

Elements of polymer physics I

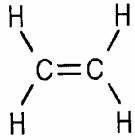
Lecture 03.05.2006

Prof. Dr. F. Kremer

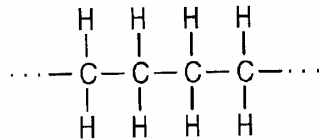
- **Structural properties of single polymer chains**
- **Ideal (Gaussian) chains**
persistence length, persistence time
contour length, radius of gyration
free energy
- **Single-chain conformations**
- **Entropy elasticity**

Structural properties of single polymer chains

Polymers are chain molecules made either out of simple organic monomer units (artificial polymers) or out of amino acids, DNA or RNA. In this lecture I will focus on artificial polymers. A typical example is Poly(ethylene), PE; it is composed out of the monomer ethylene:

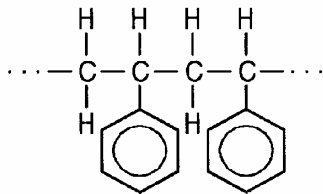


Ethylene



Poly(ethylene), PE

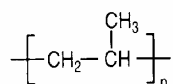
Another common polymer is polystyrene:



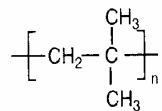
Polystyrene

A polymer is characterized by the type of the monomer unit, by the degree of polymerization N , by the molecular weight M_w and by its distribution, the poly-dispersity ("Uneinheitlichkeit").

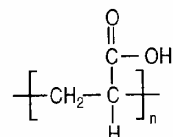
Examples of common polymers are summarized in Tab. 1:



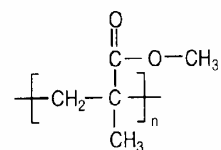
polypropylene
'PP'



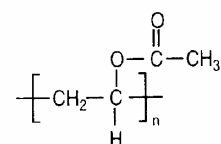
polyisobutylene
'PIB'



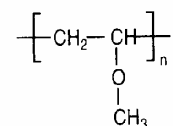
poly(acrylic acid)



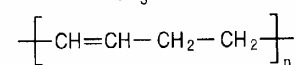
poly(methylmethacrylate)
'PMMA'



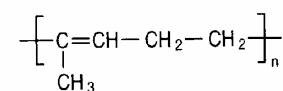
poly(vinylacetate)
'PVAc'



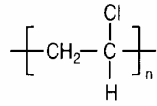
poly(vinylmethylether)
'PVME'



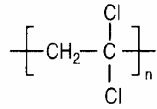
polybutadiene
'PB'



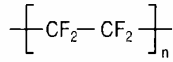
polyisoprene
'PI'



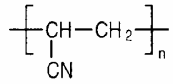
poly(vinyl chloride)
'PVC'



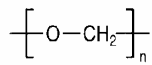
poly(vinylidene chloride)



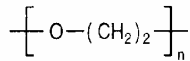
poly(tetrafluoroethylene)
'PTFE'



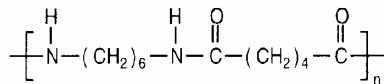
poly(acrylonitrile)
'PAN'



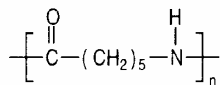
poly(oxymethylene)
'POM'



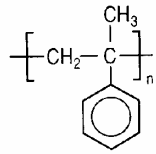
poly(ethyleneoxide)
'PEO'



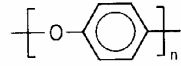
poly(hexamethylene adipamide)
nylon 6,6



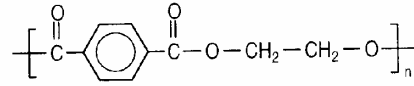
poly(ϵ -caprolactam)
nylon 6



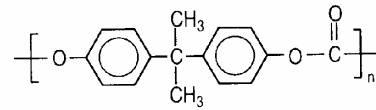
poly(α -methylstyrene)



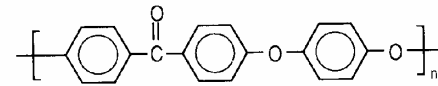
poly(phenylene oxide)
'PPO'



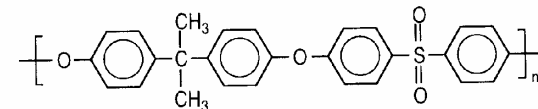
poly(ethylene terephthalate)
'PET'



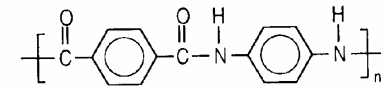
'polycarbonate'
'PC'



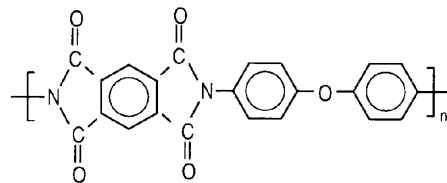
'poly(ether ether ketone)
'PEEK'



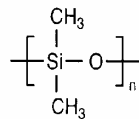
'polysulfone'



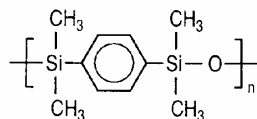
poly(p-phenylene-
terephthalamide)
'Kevlar'



'polyimide'

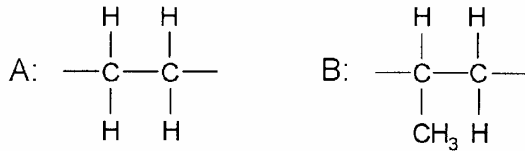


poly(dimethylsiloxan)
'silicon rubber'



poly(tetramethyl-p-silphenylene-
siloxane)
'TMPS'

The composition of polymers can be varied in a manifold manner; of special importance are statistical arrangements of two polymers A and B or polymers with block structure (Fig. 1).



.....ABAABABBAABA.....

statistical

.....AAAAABBBBBB.....

block structure

Fig. 1: Ethylene-propylene copolymers

The molecular architecture of polymers can be varied extensively; some few examples are depicted in Fig. 2:

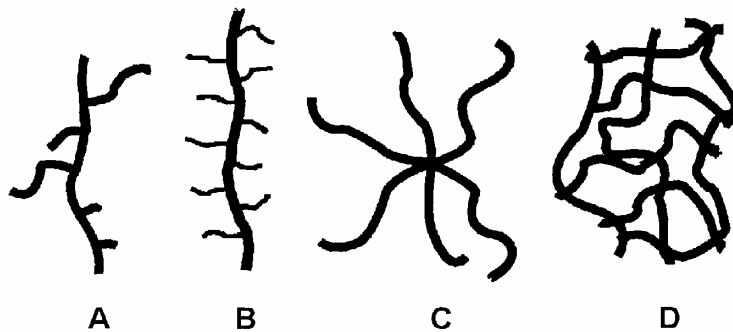


Fig. 2: Polymers with non-linear architectures: polymer with short-chain and long-chain branches (A), polymer with grafted oligomer side chains (B), star polymer (C), network of cross-linked chains (D)

Each polymer can be described vs. sequence of bonds linking successive elementary monomers. In the simple case of PE the angular variation between neighbouring carbons is defined as (Fig. 3)

$\Delta\vartheta_n = \vartheta_n - \vartheta_{n-1} = 0$, $\Delta\varphi_n = 0$, $\pm 120^\circ$ $\Delta\varphi_n = 0$ is called the **trans** configuration, $\Delta\varphi_n = \pm 120$ is a **gauche** configuration. They do not have the same energy. Similar models can be derived for other polymers.

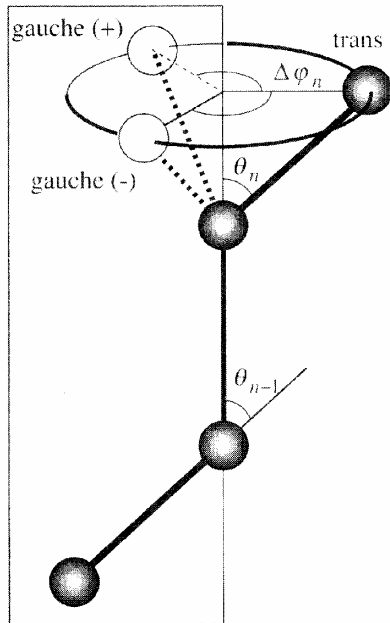


Fig. 3: Configuration parameters along a chain of ethylene groups.

Taking the successive values of $\Delta\varphi_n$ at random, the chain appears, when observed at some scale much larger than a , the elementary length of a bond, as **statistical coil**.

The **persistence length** l_p ; Let $\Delta\varepsilon = \varepsilon_g - \varepsilon_t > 0$ be the difference in energy between the **gauche** and the **trans**-conformation; then

$$l_p = a \exp\left(\frac{\Delta\varepsilon}{k_B T}\right) \quad (1)$$

is the length on which the chain has the appearance of a rigid segment; because the segments are co-linear for a succession of **trans** configurations. Hence $L = Na$ the chemical length of the chain has to be large compared to l_p for the chain to be considered as a statistical coil. This condition can be written as

$$x = \frac{l_p}{L} \approx N^{-1} \exp\frac{\Delta\varepsilon}{k_B T} \ll 1. \quad (2)$$

Phenomenological the persistence length can also be represented as a characteristic length of the thermal fluctuations carried out by an elastic rigid rod.

The **persistence time** τ_p , i.e. the characteristic time for fluctuations between **gauche**- and **trans**-conformation is

$$\tau_p = \tau_0 \exp\left(\frac{\Delta\varepsilon}{k_B T}\right) \approx 10^{-12} \text{ s}. \quad (3)$$

The conformation of single chains

There are three rotational isomeric states per bond \mathbf{t} , \mathbf{g}^+ and \mathbf{g}^- . Hence one has 3^N different configurations for a PE chain with degree of polymerisation N . Among those, some are special, as follows.

Helix configurations.

PE forms a steric structure shown in Fig. 4 with zigzag arrangements of the bonds.

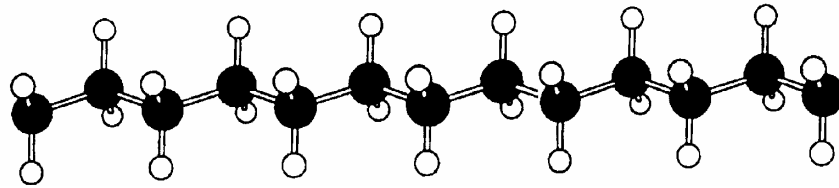


Fig. 4: Steric structure of polyethylene. Rotations about the C-C-bonds result in a change in the conformation

PTFE in the crystalline state passes a typical wound structure (Fig. 5).

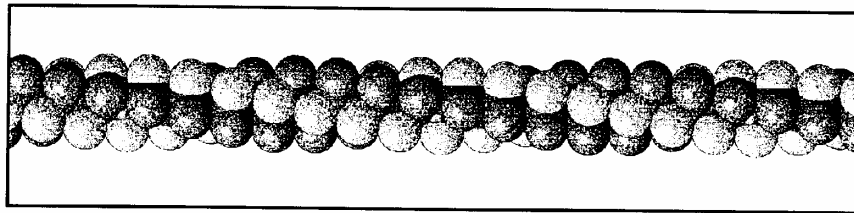


Fig. 5: PTFE in the crystalline state. The conformation corresponds to a 13/6-helix.

PTFE is obtained from PE by replacing the H-atoms by Fluoride (F)-Atoms (Fig. 4); the reason for the resulting structure change is caused by the fact, that the F-Atoms are much larger compared to H which increases the interaction energy between the CF_2 -groups of second nearest neighbours. Starting with an **all-trans** form, a uniform twist of the chain diminishes the repulsive F-F interaction energies but, at the same time, the bond rotational energy increases. There exists an energy minimum at a finite torsion angle $\varphi_{\min} = 16.5^\circ$.

Helices are characterised by the symmetry operation which maps the molecule into itself. Screw operation comprise a turn about a certain angle e.g. $\Delta\zeta$ together with a simultaneous shift, e.g. Δz . For PE one has $\Delta\zeta = 180^\circ$ and $\Delta z = 1.27 \text{ \AA}$ for PTFE $\Delta\zeta = 166^\circ$ and $\Delta z = 1.31 \text{ \AA}$.

The general helical form is described as m/n -helices which is meant to indicate that m monomeric units are equally distributed over n turns. PTFE is a 13/6 helix, indicating that 13 CF_2 units are distributed over 6 turns.

The ideal (Gaussian chain)

Assume that N elementary segments (monomers) do **not** interact and are independent from each other. Such a chain is called **ideal**. The vector that joins the origin of the chain to its end is

$$\vec{r} = \sum_{i=1}^N \vec{a}_i \quad (4)$$

Squaring \vec{r} and taking average on all possible configurations, yields

$$\langle \bar{r}^2 \rangle = \sum_i a_i^2 + \underbrace{2 \sum_{i \neq j} \langle a_i \cdot a_j \rangle}_0 = Na^2 \quad (5)$$

because two segments i and j are independent. Hence, the average separation of the ends corresponding to the average size of the ideal chain is

$$R_0 = \langle \bar{r}^2 \rangle^{1/2} = aN^{1/2} \quad (6)$$

One can show as a consequence of the central limit theorem, that the probability $P_N(\bar{r})$ for the N -link chain to terminate at \bar{r} has a Gaussian distribution

$$P_N(\bar{r}) = \left(\frac{3}{2\pi R_0^2} \right) \exp\left(-\frac{3}{2} \frac{r^2}{R_0^2} \right) \quad (7)$$

$P_w(\bar{r})$ is the ratio between the number of configurations $\Gamma_N(\bar{r})$ susceptible to bring the chain from a fixed origin 0 to a point \bar{r} , over the total number of configurations

$$\Gamma_N = \sum_{\bar{r}} \Gamma_N(\bar{r}) \quad (8)$$

The entropy S' of the ideal chain being

$$S(\bar{r}) = k_B \ln \Gamma_N(\bar{r}) \quad (9)$$

hence $S(\bar{r}) = k_B \ln P_N(\bar{r}) + k_B \ln \Gamma_N$ (10)

from which one obtains, but to an additive constant.

$$S(\bar{r}) = -\frac{3}{2} k_B \frac{r^2}{R_0^2} \quad (11)$$

which depends only on \bar{r} .

The free energy of the chain is entirely of entropic origin

$$F(R) = F_0 + \frac{3}{2} k_B T \cdot \frac{r^2}{R_0^2}$$

From this follows that the force constant of the chain if a force f is applied which leads to an elongation r

$$f = \frac{3k_B T}{R_0^2} r$$

The central limit theorem: (Der zentrale Grenzwertsatz)

The sum of N random independent variables X_i ($i = 1, \dots, N$) is a Gaussian variable; when N goes to infinity, if the moments $\langle x_i^n \rangle$ exist. A Gaussian variable ξ is a variable that follows a probability law with

$$p(\xi) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{\xi^2}{2\sigma^2}\right)$$

The quantity σ^2 is the variance

$$\sigma^2 = \int \xi^2 p(\xi) d\xi$$

If one has a random variable X as superposition of many equivalent random variable **then** X follows a Gaussian distribution.

Summary of the lecture "elements of polymer physics"

1. Most synthetic polymers are flexible chains, being characterized by a persistence length, the degree of polymerization, the molecular weight and its distribution.
2. Ideal chains have Gaussian distribution of the end-to-end vector of a chain.
3. Ideal chains have an elasticity which is of entropic origin only.