

Introduction to the Polymer Science

What is a Polymer?

Polymers are long, usually linear chains consisting of a large number ($N \gg 1$) of monomer units.

For synthetic polymers, usually $N \sim 10^2-10^4$;

For DNA $N \sim 10^9-10^{10}$.



Poly(ethylene)



Poly(styrene)



Poly(vinyl chloride)

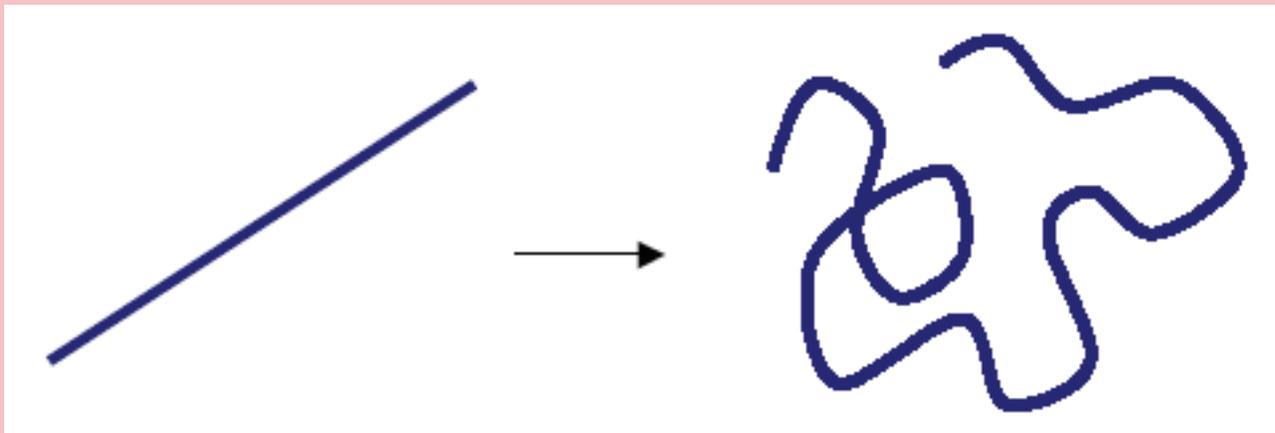
Long molecular chains.



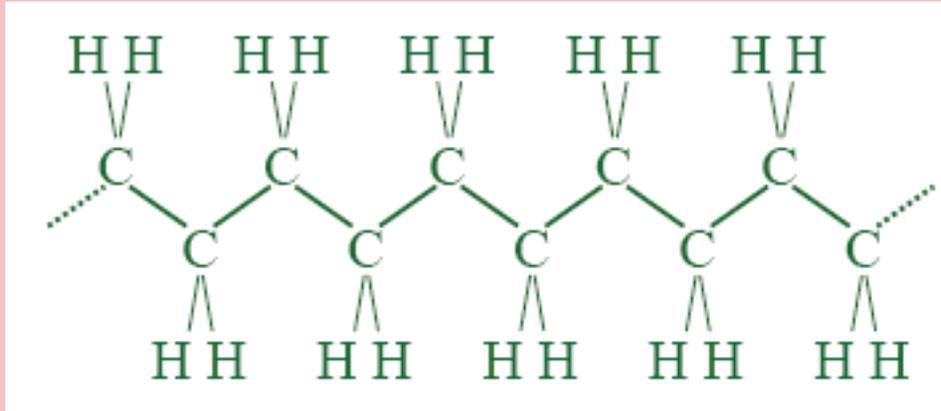
Electron microscope picture of bacterial DNA partially released from its native shell (*Dictionary of Science and Technology*, Christopher Morris, ed., San Diego, CA: Academic Press, 1992).

Three main factors which govern the physical properties of polymers.

1. The monomer units are **connected** into a chain, thus their spatial movements are not independent, contrary to those of the molecules in low-molecular fluids. This is the reason why the polymer systems are anomalously **pure in entropy**.
2. The number of monomer units per chain is large, $N \gg 1$. Existence of a large dimensionless parameter simplifies radically the construction of the theory.
3. Polymer chains are generally **flexible**:



Flexibility of a polymer chain.

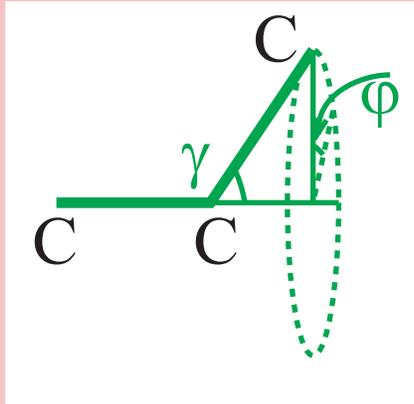


Rectilinear conformation of a poly(ethylene) chain, shown on the picture, corresponds to the **minimum of the potential energy**. All monomer units are in **trans-position**. This conformation would be an equilibrium one at $T = 0$.

However, if $T > 0$ thermal fluctuations cause the deviation from the conformation with minimal energy. According to **Boltzmann law** the probability of realisation of any conformation can be expressed in terms of its excess potential energy U :

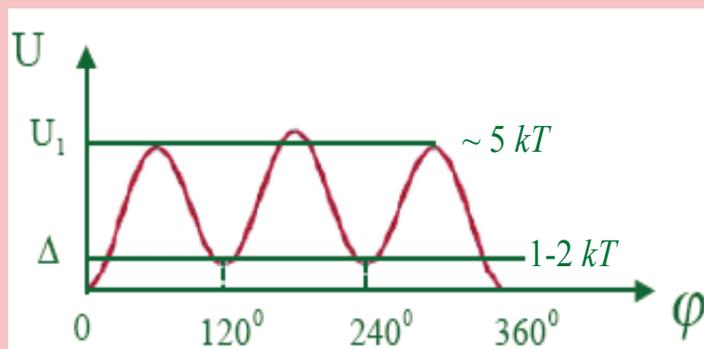
$$p(U) \sim \exp\left(-\frac{U}{kT}\right)$$

Rotational-Isomeric Flexibility Mechanism.



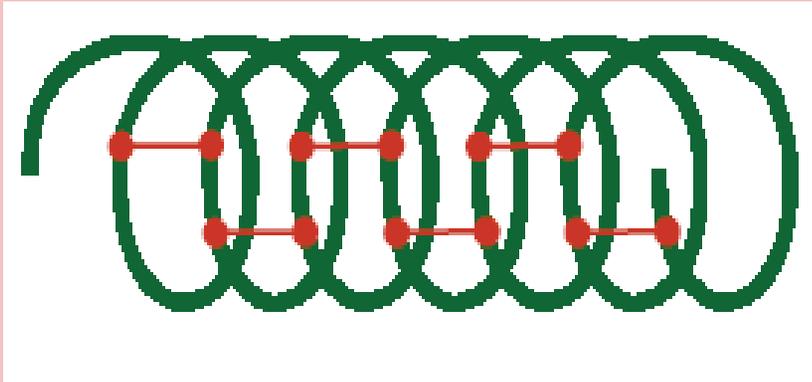
In the carbon backbone of a polymer chain the fluctuations of the **valency angle** γ are negligible (one may consider this angle to be fixed; $50^\circ < \gamma < 80^\circ$ for different chains).

However, if the backbone consists of ordinary **C-C** bonds, the angle of internal rotation ϕ can change easily (i.e., the rotation with fixed γ is possible). For any nonzero value of ϕ the chain deviates from the rectilinear conformation thus giving rise to chain **flexibility**.



Positions corresponding to $\phi = 120^\circ, 240^\circ$ are called **gauche rotational isomers**, while those with $\phi = 0^\circ$ are called **trans rotational isomers**. Gauche isomers thus make dominant contribution into chain flexibility.

Persistent Flexibility Mechanism.

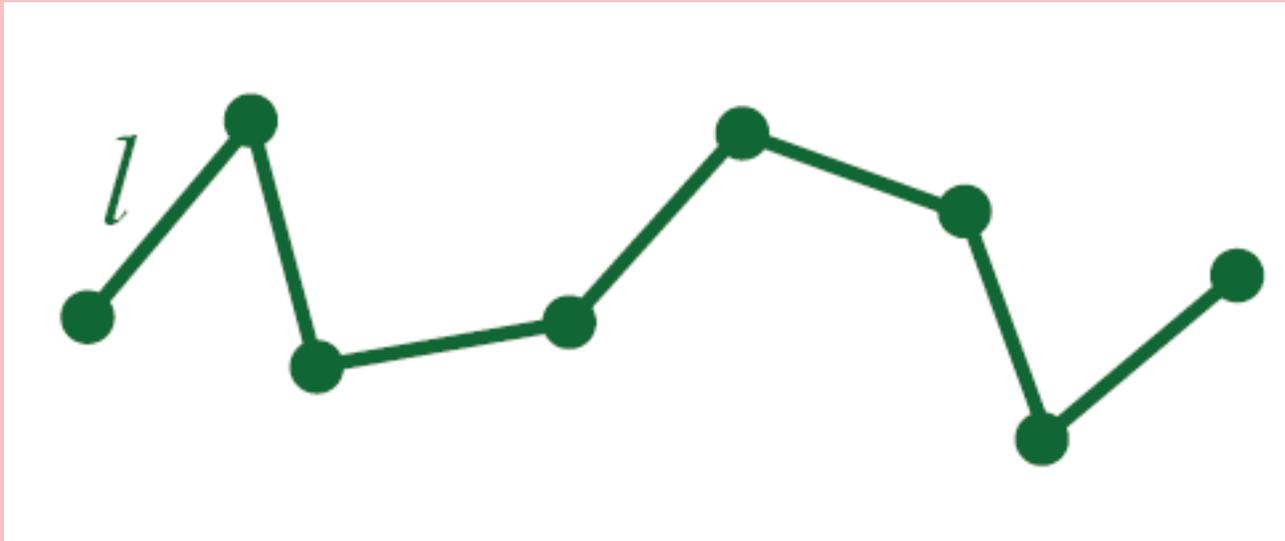


If the rotational isomers are not allowed (e.g., for α -helical polypeptides or for DNA double helix) the flexibility arises via accumulation of the **small thermal vibrations** around the equilibrium positions of the atoms.

If the chain length is long enough these small deviations would force the chain to form a tangled coil: there is only one straight conformation and exponentially large number of tangled ones.

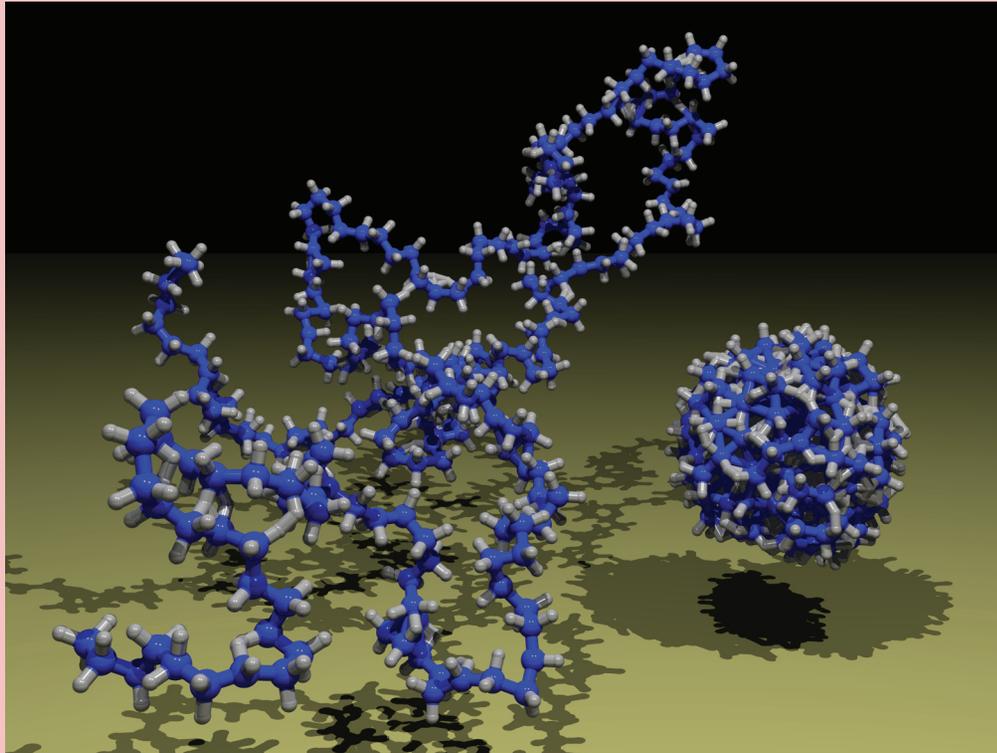
This flexibility mechanism is called **persistent**. It is, in fact, analogous to the flexibility of a **homogeneous elastic filament**.

Freely-Jointed Flexibility Mechanism.



In this mechanism the chain consists of rectilinear segments of a given length, which are connected at the freely-rotating junction points. This mechanism is normally not characteristic for real chains but it is often used for model theoretical calculations.

Portrait of a Polymer Coil.

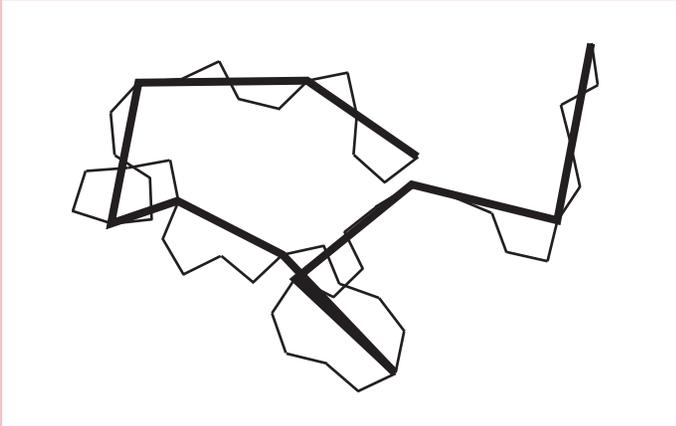


The **volume fraction** occupied by the monomer units inside the coil is **very small**, there are lots of “holes” inside.

The chain trajectory is similar to the trajectory of a **Brownian particle**.

Coil conformations of a polymer can be realized in the so-called **dilute polymer solutions** where coils do not overlap.

Self-Similarity and Scaling Laws in Polymer Physics.



A conformation of a freely-jointed chain with 50 links in 2D. The bold lines connect each fifth link (i.e., $g = 5$ in this case).

On the scales much larger than the size of a monomer unit, the polymer coil exhibits a property of **self-similarity**, i.e. the appearance and the statistical properties of a part of a coil are similar to those of the whole coil.

Formally, one can express this feature via the so-called **scaling laws**: any relationship describing the polymer coil should be invariant under the simultaneous change of variables of the type

$$N \rightarrow N/g, R \rightarrow R/f(g)$$

(one can show that the auxiliary function $f(g)$ should satisfy $f(g) = g^{\nu}$, where ν is some fixed number).

Polydispersity and Molecular Mass Distributions.

The huge majority of polymers (especially, synthetic polymers) do not have a constant, fixed once-and-for-all number of monomer units N . Instead of that, the chains with different lengths are always present in these systems. It is worthwhile, thus, to speak of a probability distribution $p(N)$ or $p(M)$ to find a chain with a given length N or molecular weight M . This probability distribution is called **molecular mass distribution (MMD)**.

By definition

$$\sum p(M) = 1$$

$$M_n = \sum Mp(M)$$

$$M_w = \sum M^2 p(M) / \sum Mp(M)$$

where M_n and M_w are called the number average and the weight average molecular masses, respectively.

The Types of Polymer Molecules

1. Homopolymers and Heteropolymers.

Homopolymers - polymers, whose monomer units are identical.

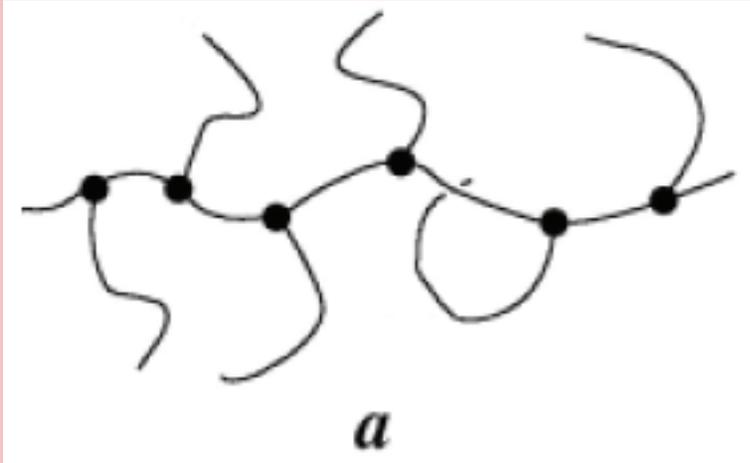
Heteropolymers - polymers, consisting of monomer units of several different types. For example, proteins consist of 20 aminoacids, DNA - of 4 types of nuclein acids.

The sequence of monomer units along the heteropolymer chain is called its **primary structure**.

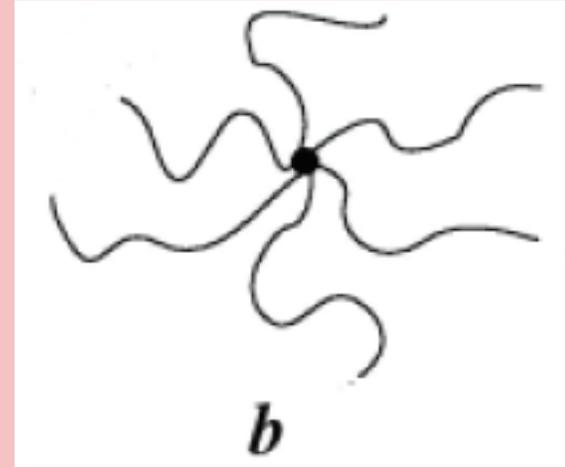
Primary structure can be both regular and random.

Types of Polymer Molecules:

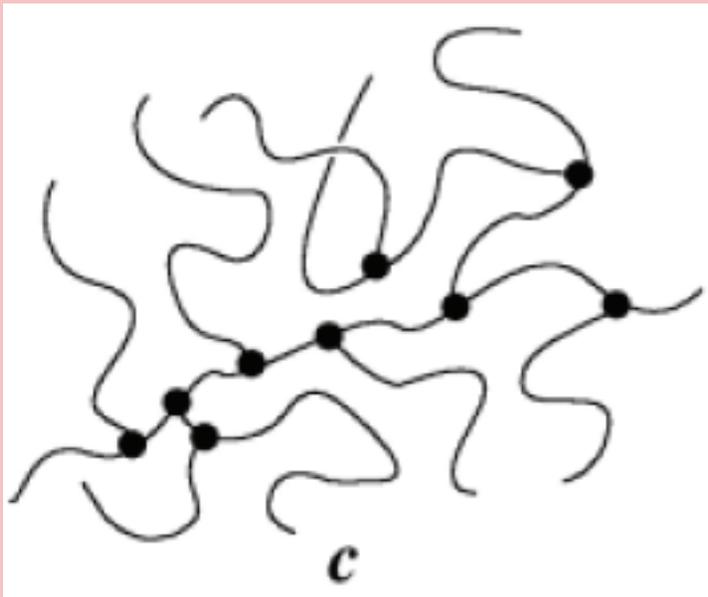
2. Branched polymers.



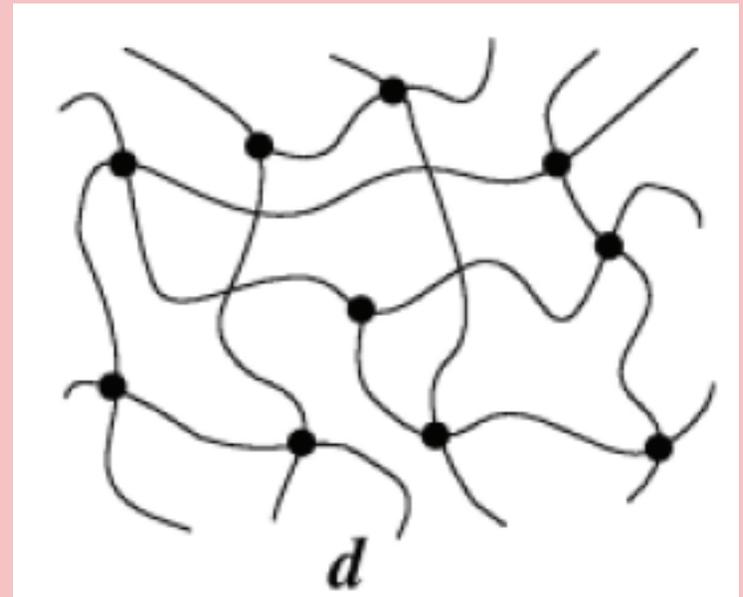
a) comb-like



b) star-like



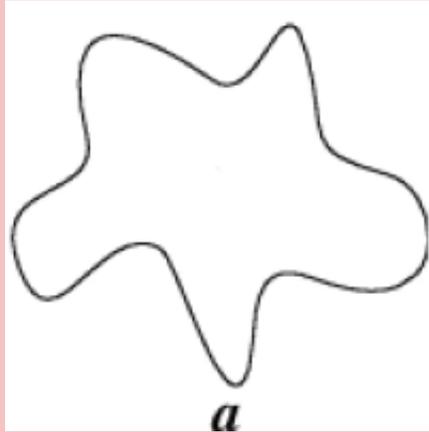
c) randomly branched



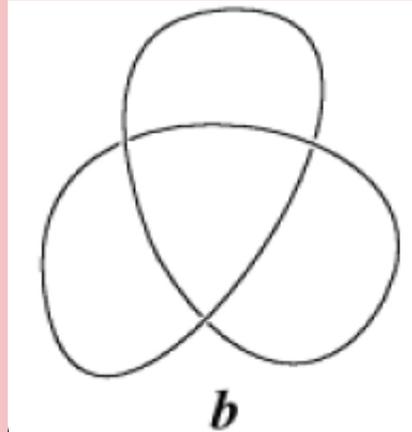
d) polymer networks

Types of Polymer Molecules:

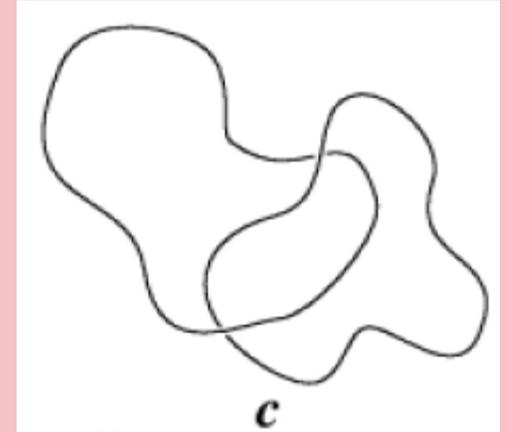
3. Ring Polymers.



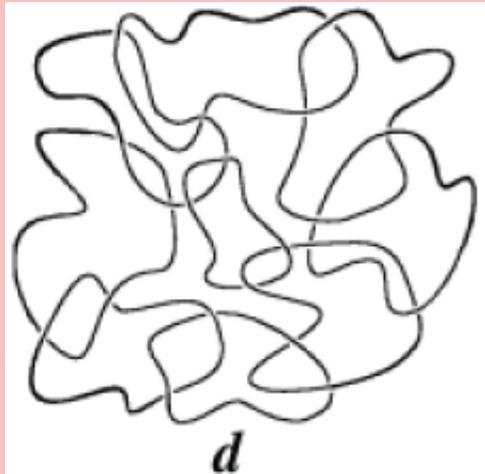
a) ring macromolecule without knots



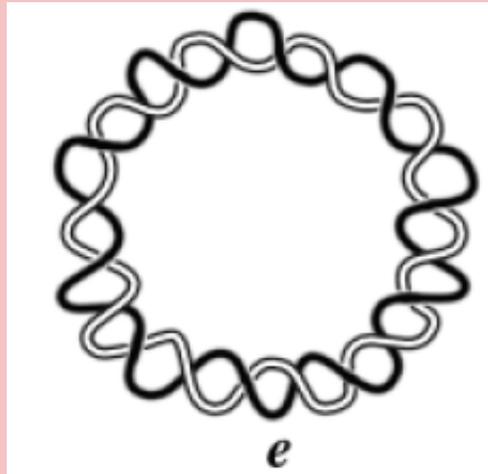
b) a simple knot



c) tangling of two polymer rings

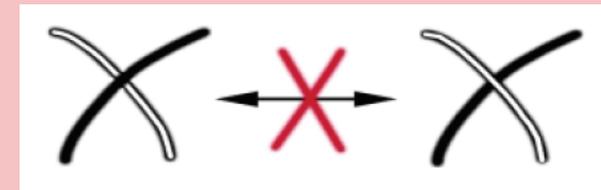


d) olympic gel



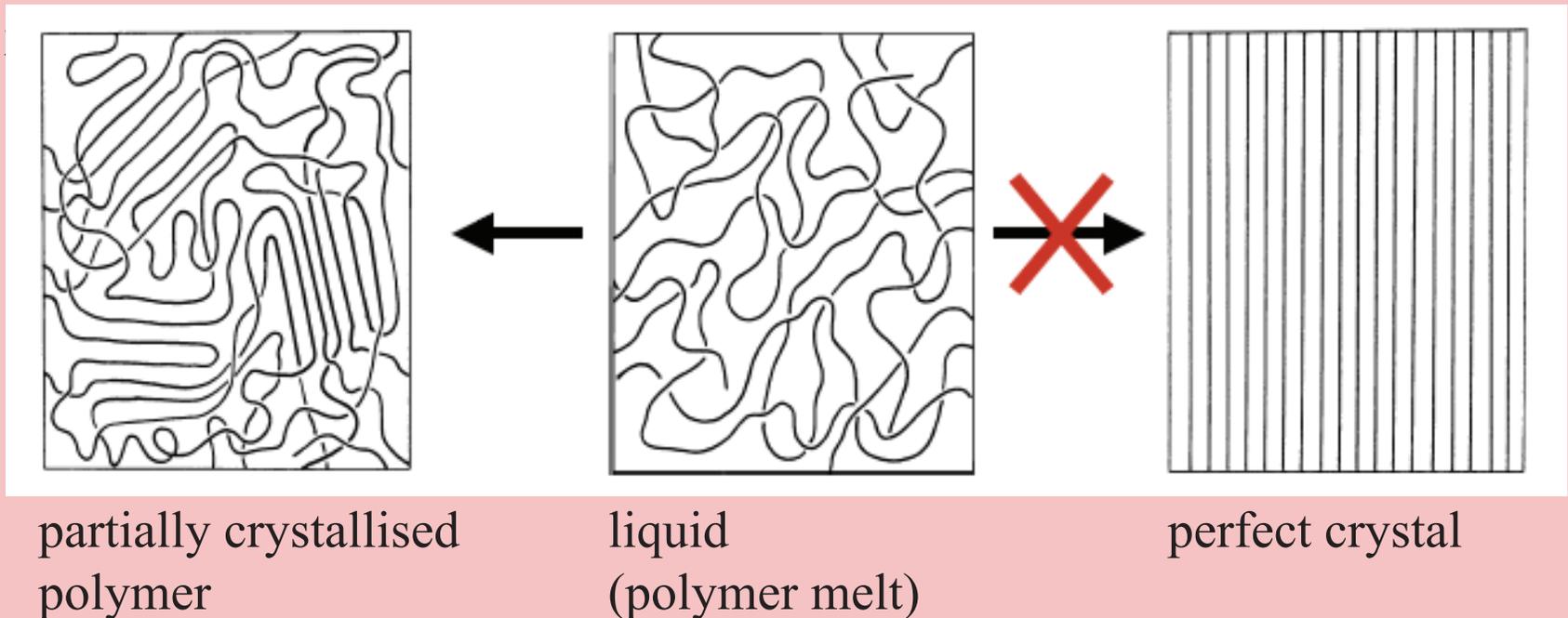
e) tangling of two complementary strains into a double helix

Topological restrictions:



Physical States of Polymer Materials.

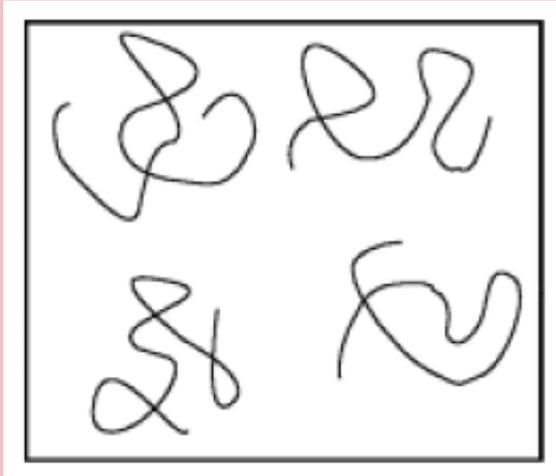
Traditional classification of physical states (gases, liquids, crystals) is irrelevant in polymer systems



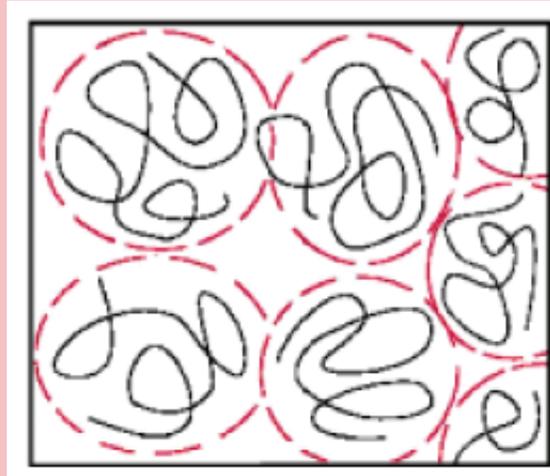
Classification of states for polymer materials:

1. **Partially crystalline** state
2. **Viscoelastic** state (polymer melt)
3. **Highly elastic** state (e.g., **rubbers**)
4. **Glassy** state (e.g., organic glasses from **poly(styrene)**, **poly(methylmethacrylate)**, etc.)

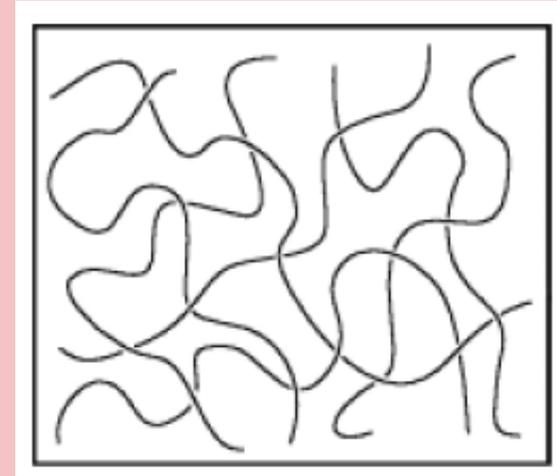
Polymer solutions.



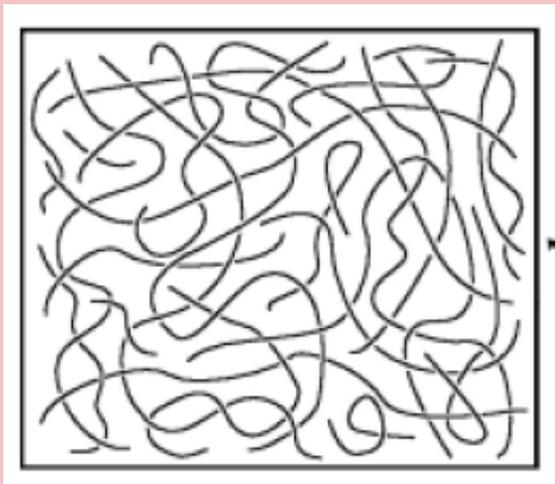
dilute solution



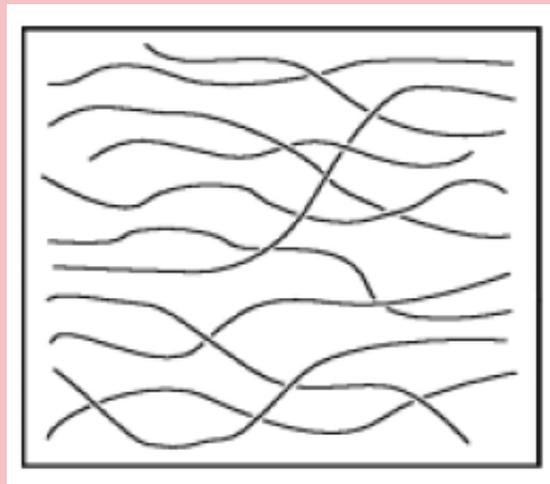
crossover from the dilute to the semidilute regime



semidilute solution



concentrated solution
(polymer melt)



liquid-crystalline
solution

History of Polymer Physics

- Discovery of the chain structure of a polymer molecule

H. Staudinger, 1920-1930

- First works in polymer physics: molecular explanation of the high elasticity of rubbers

W. Kuhn, E. Guth, H. Mark, 1930-1935

- “Physico-chemical” period

P. Flory, V.A. Kargin, 1935-1965

- Discovery of the DNA double helix

J.D. Watson, F. Crick, 1953

- The theoretical physics methods permeate into polymer science

I.M. Lifshits, P.-G. de Gennes, S. Edwards, 1965-...

Nowadays, polymer physics is an important subfield of general condensed matter physics, the basis of a so-called “*Soft Condensed Matter Physics*”.