Methane: CH_4

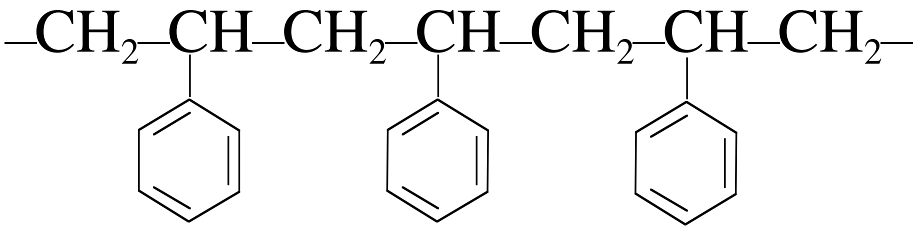
Ethane: $CH_3{-}CH_3$

Propane: $CH_3{-}CH_2{-}CH_3$

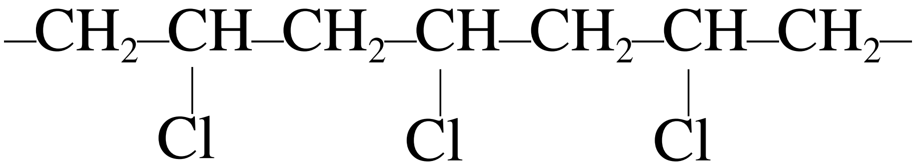
Polyethylene: ${-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}$

A polymer chain is a sequence of chemical repeating units (called monomers) connected by covalent bonds

Polystyrene



Polyvinychloride:



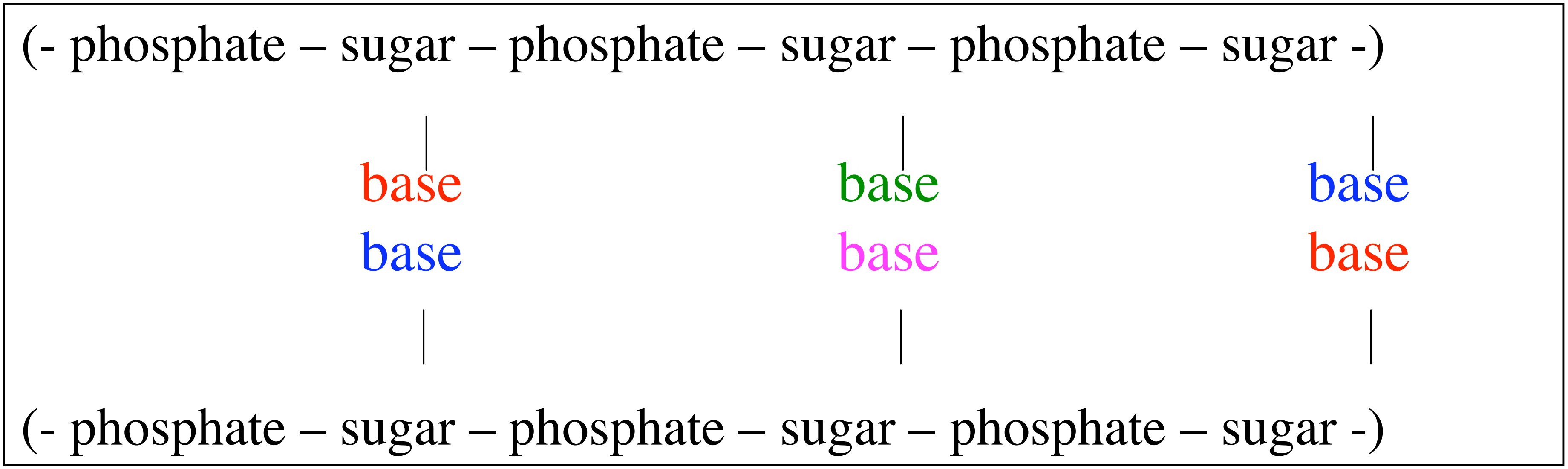
$$-CH_2-\underset{|\atop Cl}{CH}-CH_2-\underset{|\atop Cl}{CH}-CH_2-\underset{|\atop Cl}{CH}-CH_2-$$

$N=2$ “dimer”

$10^2<N<10^4$ “small polymer”

$N\sim10^{10}$ “the limit”

What polymer is this? It has N = 10^9!



(- phosphate – sugar – phosphate – sugar – phosphate – sugar -)

base base base

base base base

(- phosphate – sugar – phosphate – sugar – phosphate – sugar -)

4 different monomers, each containing a base

Adenine (A)

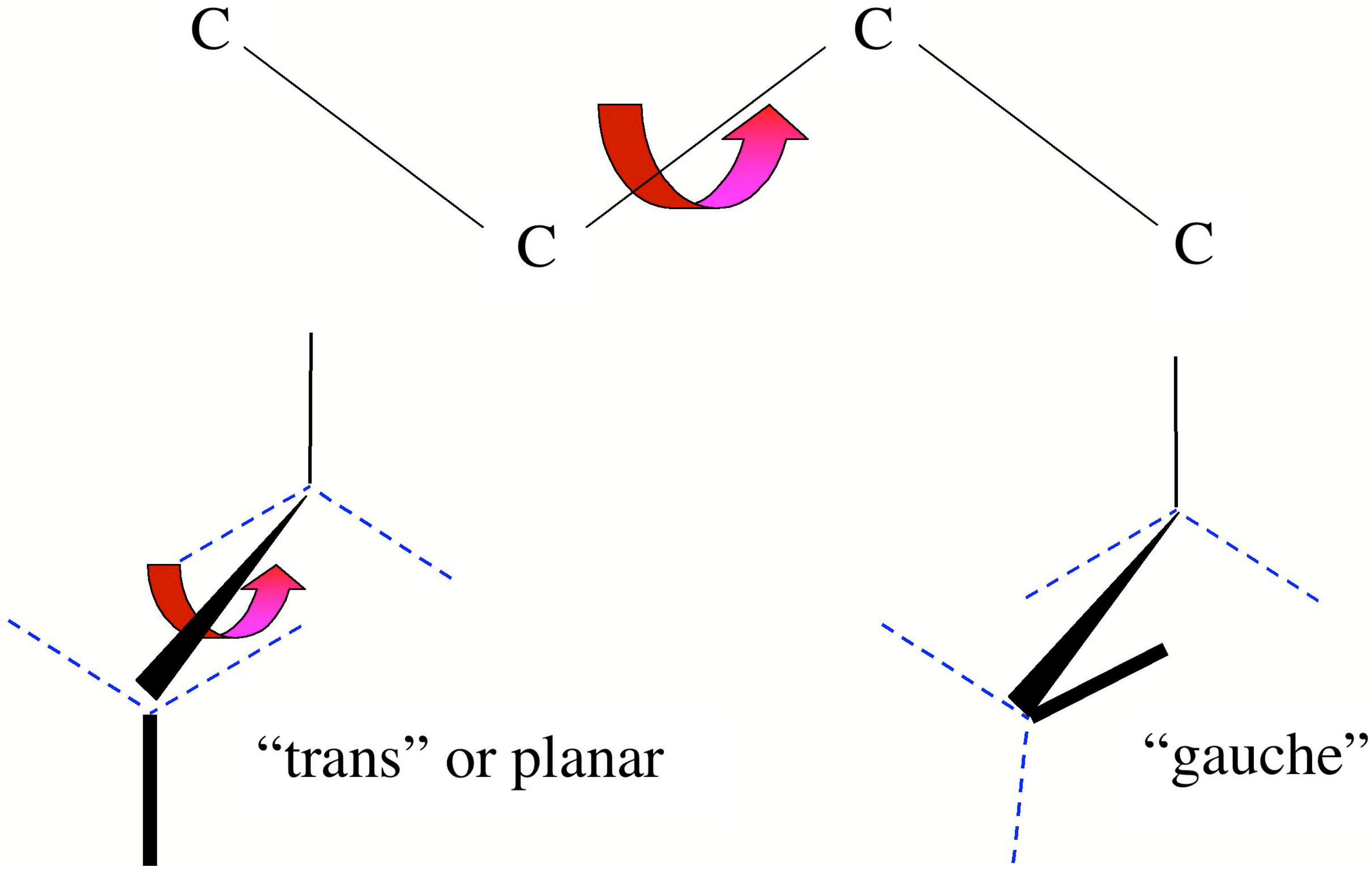
Cytosine (C)

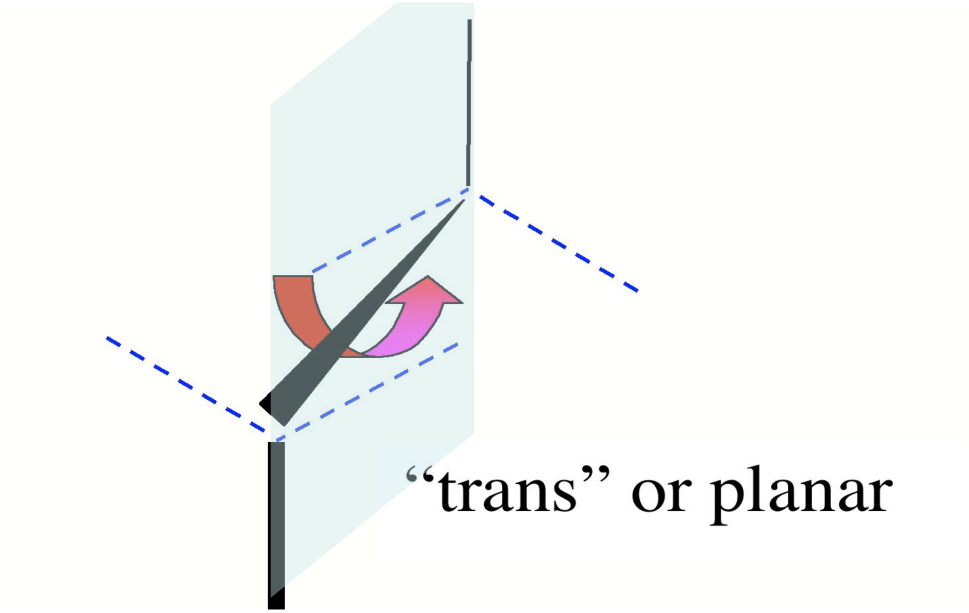
Guanine (G)

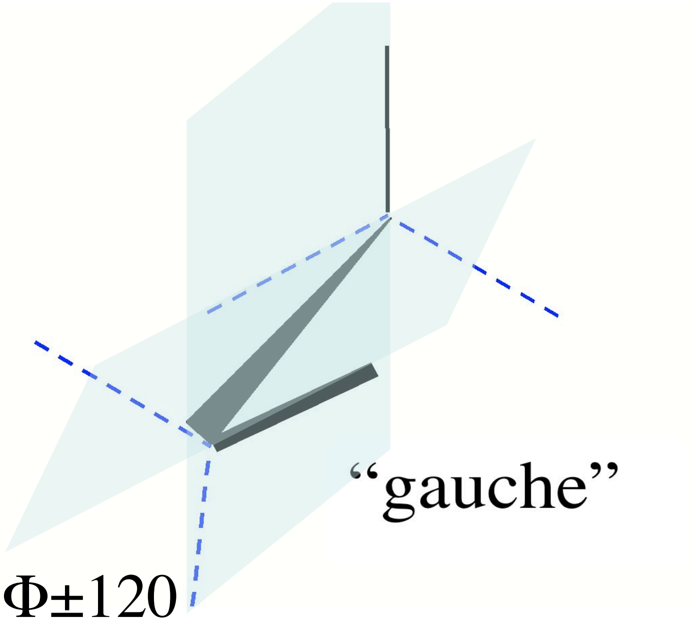
Thymine (T)

Bacterial DNA partially escaped from its native shell (from *Dictionary of Science and Technology*, Christopher Morris, ed., San Diego CA: Academic Press, 1992)

The size and shape of a polymer is always changing . . . . .







Minimal energy
conformation: $U(\Phi = 0) = 0$

Secondary minimum:
$U(\Phi = \pm 120) \sim 1$ kcal/mol

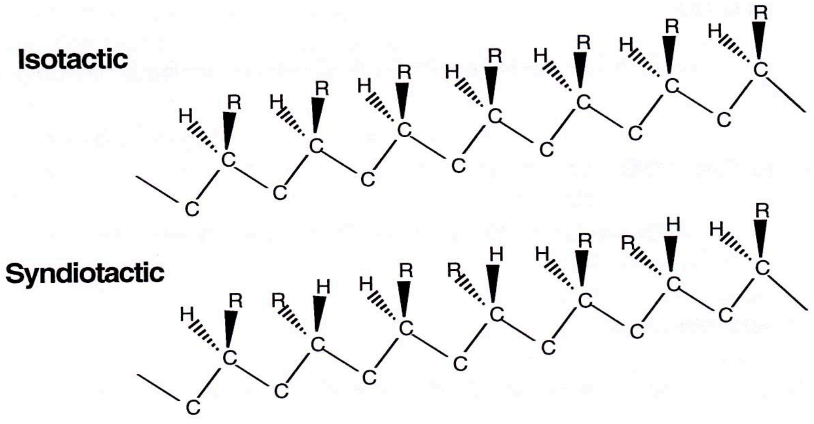
Energy barrier between Φ=0 and Φ=±120 is ΔU=3 kcal/mol
($k_B T = 0.6$ kcal/mol)

- the population of conformers
- the rate at isomerisation of conformers

The backbone of a computer generated N=1,000,000 polymer

Alexander Yu.Grosberg and Alexei R. Khokhlov, Giant Molecules: Here, There, and Everywhere, Academic Press, 1997

Tacticity of a linear polymer chain



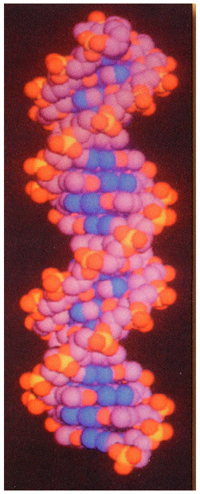
trans conformation

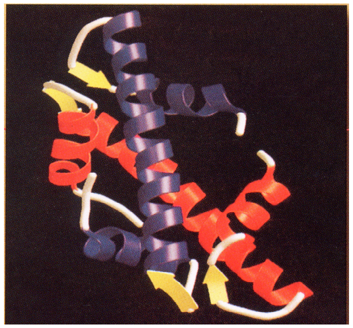
. . .breakage of covalent bonds
required to change configuration/tacticity

Isotactic: -R groups on the same side of the C-C plane
Syndiotactic: -R groups on alternating side
Atactic: -R groups on either side of the C-C plane

Flexibility in polymers where rotational isomerisation is hindered/disallowed

1. DNA
2. Proteins (20 amino acids = monomers)
3. Triple/double carbon bond backbones

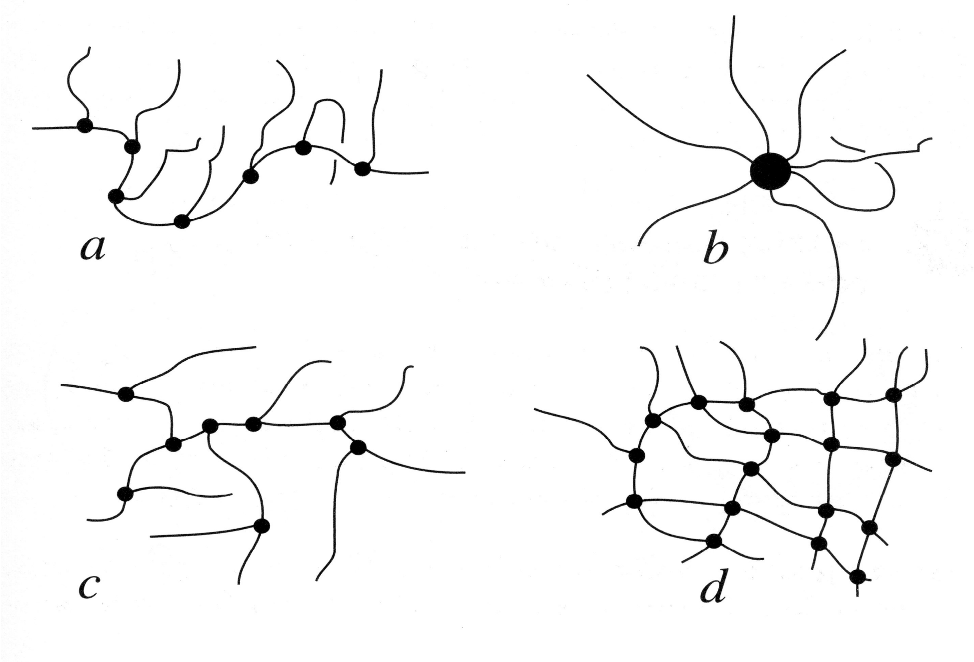




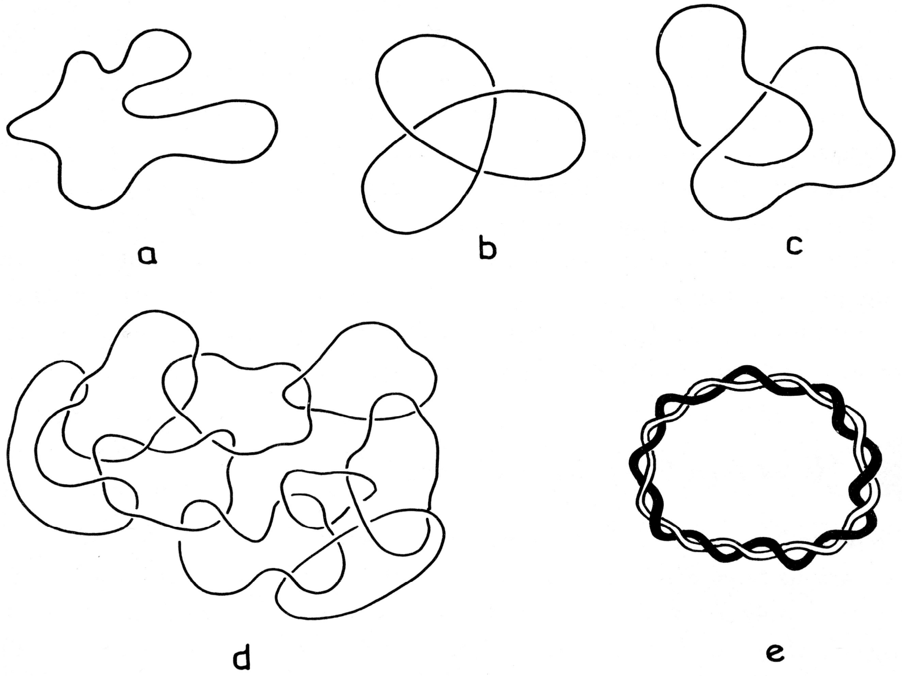
Bond angles can still change; atoms can fluctuate in position providing very limited flexibility along small distances long the chain, but significant flexibility over long distances

no kinks, garden hose or worm-like models

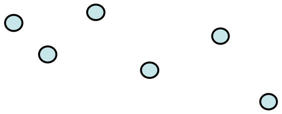
Non-linear chains are also of interest

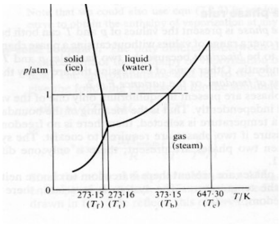


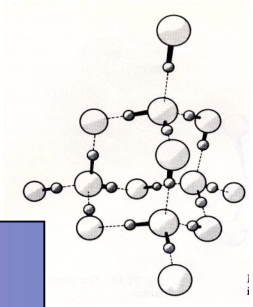
Circular chains



States of polymers

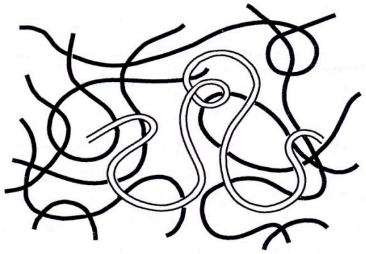


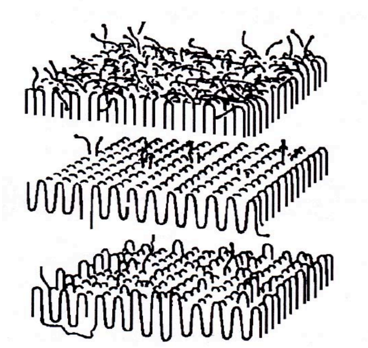




Gaseous Liquid Solid

“melt”& solutions “glasses” semi-crystalline

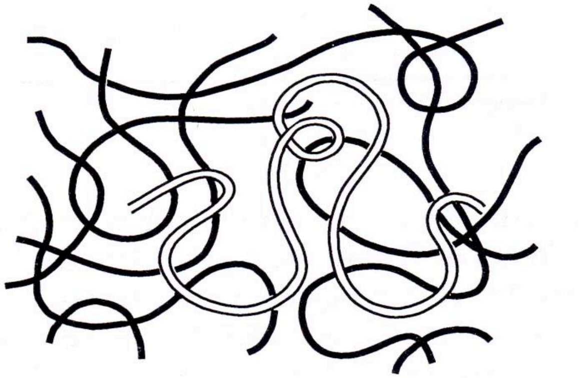




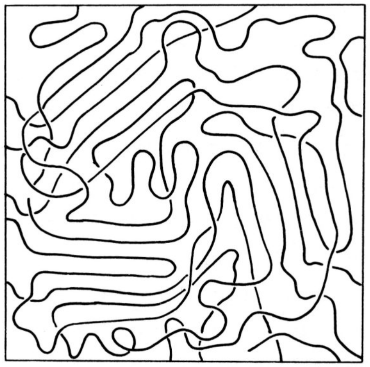
→

decrease temperature or thermal motion

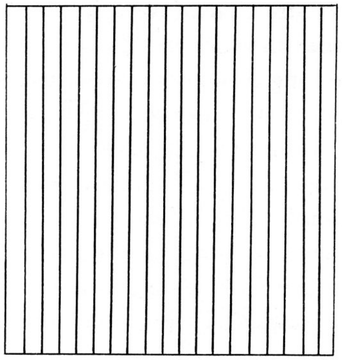
Melts (pure polymer “liquid”) towards crystalline solids



. towards crystalline state
  - motion frozen on scale of polymer
  - segmental motion persists

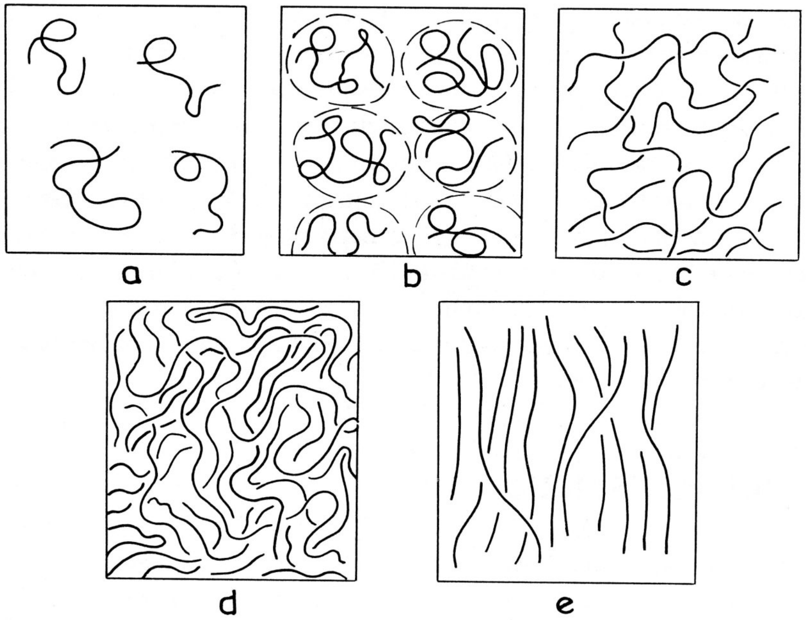


c



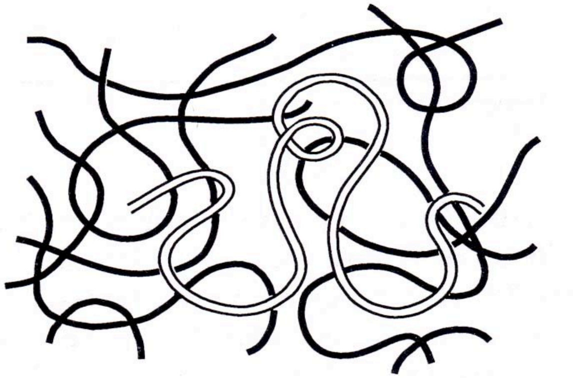
b

Polymer solutions “dilute”, semi-dilute, through to concentrated



Rheology: a study of the flow of polymer melts and solutions
(shear-thinning, die swell, energy requirements
for mold filling, design of mixers, extruders

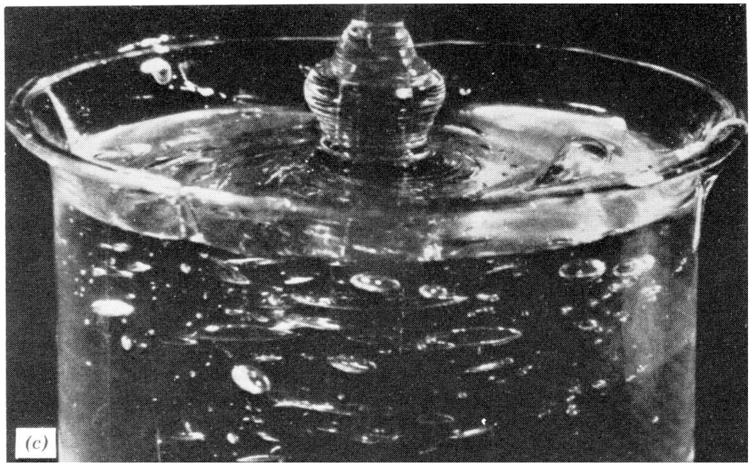
Polymer melt



polymer melt is like a bowl of spaghetti

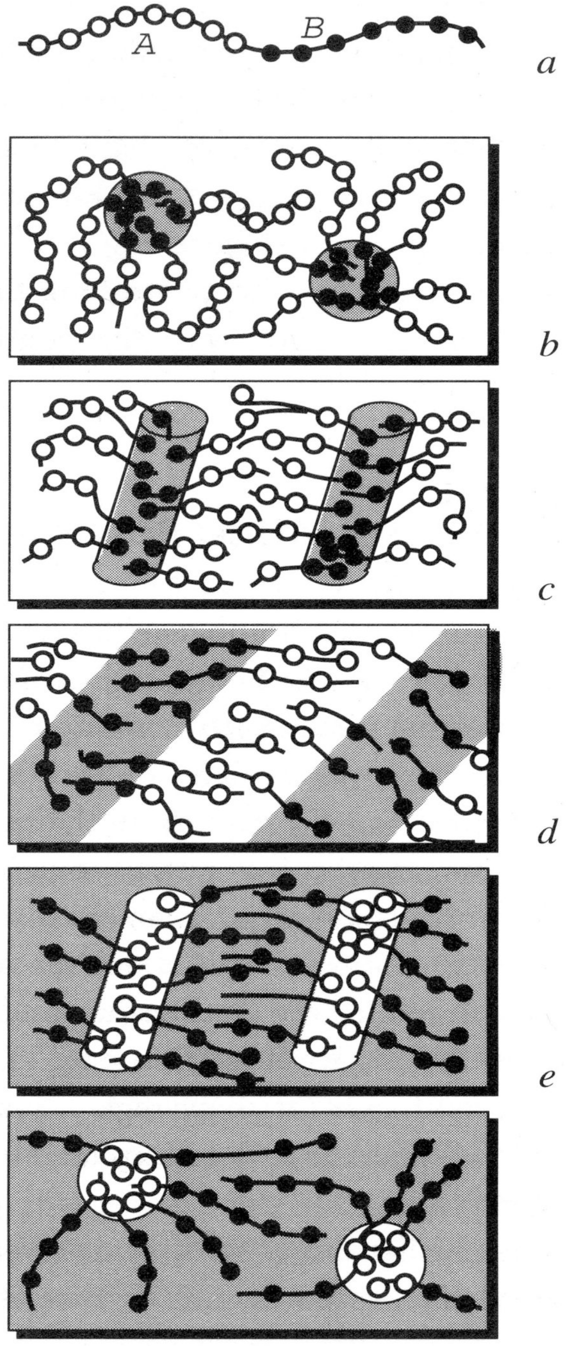
- entanglements limit motion
- flows on long-timescales (reptation)
- elastic on short-timescales

viscoelasticity



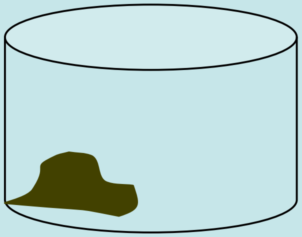
Block copolymer solutions and melts:

making patterned surfaces and
ordered melt morphologies

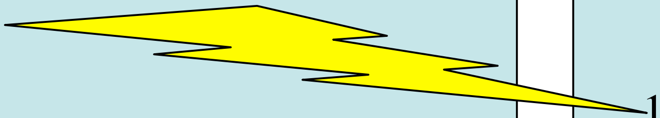


Scientists, academics < 1930s

“A damned gooey mess”



Another failed synthesis



Industrialists

1830 Charles Goodyear,: vulcanised rubber

Hevea brasiliensis + Δ + S → elastomeric material

1847 Christian Schonbern

Cellulose + nitric acid → cellulose nitrate

1860 Leo Baekeland (Bakelite)
phenol-formaldehyde resin

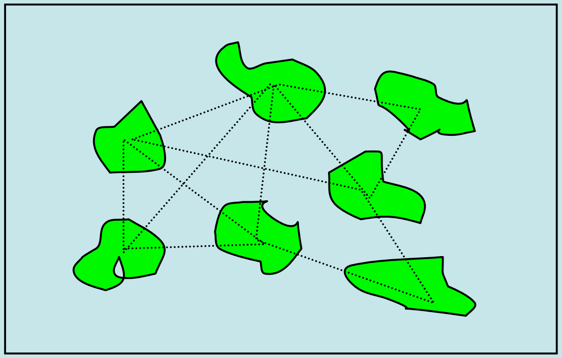
1930s DuPont (USA) nylon, teflon
1938Dow (USA) polystyrene
1939 ICI (UK) LDPE

WWII: shortage of natural rubber!

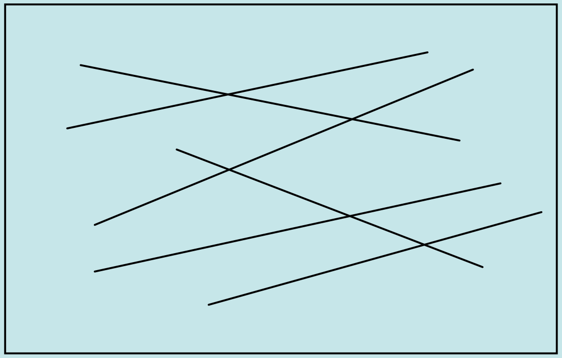
Scientists begin to look at complex systems . . . .

1920's Hermann Staudinger, German Physical Chemist

"long-chained molecules or macromolecules"

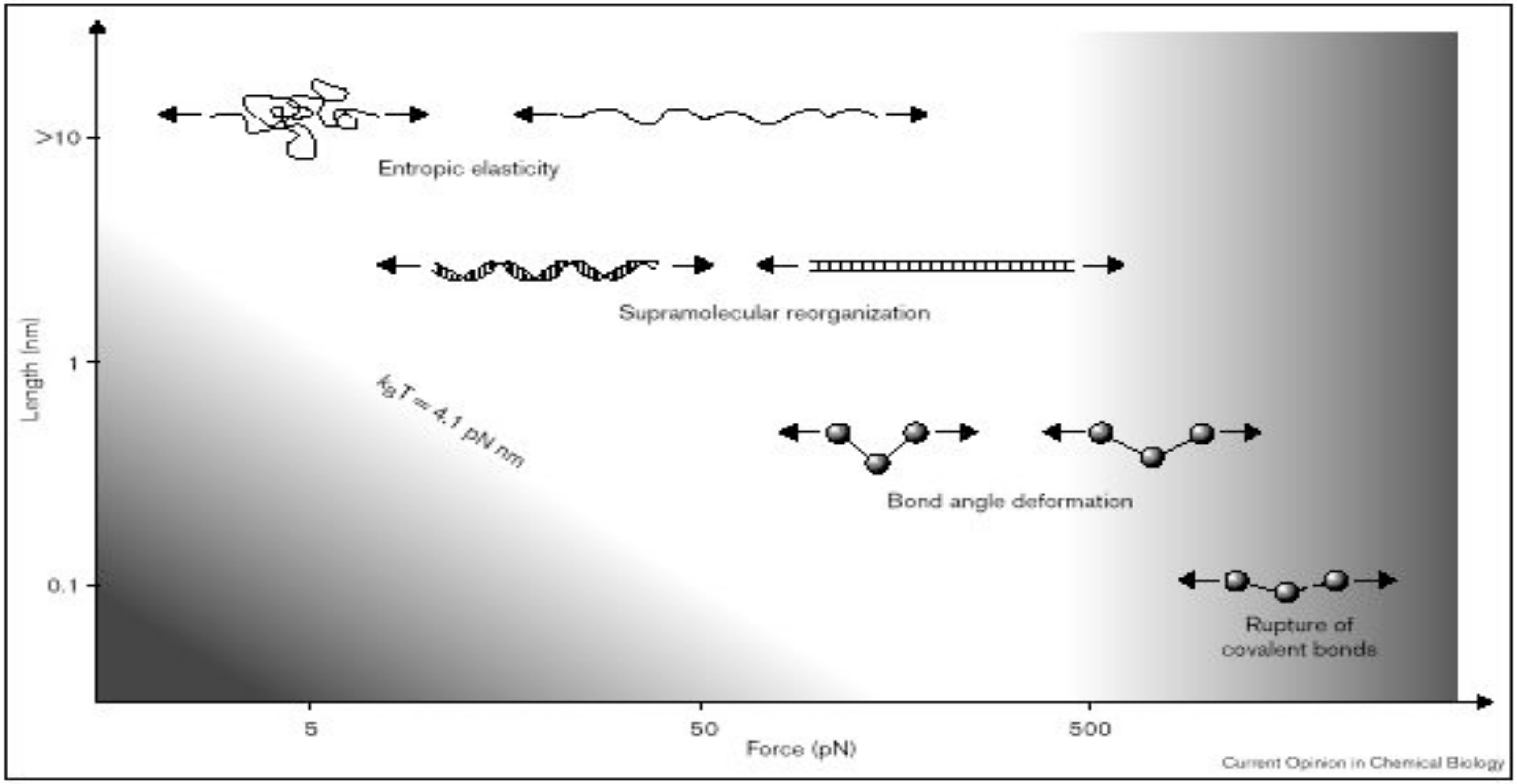


interacting, separate
intermediate species
e.g., T_m, flow behaviour



very long, alkane-like
but misunderstood .
flexibility

Clausen-Schaumann, 2000



Large forces (100’s of picoNewtons) over small distances (Å)
needed to break covalent bonds

Small forces (~1 picoNewton) over large distances (μm)
needed to stretch a polymer