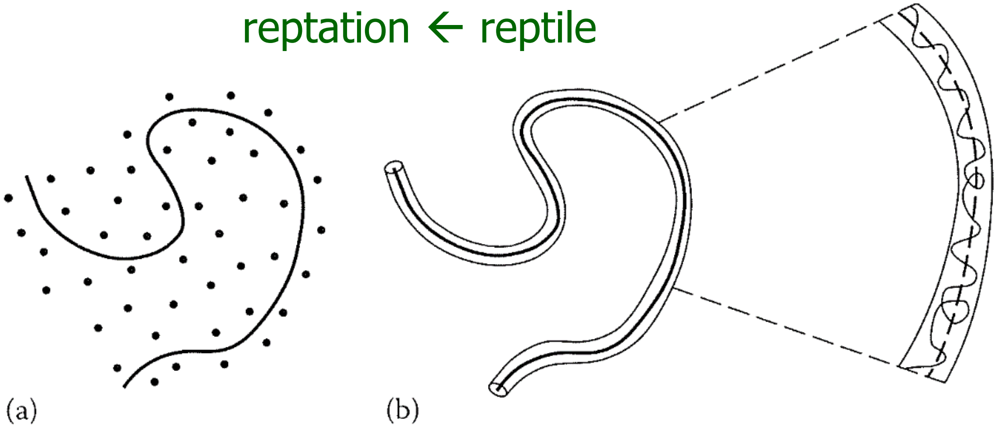
entanglement

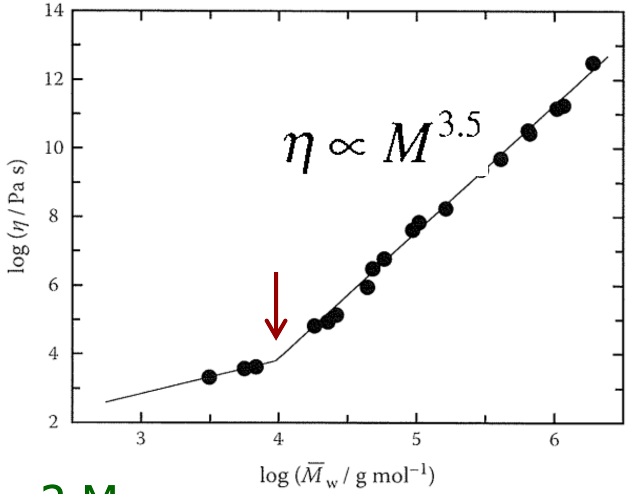
- reptation theory (by de Gennes) Nobel prize 1991
  - considers entanglement [= interchain interaction]
  - for concentrated solution, bulk
  - 'chain in a tube'
    - time for motion of chain in tube ∝ M_w
    - time for motion of tube ∝ $L^2 \propto M_w^2$

→ $\eta \propto M_w^3$



reptation ← reptile





$M_{cr} \approx 2\ M_e$

M_e from G_N^0

$M_{cr(itical)}$