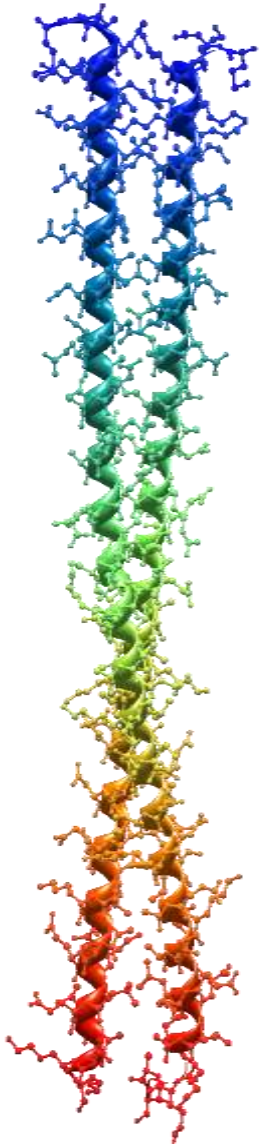


Struktura polimerów i biopolimerów (2)



Andrzej Koliński

Pracownia Teorii Biopolimerów
Wydział Chemii, Uniwersytet Warszawski

kolinski@chem.uw.edu.pl

<http://www.biocomp.chem.uw.edu.pl>

Podsumowanie poprzedniego wykładu

LITERATURA UZUPEŁNIJĄCA (do chemii polimerów):

1. M.P.Stevens, Wprowadzenie do chemii polimerów, PWN, Warszawa 1983
2. Z.Florjańczyk, S.Penczek, (red.) Chemia polimerów, tom 1, Makrocząsteczki i metody ich otrzymywania, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1995
3. Z.Florjańczyk, S.Penczek, (red.) Chemia polimerów, tom 2, Podstawowe polimery syntetyczne i ich zastosowania, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 1997

PODZIAŁ PROCESÓW POLIMERYZACJI

Staudinger (polireakcje)

- Polimeryzacja (łańcuchowa)
- Polikondensacja (stopniowa)
- Poliaddycja (stopniowa)

Flory (podział ze względu na stechiometrię)

- Polimeryzacja addycyjna (poliaddycja) łańcuchowa lub stopniowa
- Polimeryzacja kondensacyjna (polikondensacja) stopniowa

IUPAC, PTChem

- Polimeryzacja łańcuchowa (łańcuchowa)
- Polimeryzacja addycyjna (poliaddycja) stopniowa
- Polimeryzacja kondensacyjna (polikondensacja) stopniowa

POLIMERYZACJA MONOMERÓW Z WIĄZANIEM PODWÓJNYM - Polimeryzacja łańcuchowa

Inicjowanie

$I \rightarrow I^*$ (wytworzenie centrum aktywnego)

* = . polimeryzacja wolnorodnikowa (rodnikowa)

* = + polimeryzacja jonowa kationowa

* = - polimeryzacja jonowa anionowa

Propagacja (wzrost)

$I-CH_2-CHR^* + CH_2=CHR \rightarrow I-CH_2-CHR-CH_2-CHR^*$

$I-CH_2-CHR-CH_2-CHR^* + CH_2=CHR \rightarrow I-(CH_2-CHR)_2-CH_2-CHR^*$

$I-(CH_2-CHR)_2-CH_2-CHR^* + CH_2=CHR \rightarrow I-(CH_2-CHR)_3-CH_2-CHR^*$

I tak dalej.....

Zakańczanie (terminacja) w polimeryzacji rodnikowej

Rekombinacja

$I-(CH_2-CHR)_n-CH_2-CHR^* + ^*CHR-CH_2-(CH_2-CHR)_m \rightarrow I-(CH_2-CHR)_{n+m+2}-I$

Dysproporcjonowanie

$I-(CH_2-CHR)_n-CH_2-CHR^* + ^*CHR-CH_2-(CH_2-CHR)_m \rightarrow$

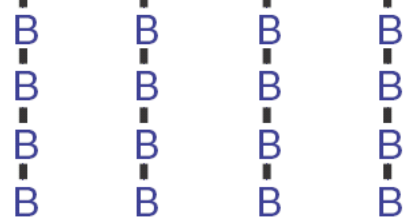
$I-(CH_2-CHR)_n-CH=CHR + CH_2R-CH_2-(CH_2-CHR)_m \rightarrow$

I inne reakcje....

A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A

A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B

A-A-A-A-A-A-A-A-A-A-A-A-A-A

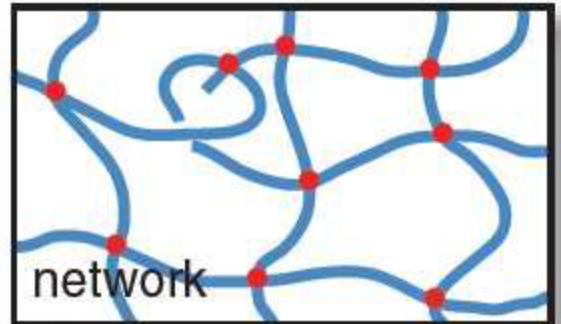
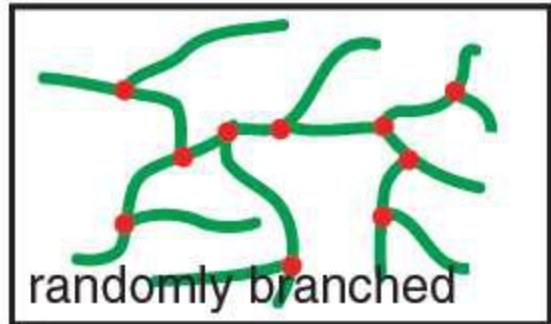
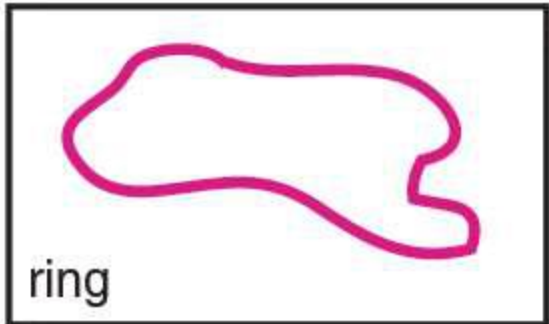
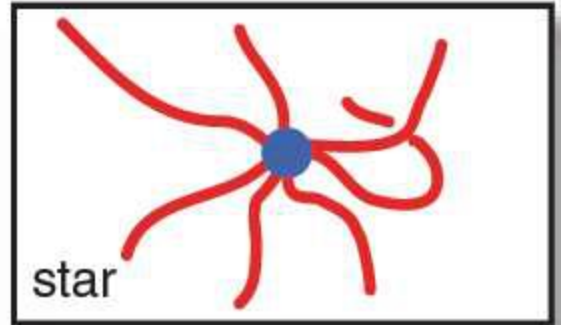
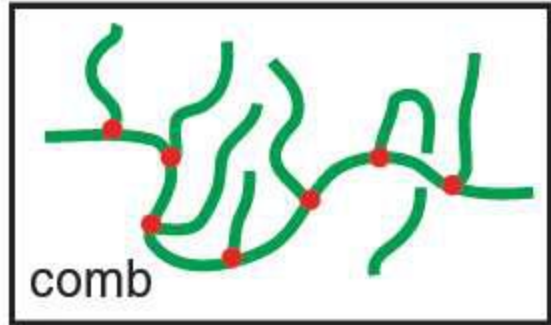


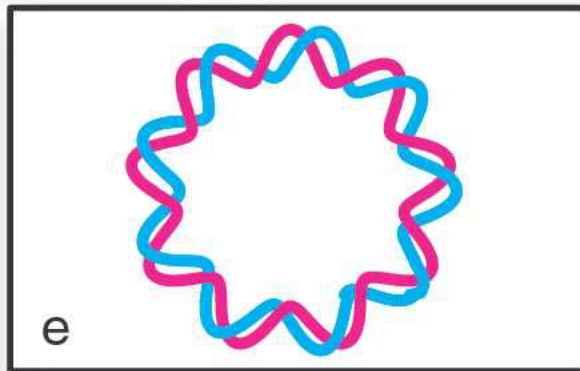
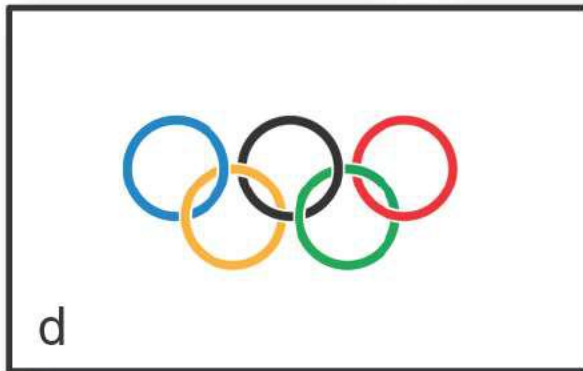
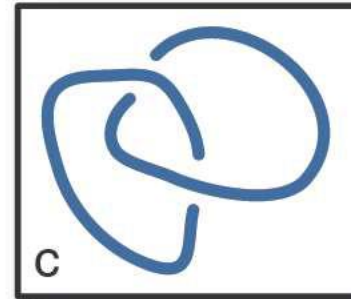
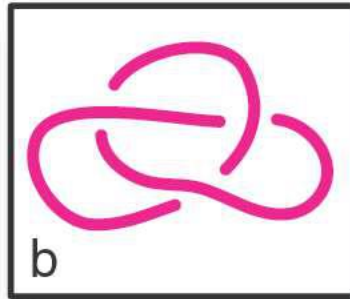
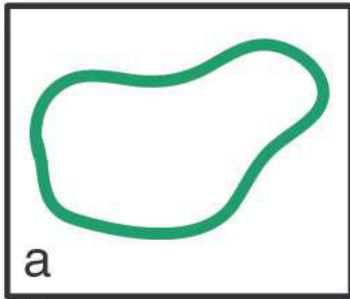
A-A-A-B-B-A-B-B-B-B-A-B-A-A-B-A

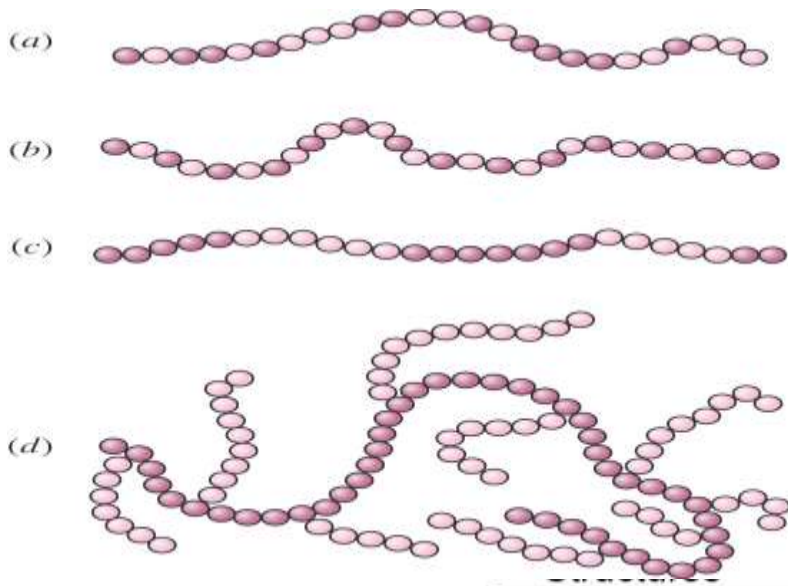
A-A-A-A-A-A-A-B-B-B-B-B-B-B-B

A-A-A-A-B-B-B-B-B-B-B-A-A-A-A



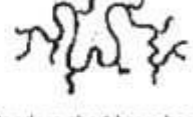
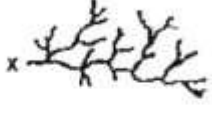

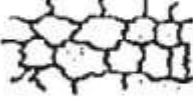
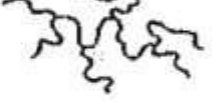
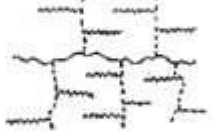







A-A-A-B-B-A-A-A-B-B-A-A-A-B-B-A-A-A-B-B



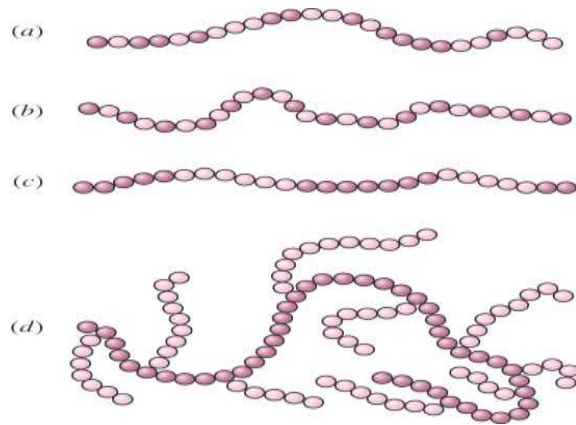




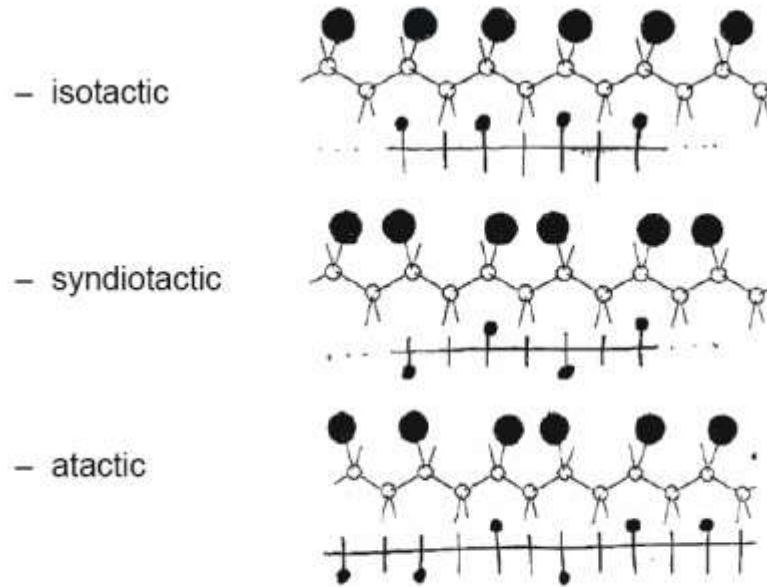
Roźnorodność sekwencyjno-strukturalna

Linear	Cross-linked	Branched	Dendritic
			
Flexible coil	Lightly cross-linked	Random short branches	Random hyperbranched
			
Rod	Densely cross-linked	Random long branches	Controlled hyperbranched
			
Cyclic	Interpenetrating networks	Regular comb	Dendron
			
Polyrotaxane		Regular star	Dendrimer
1930's -	1940's -	1960's -	1980's -

Rożnorodność sekwencyjno-strukturalna

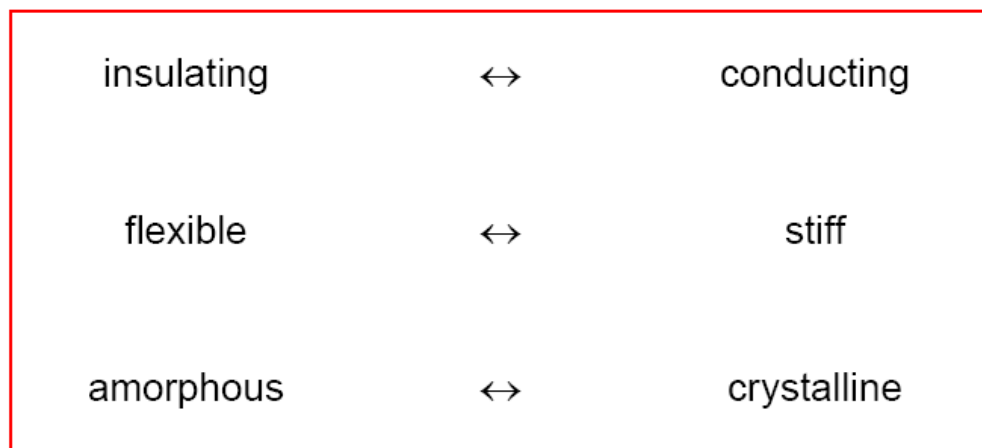


- Tacticity = stereochemical handedness

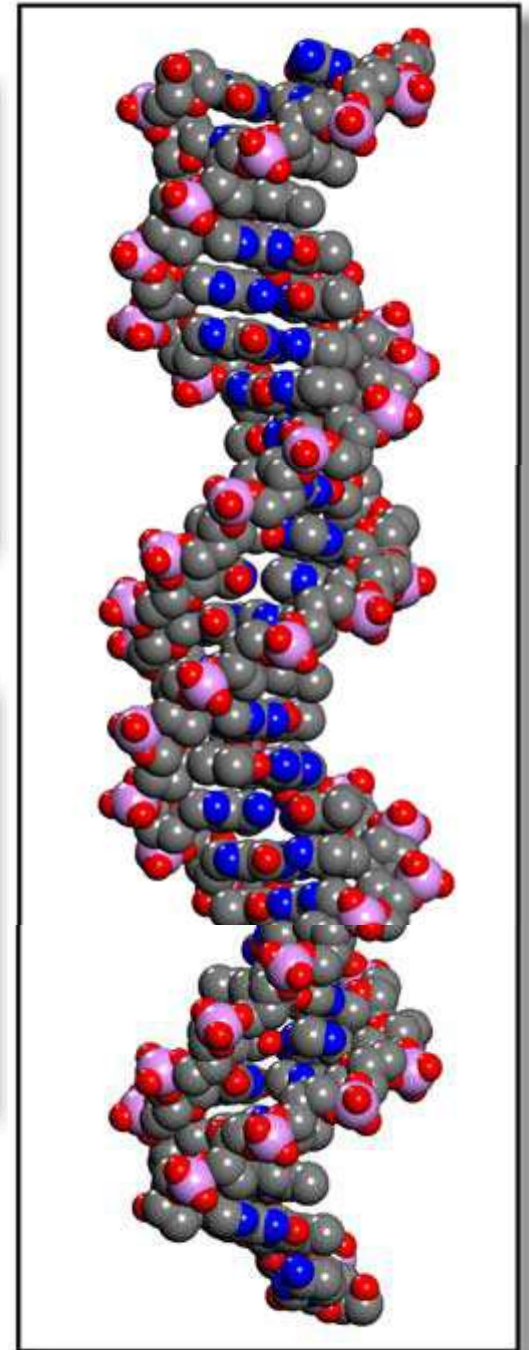
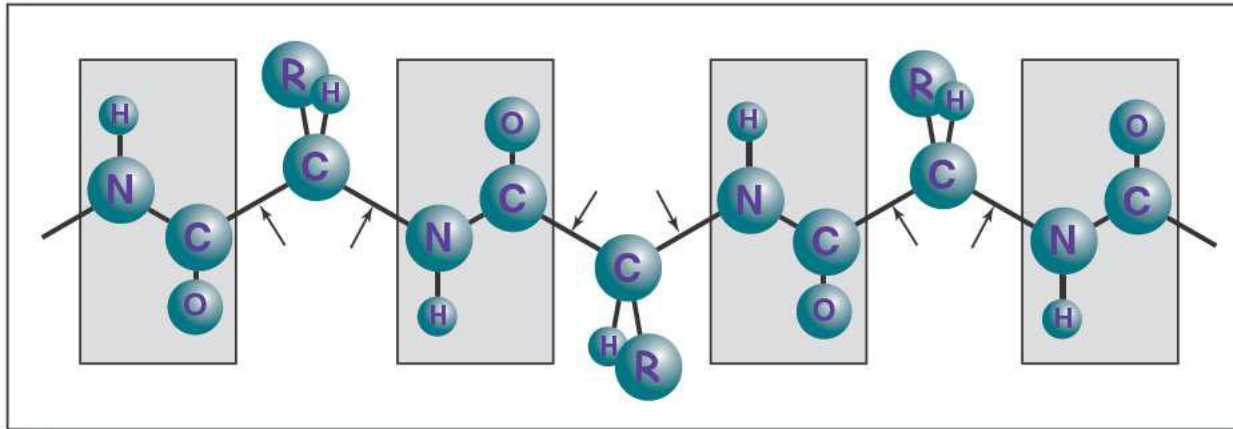
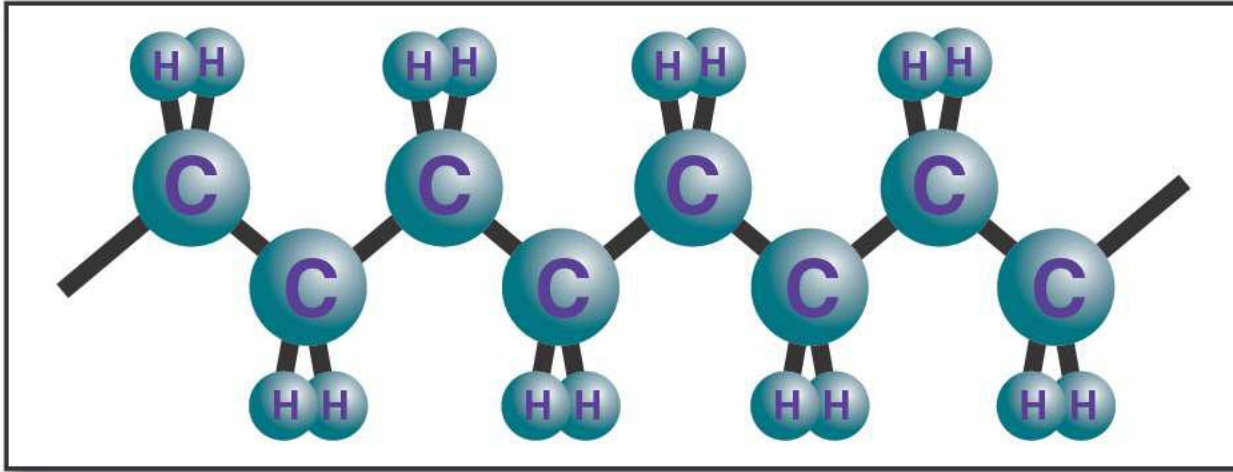


Introduction

- Enormous range of physical properties



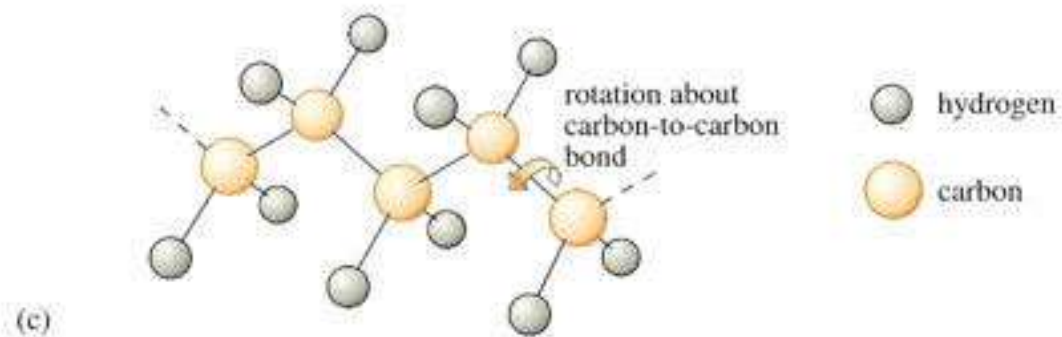
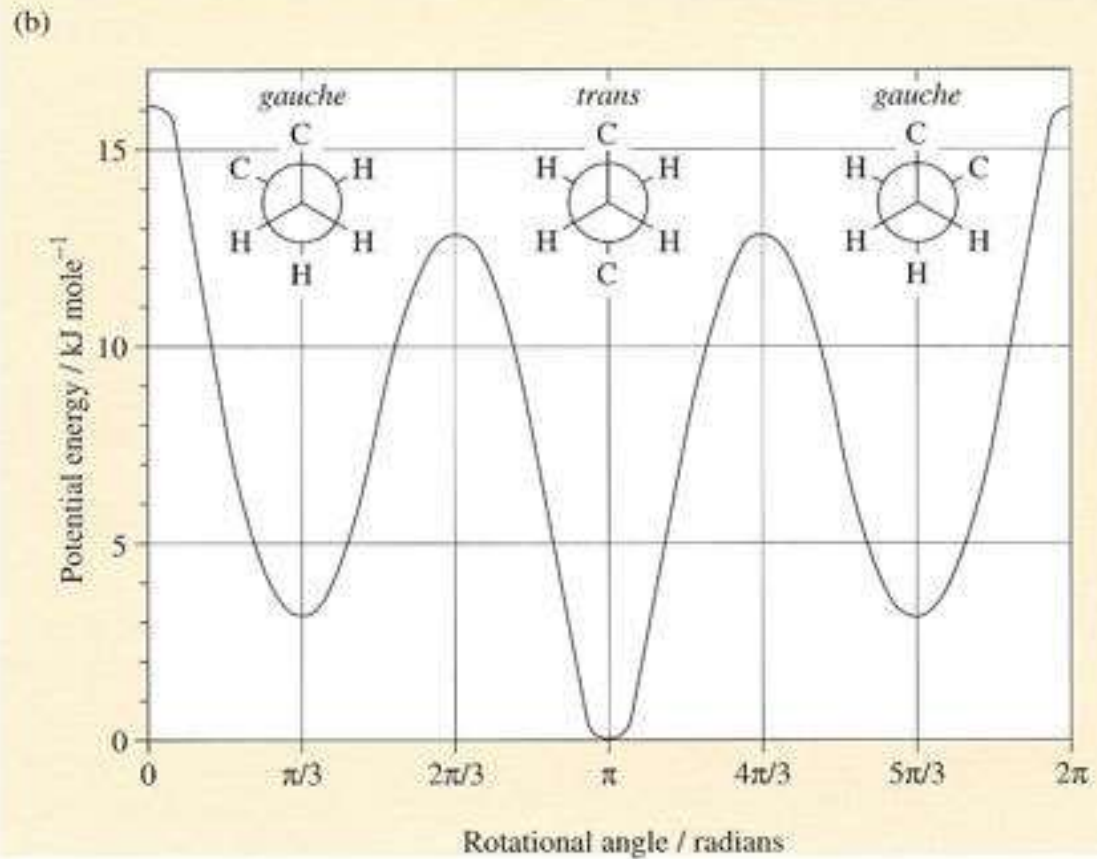
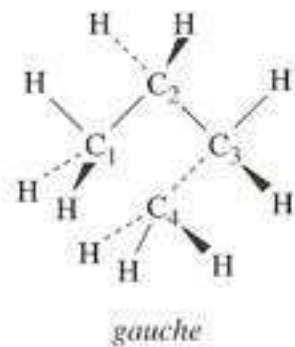
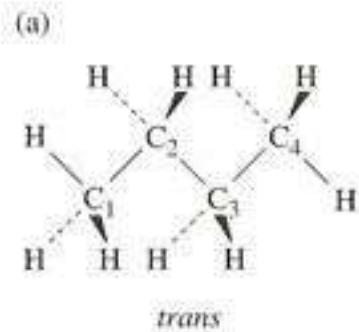
- Tunable properties: weak interactions easily altered



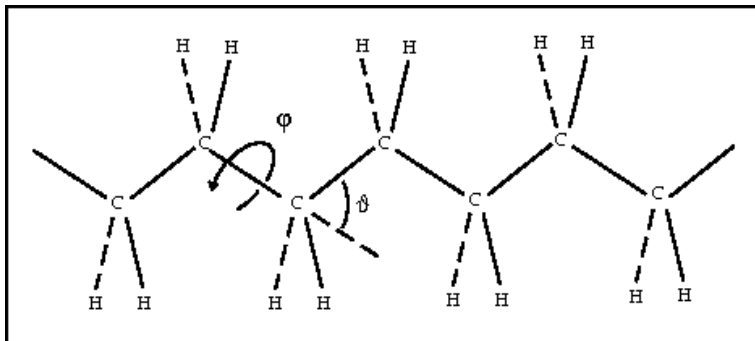
Conformational statistics of chain molecules



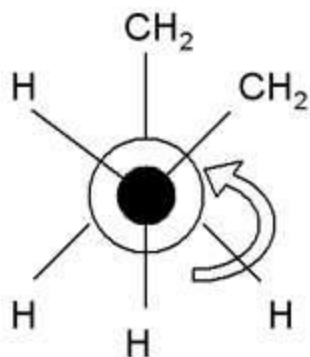
Paul Flory



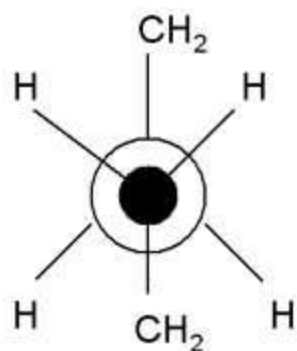
Bond rotations and chain flexibility



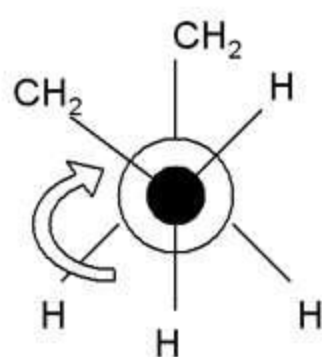
$$\Omega = 3^N$$



Gauche(-)



Trans



Gauche(+)

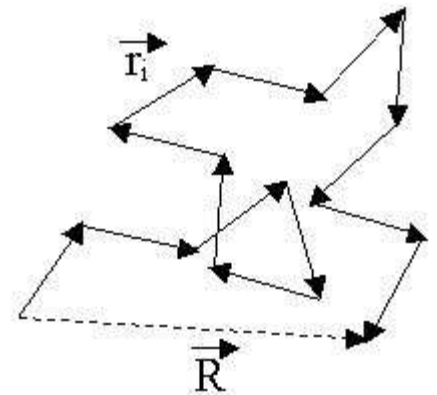
Ideal Polymer Coil (Freely jointed chain)

- n segments of equal length L
- Unrestricted (and uncorrelated) angles

$$\begin{aligned}\langle R^2 \rangle &= \langle (\sum \mathbf{r}_i)^2 \rangle \\ &= \langle \sum \mathbf{r}_i^2 + \sum \mathbf{r}_i \mathbf{r}_j \rangle = L^2 n\end{aligned}$$

$$\langle S^2 \rangle = \langle R^2 \rangle / 6$$

$$\text{Def: } \langle S^2 \rangle = n^{-1} \sum (\mathbf{w}_{\text{CM}} - \mathbf{w}_i)^2$$



Ideal Polymer Coil



Random walk distribution for ideal polymer chain:

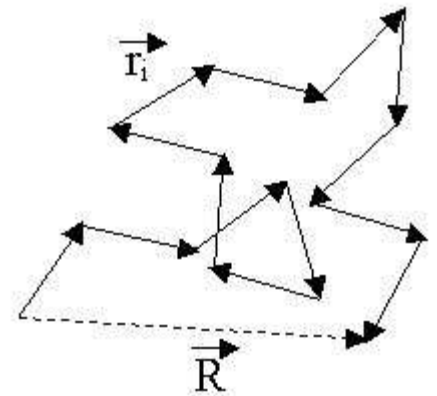
$$P_n(R) = [3/2\pi nL^2]^{3/2} \exp(-3R^2/2nL^2)$$

L = Kuhn length, n = # Kuhn steps, R = end-end vector

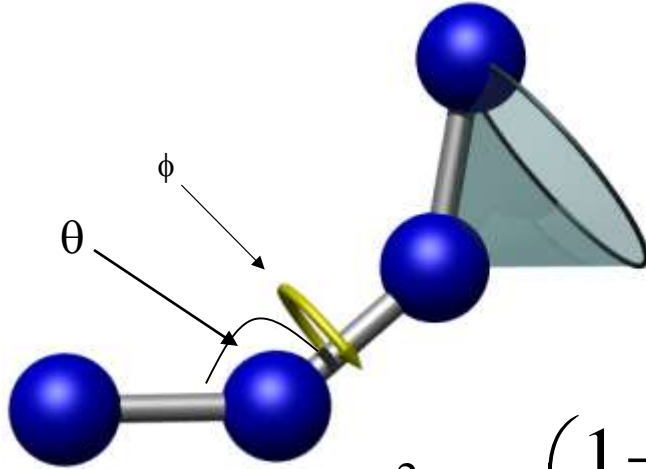
RMS end-to-end distance for ideal polymer chain:

$$\langle R^2 \rangle \sim L^2 n$$

(Einstein- Smoluchowski Brownian motion $\langle r^2 \rangle \sim 6D t$)



Ideal Chain: *angle restrictions*



$$\langle R^2 \rangle = \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + \cos \langle \phi \rangle}{1 - \cos \langle \phi \rangle} \right) N b^2 = N b_{eff}^2$$

In general we can write:

Involving the lattice details has no effect on the scaling behavior.

$$\langle R^2 \rangle = C_{\infty} N b^2 = N b_{eff}^2$$

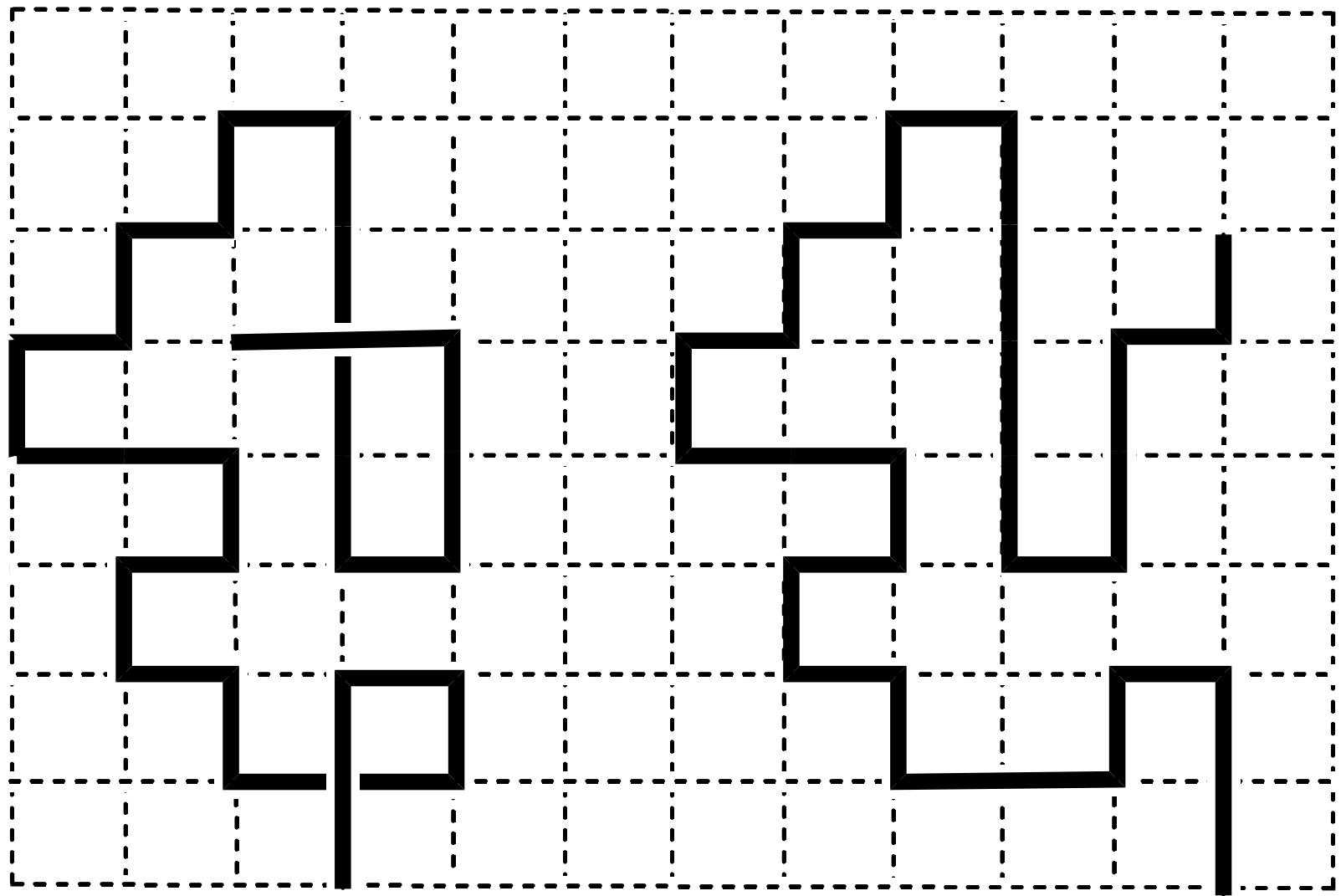
Where C_{∞} is the polymer stiffness

Ideal Chains

- Freely jointed chain
- Chain with constant bond angle
- Chain with flexible bond length
- Chains on lattices (random walk on a lattice)
-
- Manhattan random walking (forget Broadway)
- Particle Brownian motion (self diffusion)
-

Always for large n : $\langle R^2 \rangle \sim n$ and $\langle S^2 \rangle = \langle R^2 \rangle / 6$
and Gaussian distribution of segment density

Ideal chains are analytically tractable (Markov process)

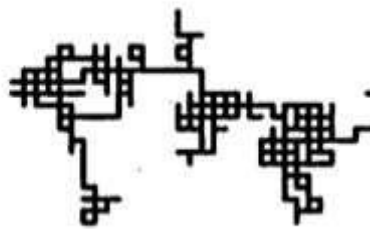


Visualisation of the Self-Avoiding Walk

2-D Random walks



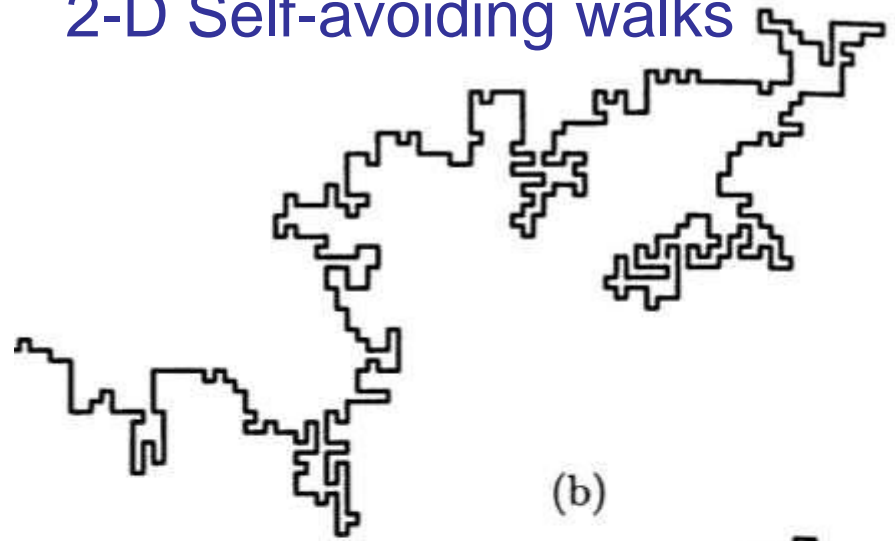
(a)



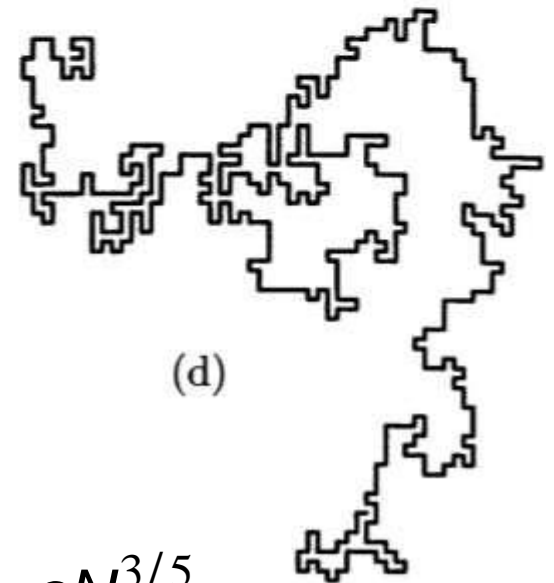
(c)

$$\langle R^2 \rangle^{1/2} = aN^{1/2}$$

2-D Self-avoiding walks



(b)



(d)

$$\langle R^2 \rangle^{1/2} = aN^{3/5}$$

Real Polymer Coil

- Excluded volume effect (collisions): repulsion at small distances

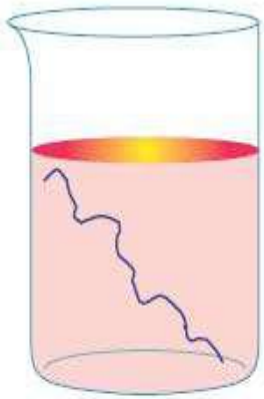
RMS end-to-end distance for self-avoiding random walk:

$$\langle R^2 \rangle^{1/2} \sim n^{6/5}$$

- Solvent effects: balance of repulsive effects and attractive effects (entropic elasticity)

$$F = U_{\text{rep}} - TS$$

- We can immediately see how temperature is involved in 'solvent quality' (affinity of the polymer for the solvent).

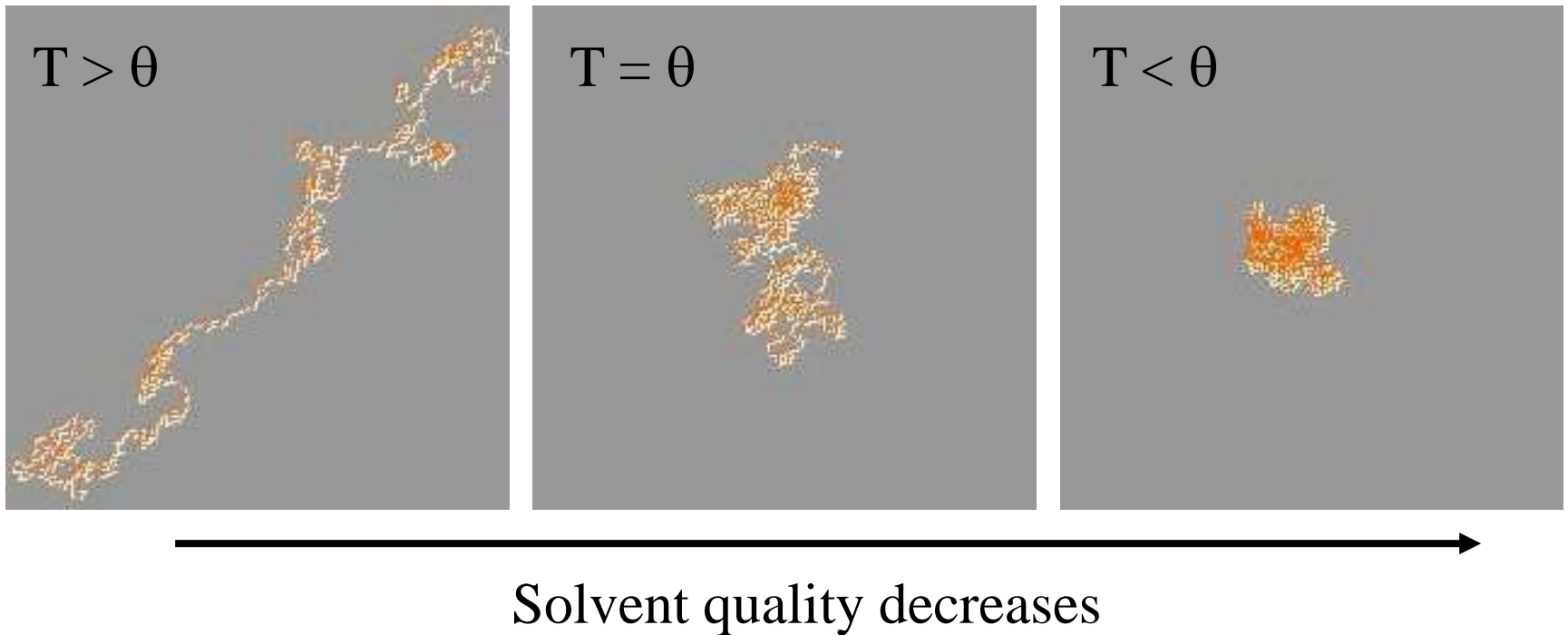


Environment change



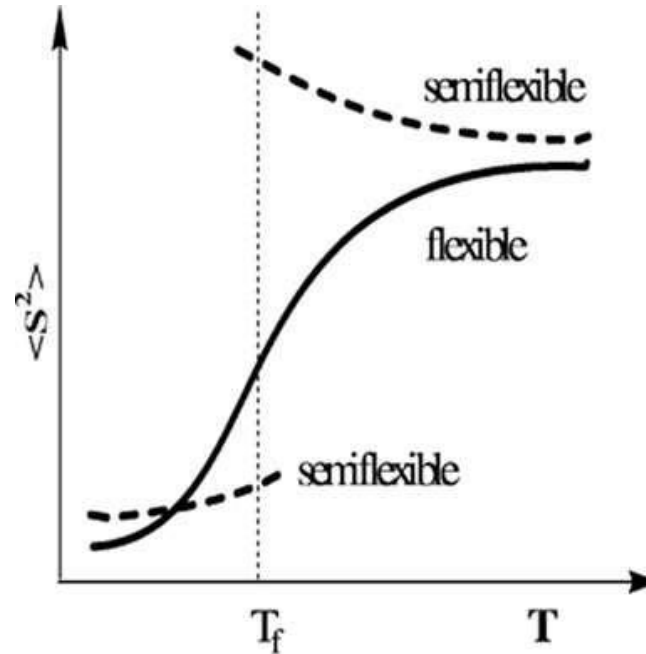
Solvent Effects: Coil-Globule

- In 'good solvent', polymer interacts with solvent.
- In 'bad solvent', polymer prefers to interact with self.
- At θ point, polymer acts ideal.



Images from: "Giant Molecules" software (Grosberg).

Flory's theory of polymer chain in dilute solution



$$\alpha^2 = \langle R^2 \rangle / \langle R^2_0 \rangle$$

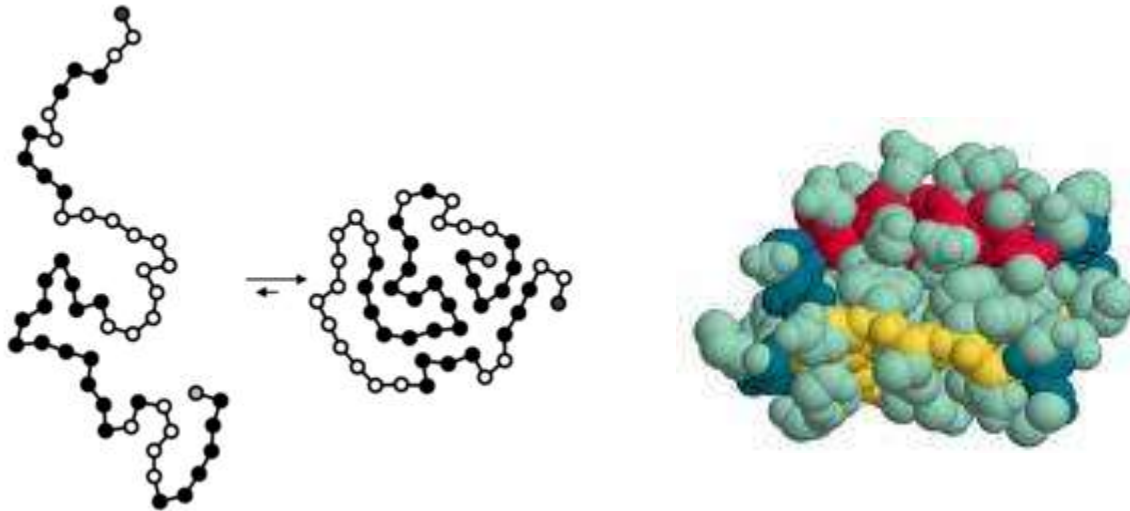
$$\alpha^5 - \alpha^3 = \text{const.} (1 - \Theta/T) n^{1/2}$$

$$\langle R^2 \rangle^{1/2} = aN^{3/5}$$

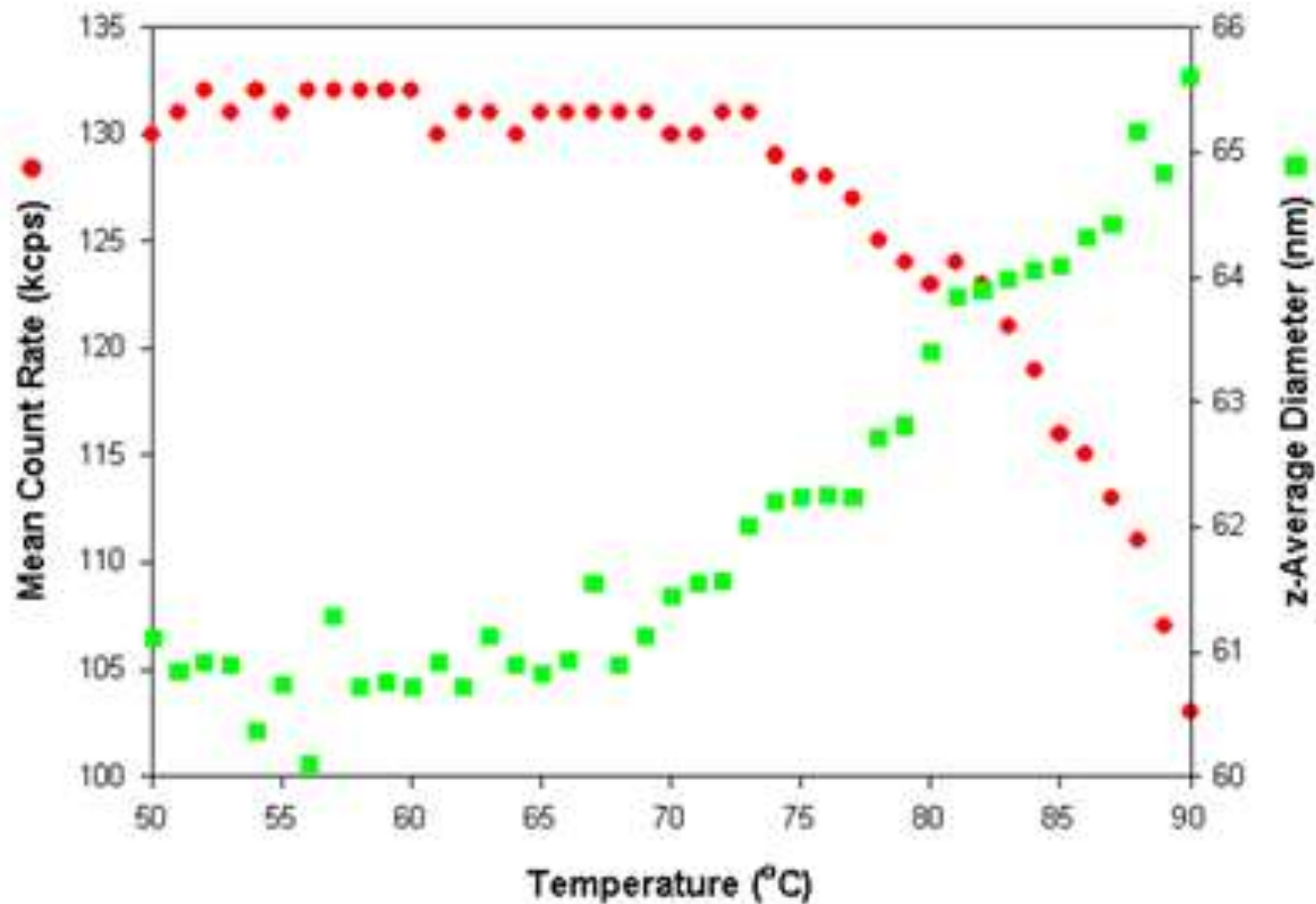
$$\langle R^2 \rangle^{1/2} = aN^{1/2}$$

$$\langle R^2 \rangle^{1/2} = aN^{1/3}$$

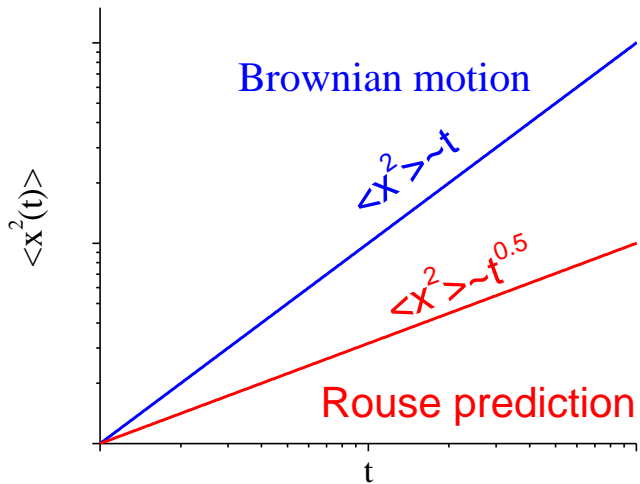
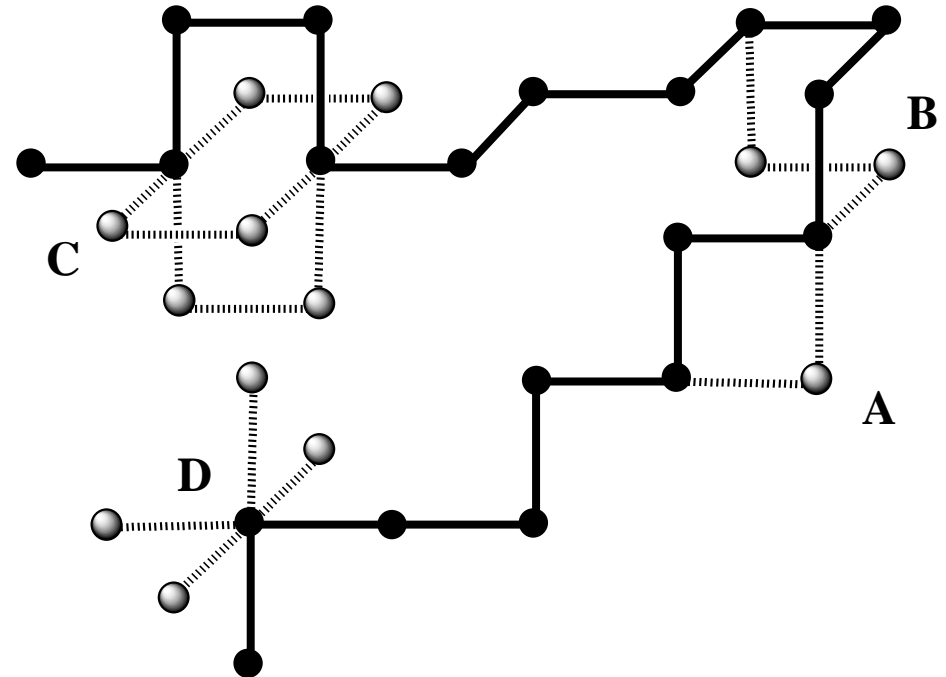
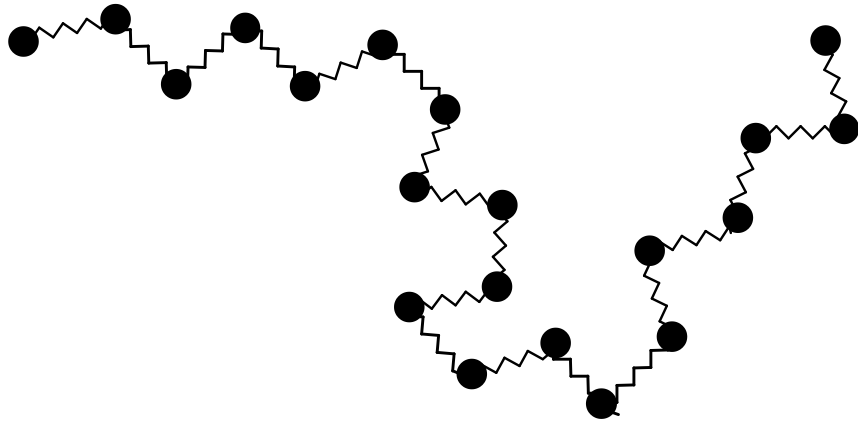
Protein Folding



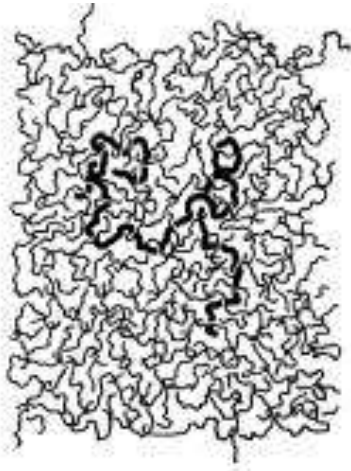
Light scattering measurement of a polymer coil-globule transition



Polymer dynamics – Rouse chain and Verdier-Stockmayer chain



Polymer solutions and melts

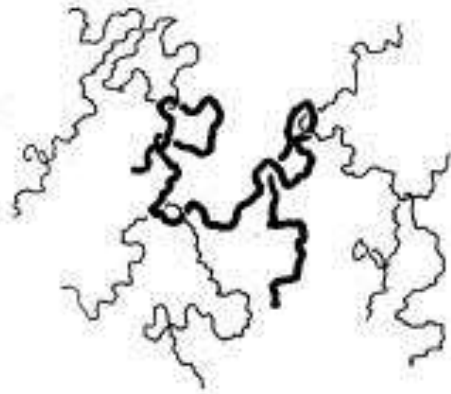


melt

$$\phi = 1$$



semi-crystalline solid



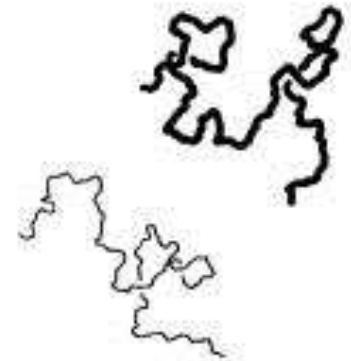
semi-dilute solution

$$\phi \approx \phi_{\text{overlap}}^*$$

$$\approx |\eta|^{-1}$$



gel



dilute solution

$$\phi < \phi^*$$



single crystal
dispersion

