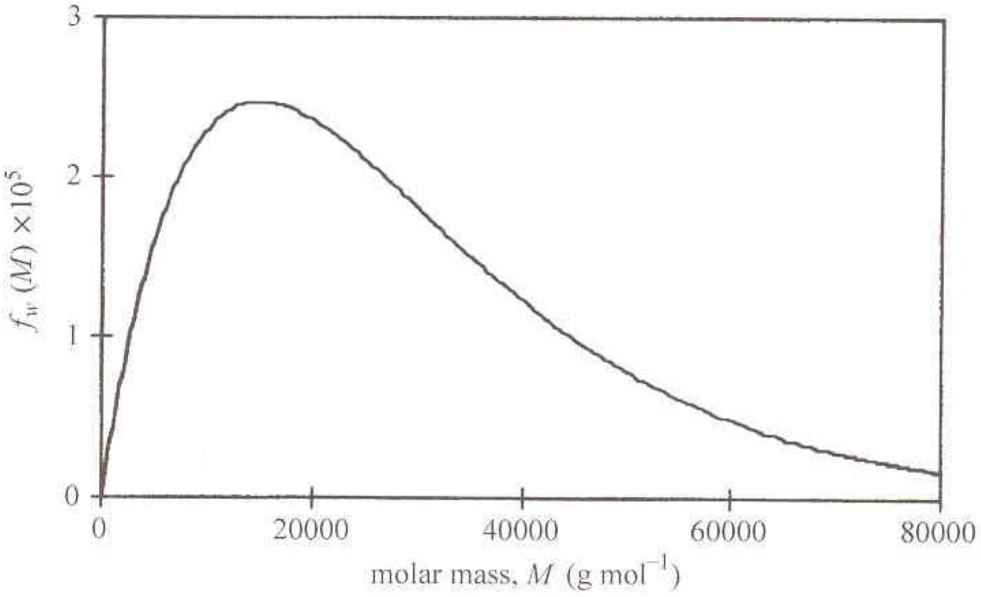
Chapter 3 ~ 5

Amorphous and Crystalline Structures

Chapter 3

Molecular size, Shape, and Ordered structures

Fig. 3.1 The theoretical molar-mass distribution for a self-condensation polymer with a chemical repeat of $M = 150$ g mol^{-1} assuming that 99% of all end groups have reacted. $f_w(M)\,dM$ is the fraction by weight of the polymer that consists of chains with molar mass in the interval dM at M.



	# of chains	f(number)	f(num x Mi)	f(weight)
500	20	0.25	10000	0.125
1000	40	0.5	40000	0.5
1500	20	0.25	30000	0.375

sum of weight 80000

Mn= 1000
Mw= 1125

Structure of polymers

- chemical structure
  - atomic structure
  - isomers ~ configuration
  - architecture

- physical structure
  - single chain structure ~ conformation
  - aggregation structure
    - amorphous state ← conformation in unperturbed state
    - semicrystalline state ← preferred conformation

Single chain structure ~ Conformation

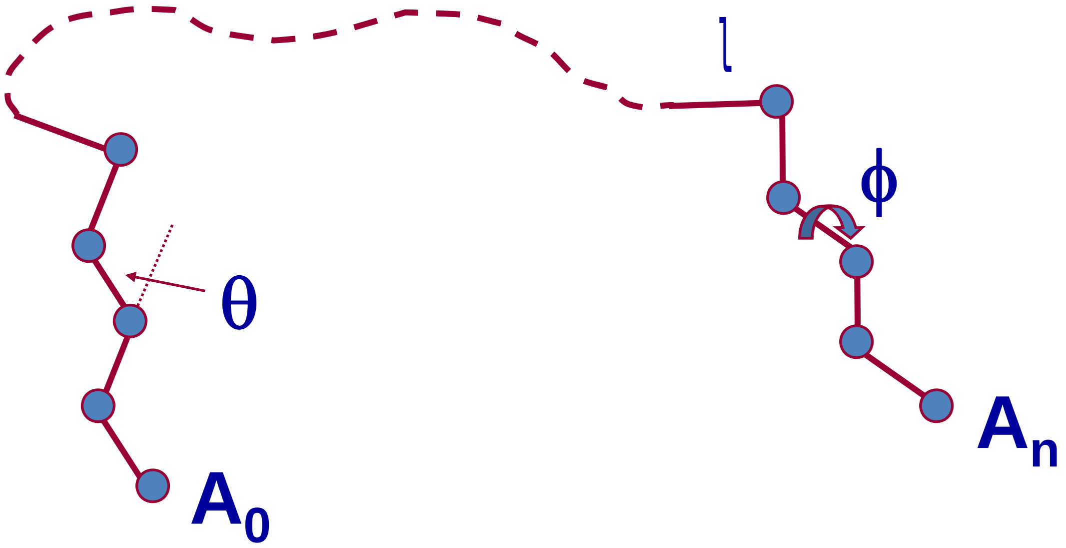
- configuration ~ breaking single bond
  - isomers, copolymers, branches

  conformation ~ rotation about single bond
  - syn-anti, trans-gauche, staggered-eclipsed

- by Flory
  - spatial configuration
  - rotational isomers

A polymer chain

- (n+1) atoms
- n bonds (length l)
- (n–1) bond angles ~ t = 180 - q
- (n–2) rotational angles ~ angle f



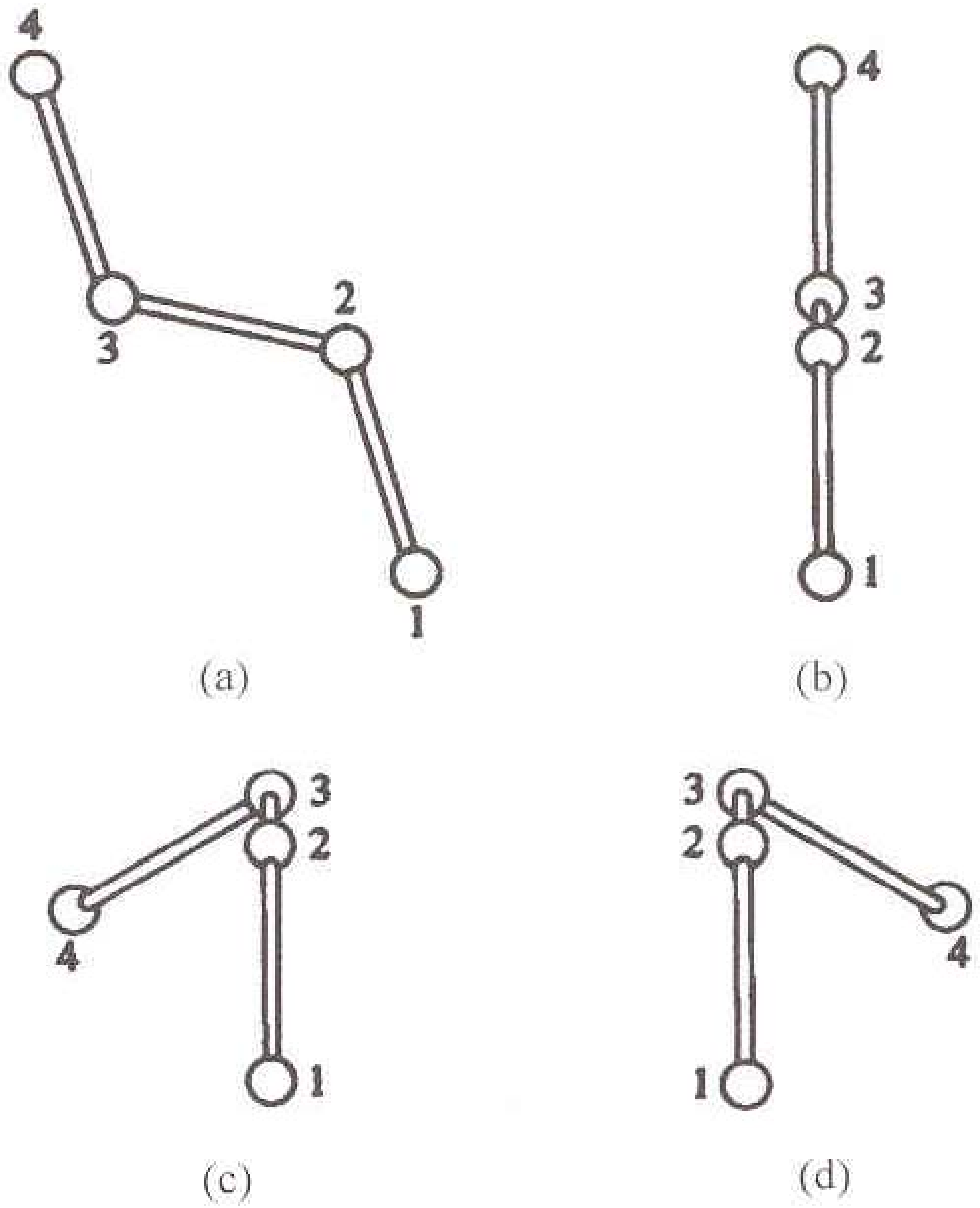


Fig. 3.3 *Trans/gauche* isomerism: (a) a *trans* bond viewed normally to the plane of the three bonds required to define it; (b) a view of (a) from the right-hand side, looking almost end-on to the *trans* bond; (c) and (d) nearly end-on views of left- and right-handed *gauche* bonds, respectively. (Reproduced from *The Vibrational Spectroscopy of Polymers* by D. I. Bower and W. F. Maddams. © Cambridge University Press 1989.)

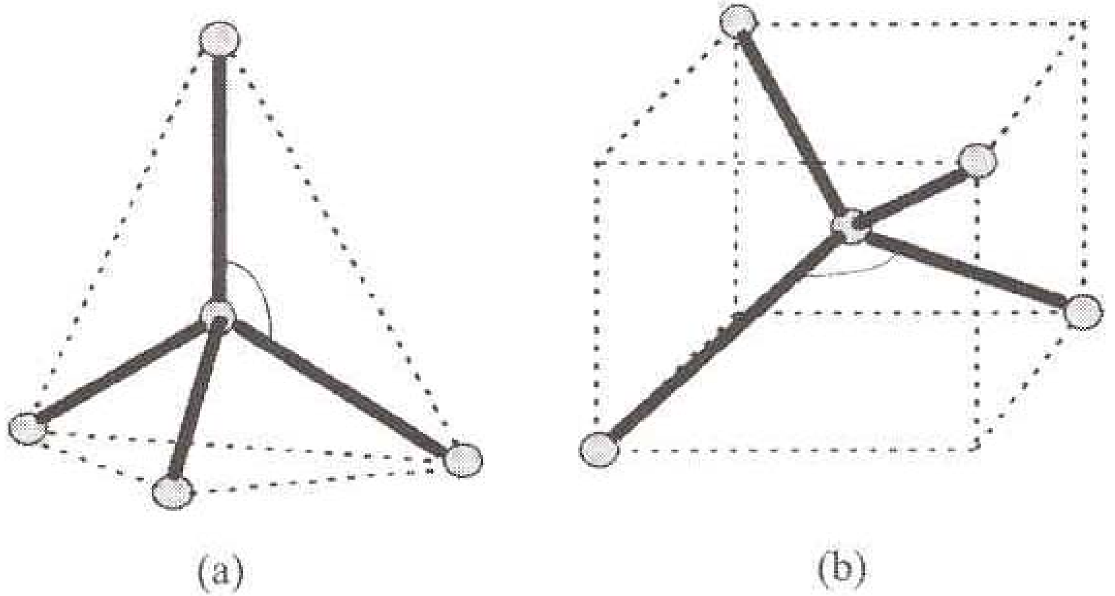


Fig. 3.2 Two ways of visualising the tetrahedral angle, (a) by means of a regular tetrahedron and (b) by means of a cube. The angles marked (and all similar angles) are equal to the tetrahedral angle, which is approximately 109.5°.

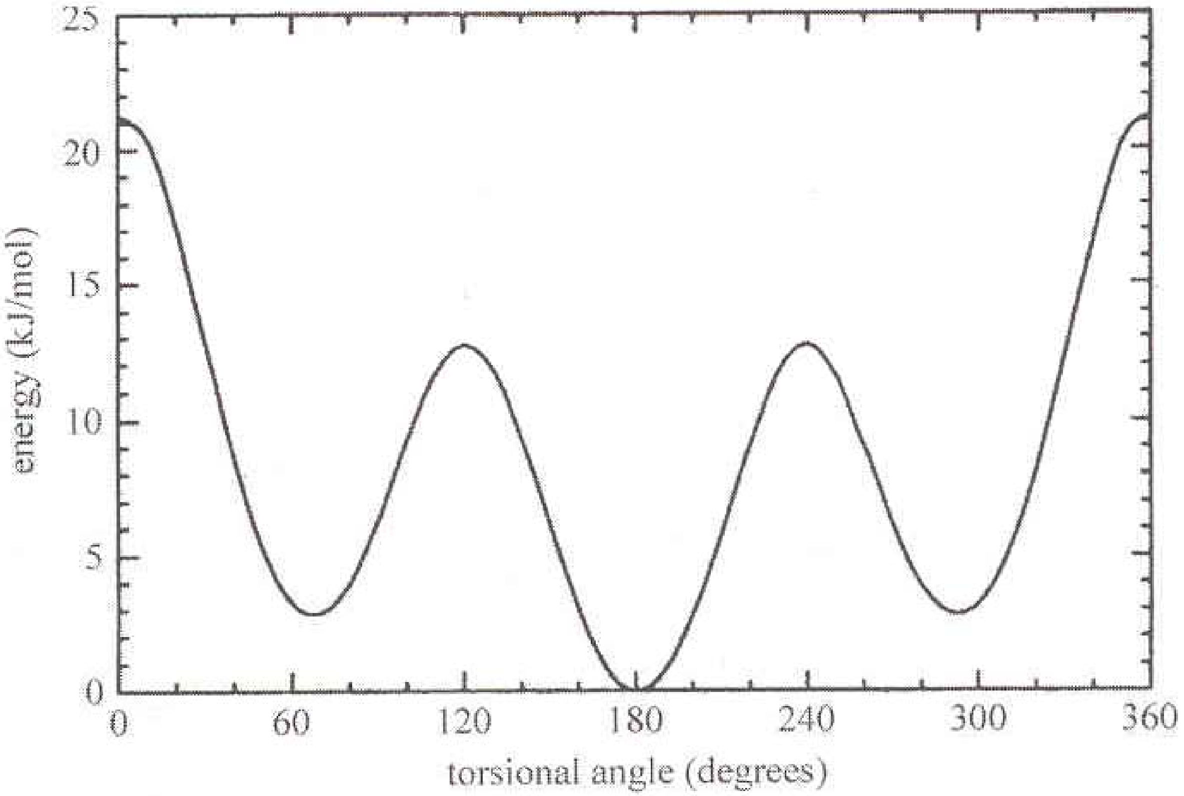
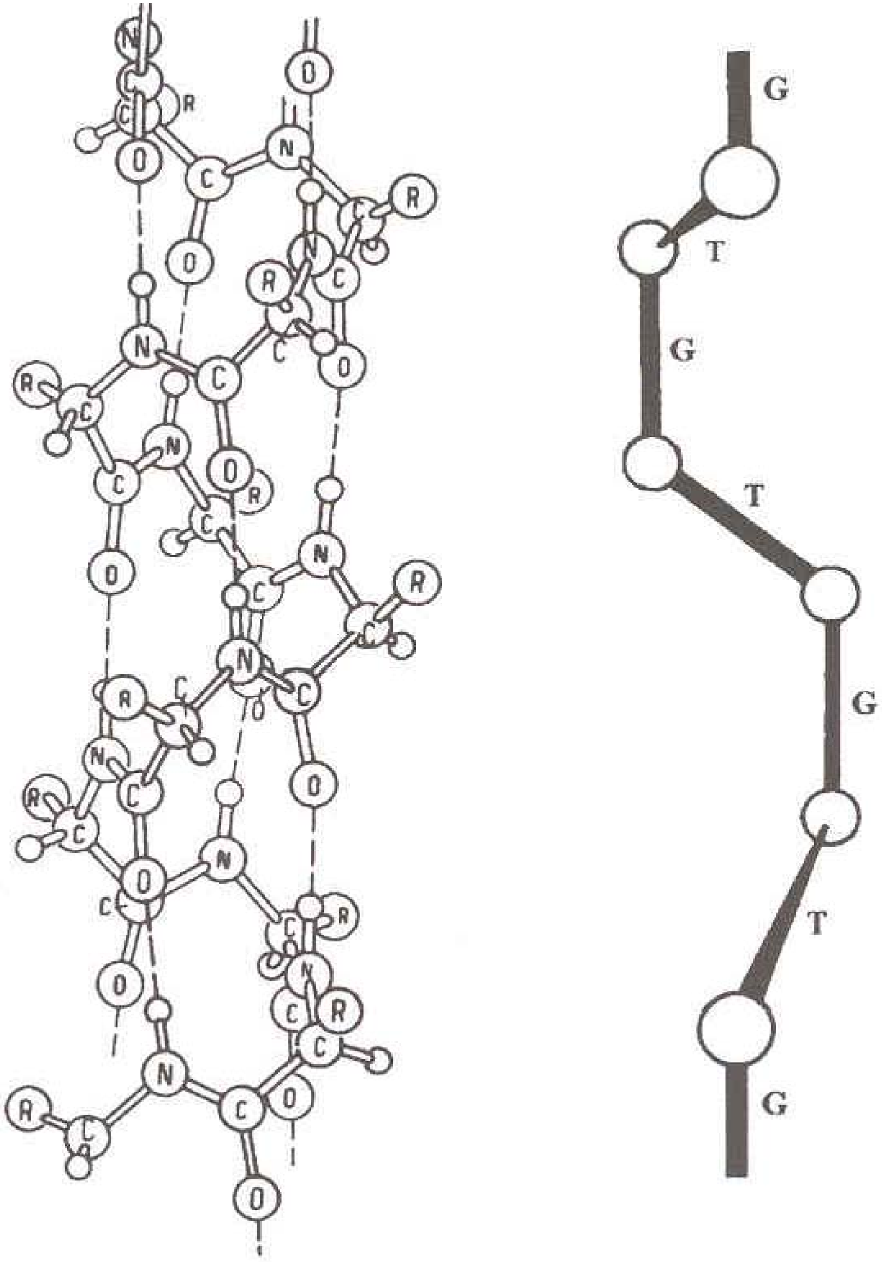


Fig. 3.4 The variation of the energy of the n-butane molecule $CH_3—CH_2—CH_2—CH_3$ as a function of the torsion angle of the central C—C bond measured from the *eclipsed* conformation. (Reproduced from *The Science of Polymer Molecules* by R. H. Boyd and P. J. Phillips. © Cambridge University Press 1993.)

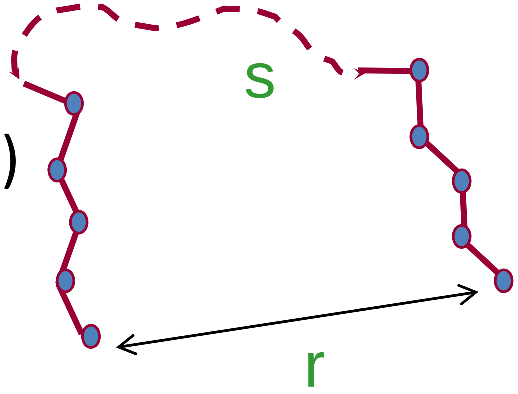


(a) (b)

Fig. 3.5 (a) The α-helix of a polypeptide, with intramolecular hydrogen bonds shown by dashed lines. (b) The carbon backbone of a 3_1 TGTGTG helix. ((a) Reproduced by permission of Springer-Verlag.)

Size of a chain

- end-to-end distance, r
  - $<r^2>^{½}$ ~ root-mean-square end-to-end distance
    - a measure of chain dimension
- radius of gyration, s
    - another measure of chain dimension
  - $<s^2>^{½}$ ~ root-mean-square end-to-end distance to the atoms from CM
- $<r^2>_{(0)} = 6 <s^2>_{(0)}$
    - for (infinitely) long chain (very large n)
    - in unperturbed state (0)



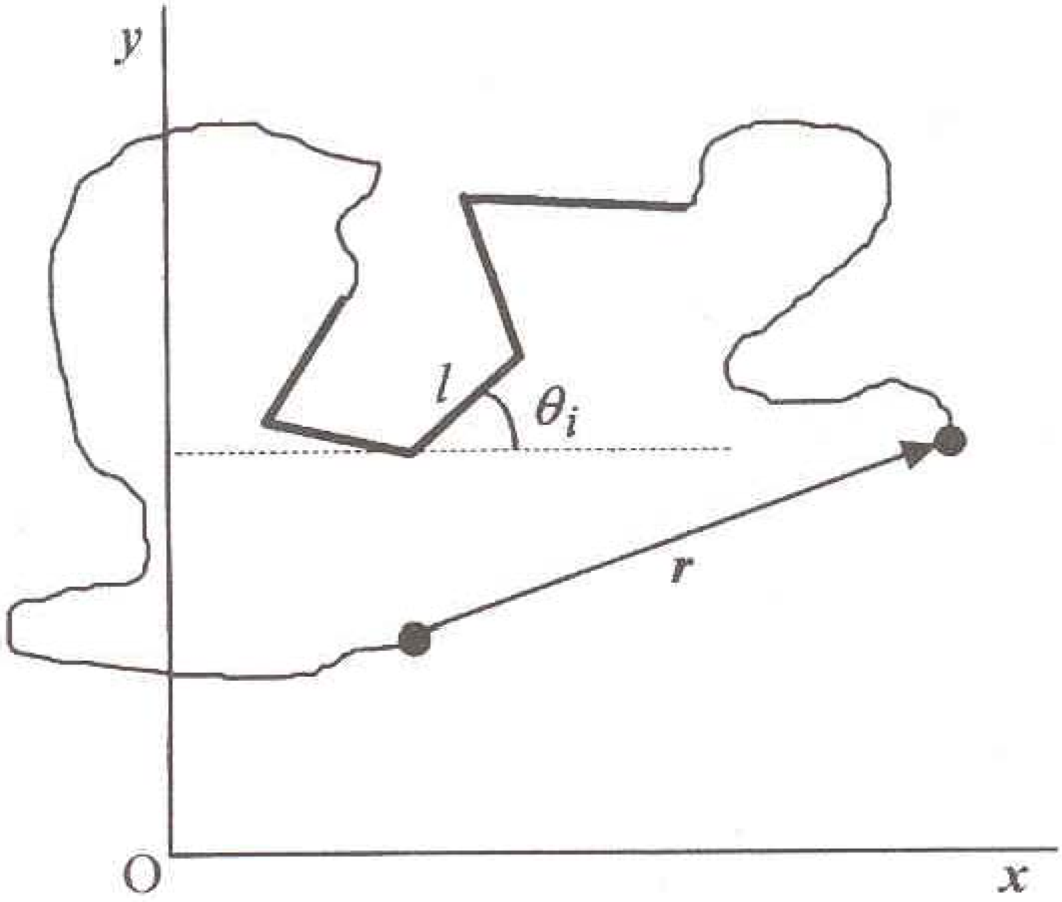


Fig. 3.6. Calculation of the RMS chain length. The thick lines represent five actual links somewhere in the chain, the rest of which is represented by the curved lines. The angle θ_i is the angle between the *i*th link and the O*x* axis.

RMS end-to-end distance

$$r_x = \sum_i l \cos\theta_i$$

$$r_x^2 = l^2\left(\sum_i \cos^2\theta_i + \sum_{i\neq j}\cos\theta_i\cos\theta_j\right)$$

$$\left\langle r_x^2\right\rangle = \left\langle r^2\right\rangle/3 = nl^2/3$$

$$\left\langle r^2\right\rangle = \left\langle r_x^2\right\rangle + \left\langle r_y^2\right\rangle + \left\langle r_z^2\right\rangle, \left\langle r_x^2\right\rangle = \left\langle r_y^2\right\rangle = \left\langle r_z^2\right\rangle$$

$$r_{rms} = \sqrt{\left\langle r^2\right\rangle} = \left\langle r_0^2\right\rangle^{1/2} = l\sqrt{n}$$

Parameters expressing chain characteristics

- characteristic ratio

$$\langle r^2 \rangle = nl^2 + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \bar{\mathbf{r}}_i \bar{\mathbf{r}}_j \rangle$$

$$\langle r^2 \rangle_0 = Cnl^2$$

  - $C_{(\infty)} = \langle r^2 \rangle_{(0)} / n\, l^2$ ~ definition
  - a measure of chain stiffness

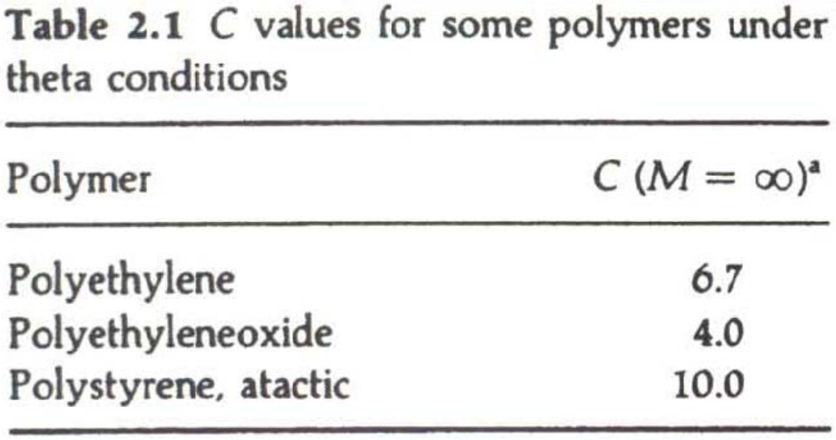


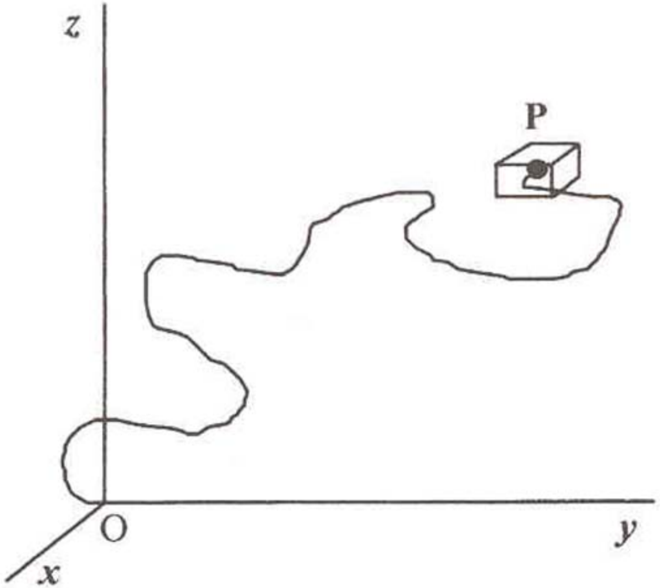
Table 2.1 *C* values for some polymers under theta conditions

Polymer	$C\ (M = \infty)^a$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Gaussian Chain

$$P(x,y,z)dxdydz = (b^3/\pi^{3/2})\exp(-b^2r^2)dxdydz$$

where $b^2 = 3/2nl^2$ and $r^2 = x^2 + y^2 + z^2$



$$P(r)dr = 4\pi r^2 p(r)dr = (b^3/\pi^{3/2})\exp(-b^2r^2)dr$$

$$P(br)dbr = (4/\pi^{1/2})(br)^2\exp(-(br)^2)d(br)$$

Distribution of r

Peak Max

$$r_{\max} = \frac{2}{3} r_{rms} = 1/b$$

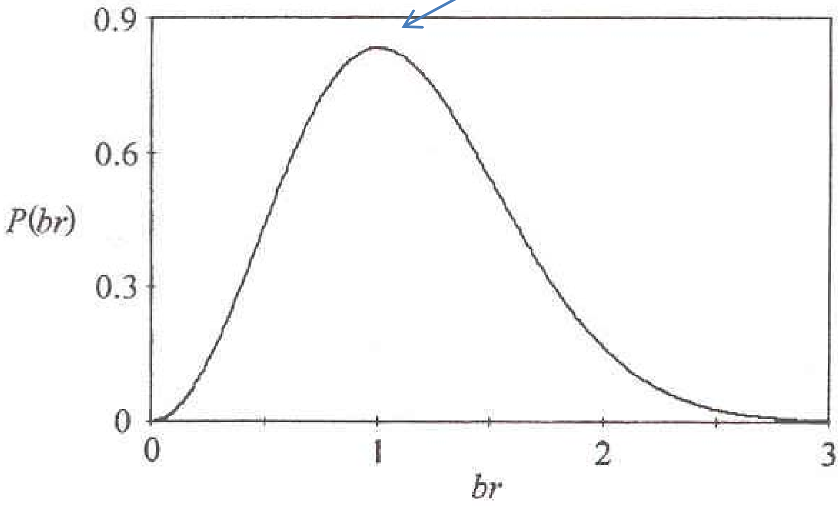
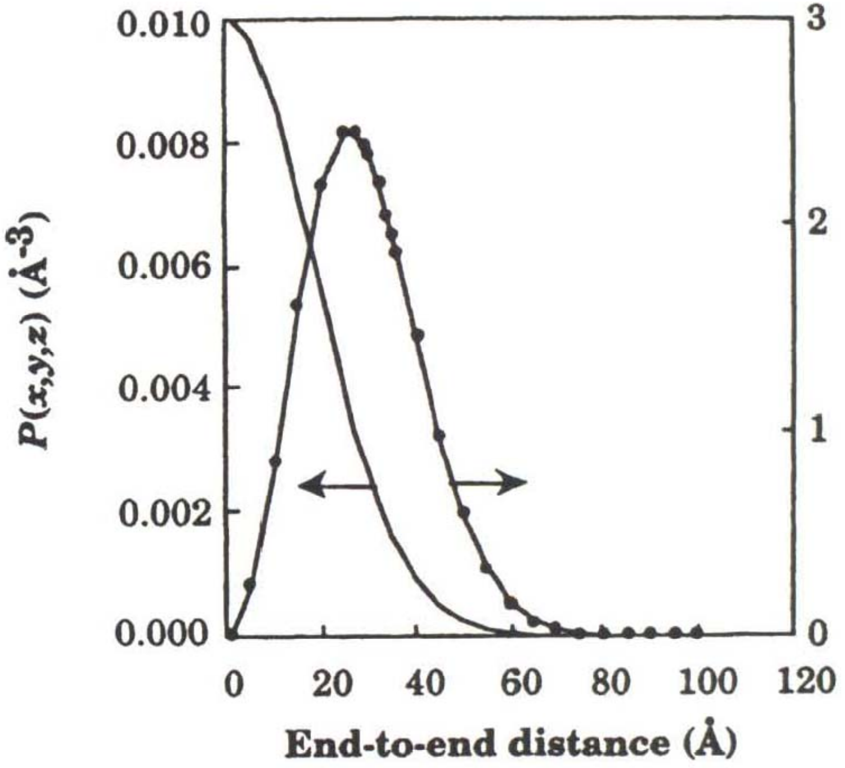
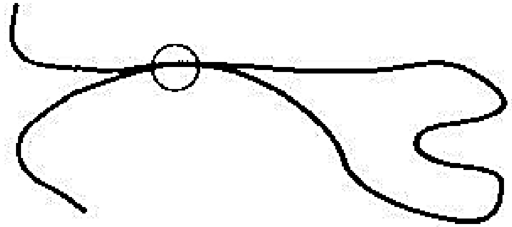
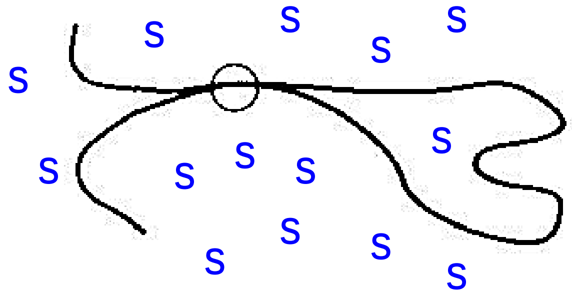


Fig. 3.8 The probability for a chain of length *r* in the Gaussian approximation. See the text for discussion.

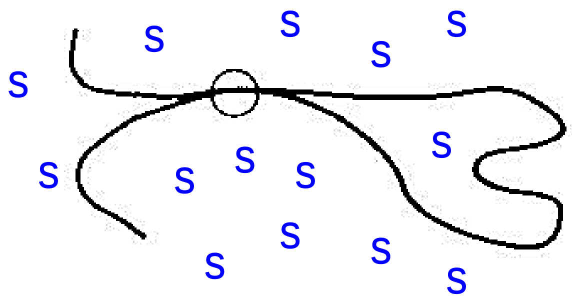


Excluded volume effect





- $<r^2>_{EV} = \alpha^2 <r^2>_{RIS}$
  - in good solvent
    - repulsion(polymer-polymer) > repulsion(polymer-solvent)
    - chain expands, $\alpha > 1$
    - by Flory-Krigbaum, $\alpha^5 - \alpha^3 = C\, n^{½}\, \psi\, (1 - \theta/T)$
      - » C ~ const, ψ ~ entropy factor, θ ~ theta temp
  - $\alpha^5 >> \alpha^3 \rightarrow \alpha \propto n^{0.1}$; $<r^2>_{RIS} = C_\infty\, n\, l^2$
  - $<r^2>^{½}_{EV} \propto n^{0.6}$



- $<r^2>_{EV} = \alpha^2 <r^2>_{RIS}$
  - in poor solvent
    - repulsion(polymer-polymer) < repulsion(polymer-solvent)
    - chain shrinks, $\alpha < 1$
  - in a condition between good and poor solvent
    - where $\alpha = 1$
    - repulsion(polymer-polymer) = repulsion(polymer-solvent)
    - chain neither expands nor shrinks
    - ‘phantom’ or ‘ghost’ chain
    - ‘theta (Θ) condition’
      - in a theta solvent/temperature
    - polymer is in ‘unperturbed state’
      - unperturbed by environment (solvent)
    - $<r^2>_{EV} = <r^2>_{RIS} = <r^2>_0$

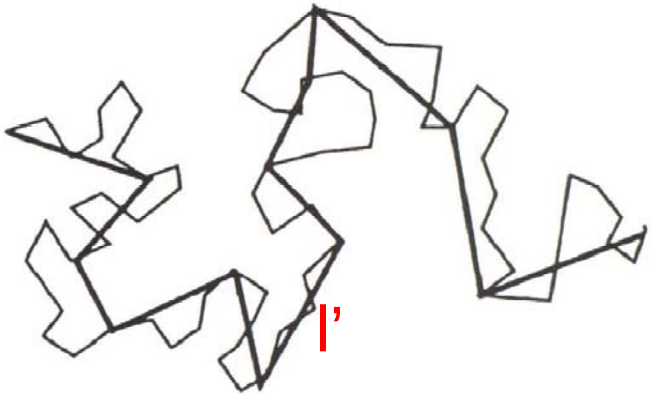
Real chain in bulk ~ ‘random coil’

- in bulk amorphous state
    - Chains are in unperturbed states.
    - $\langle r^2 \rangle = \langle r^2 \rangle_0 = r_q^2 = \langle r^2 \rangle_{RIS}$
    - proposed by Flory; proved by SANS exp’t
    - also in the melt state
    - also in the semicrystalline state (dimension)

Kuhn chain

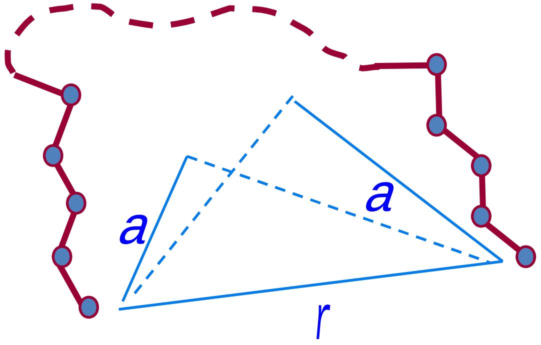
- Kuhn chain = statistical segment
  = (statistically) equivalent (freely jointed) chain
- Kuhn (chain) length, l’
  - $n' l'^2 = \langle r^2 \rangle_0 = r_\theta^{\,2} = C_\infty\, n\, l^2$
  - $n' l' = r_{max}$ (max or contour length) $= f\, nl$
  - $l' = r_\theta^{\,2} / r_{max} = (C_\infty / f)\, l$
  - a measure of axial correlation length

  - for PE
    - $C_\infty = 6.7$, $r_{max} = (\cos 35)\, n\, l = .83\, n\, l$
    - $l' = 8.2\, l$, $n' = 0.1\, n$



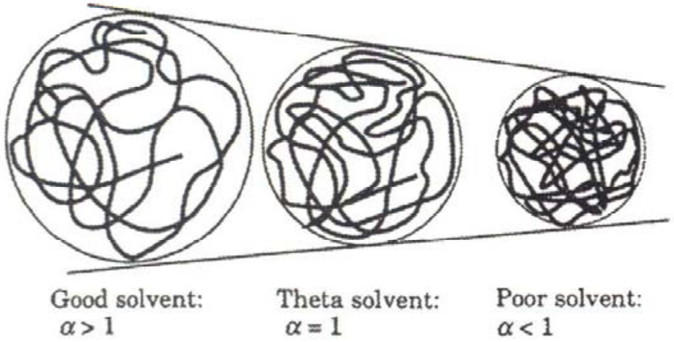
Persistence length

- Persistence length, *a*
  - average projection of r to a bond
  - length over the chain persists in one direction
  - a measure of axial correlation length also
  - $a = [(C_\infty + 1)/2]\, l$
  - for PE, $a \sim 4\, l$



Determ'n of chain dimension

- size depends on solvent
  - good or poor solvent
  - theta solvent (theta condition) ~ unperturbed state



- in dilute soln
  - viscometry
  - light scattering
- in conc. solution, melt, or solid state
  - SANS

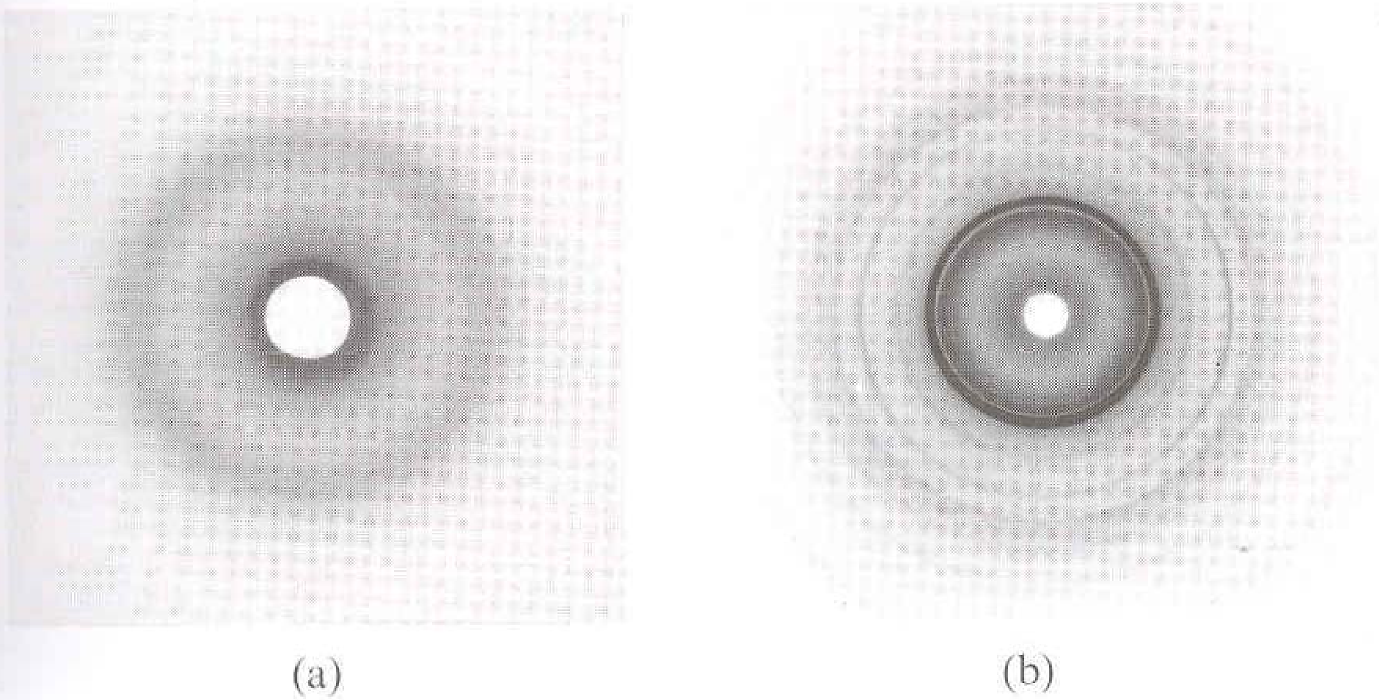


Fig. 3.9 Wide-angle X-ray scattering from (a) polystyrene, showing a diffuse halo from an amorphous sample; and (b) highly crystalline polyethylene, showing sharp 'powder' rings. (Courtesy of Dr A. P. Unwin.)

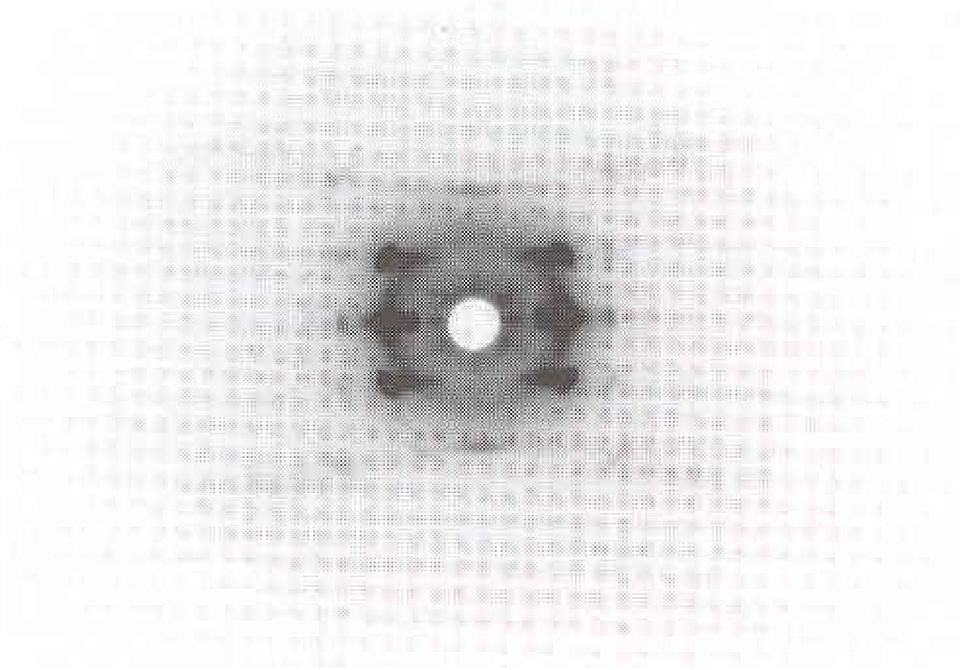


Fig. 3.10 A fibre pattern from oriented syndiotactic polypropylene, drawn to a draw ratio of about 5 at 109 °C. (Courtesy of Dr A. P. Unwin.)

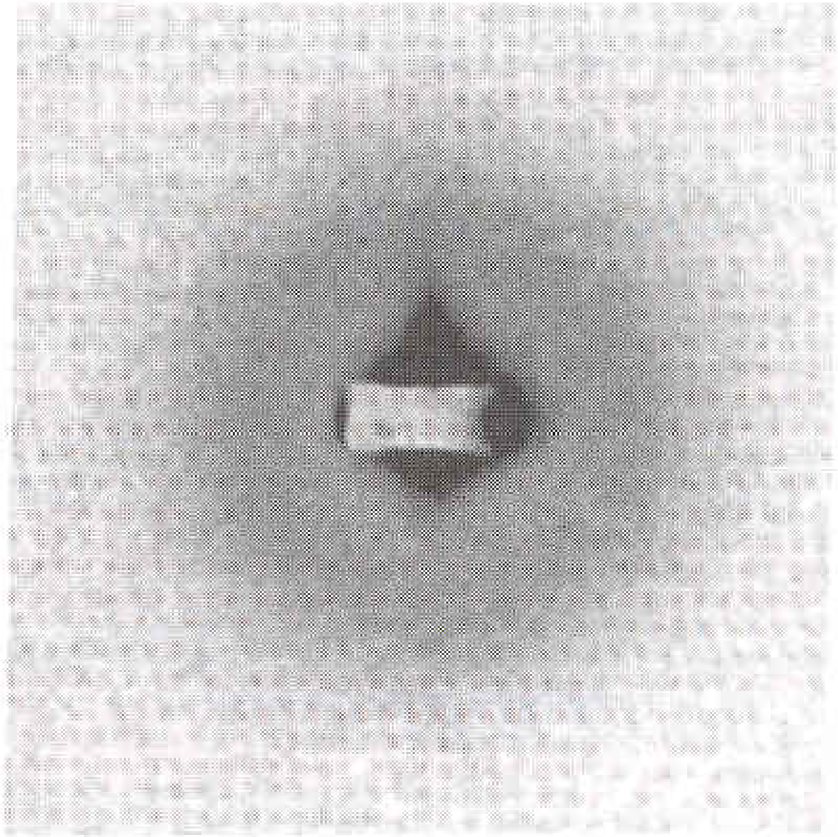


Fig. 3.11 Small-angle X-ray scattering from unoriented polypropylene. The SAXS scattering is the dark halo of diameter at its darkest equal to about half the side of the outer square. This diameter corresponds to about 1°. (Courtesy of Dr A. P. Unwin.)

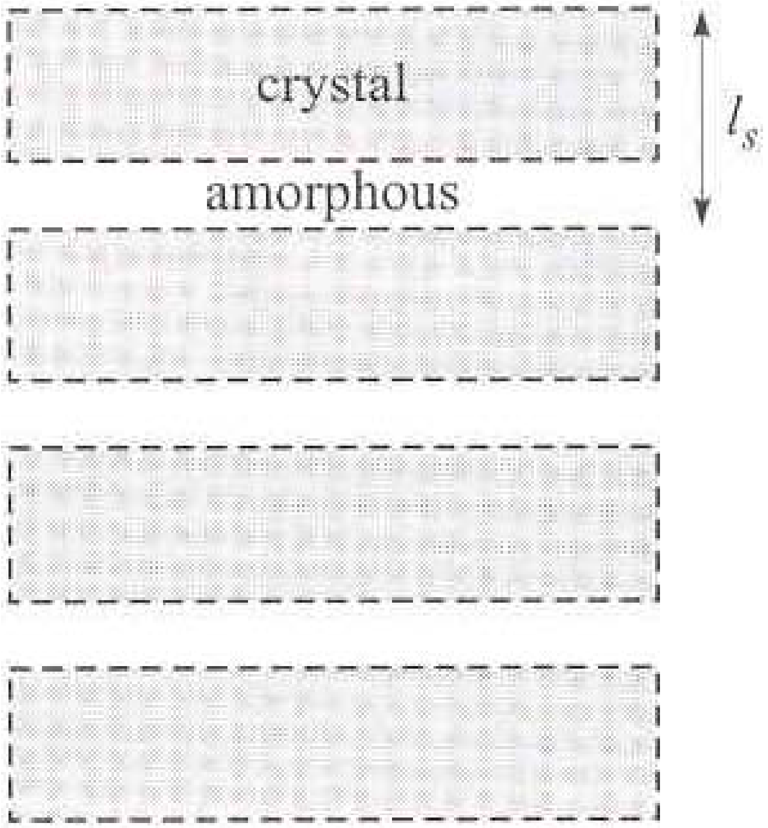


Fig. 3.12 A stack of crystal lamellae, shown schematically. The separation l_s determined by X-ray scattering is the repeat distance shown.

Fig. 3.13 An optical micrograph of spherulites of poly(propylene terephthalate) grown from the melt. (Courtesy of Dr M. A. Wilding.)