Leibniz-Institut für Polymerforschung Dresden

Polymers in Solution

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Bioactive and Responsive Polymers
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DRESDEN concept

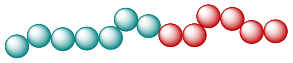
Leibniz Gemeinschaft

2. The isolated macromolecule:
constitution, configuration, conformation

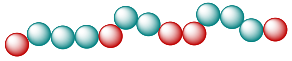
1. **Constitution**
2. Chemical **configuration**
3. **Conformation** ➔ Microconformation
4. **Conformation** ➔ Macroconformation
5. Example Questions
6. Books recommended

1. Constitution

Homopolymer



Block copolymer



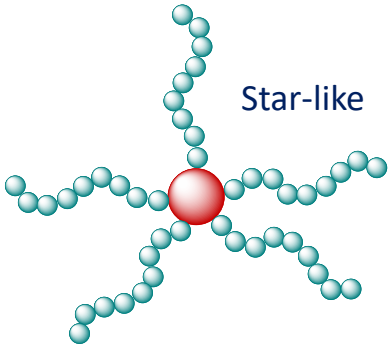
Heteropolymers

- **Monomer units**

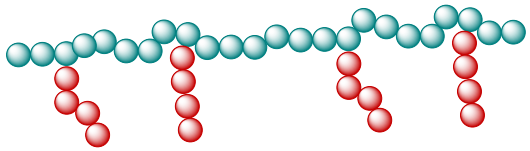
- **Homo-, Heteropolymers, Copolymers**
Alternating (ababab); periodic (abbabbabba); random (abbbababaaabbbbabab); biblock polymer; graft polymer

Block copolymer- is obtained by a **copolymerization** of a mixture of different types of momoners

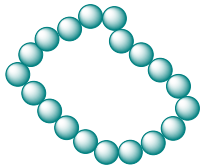
Block polymers- by **coupling** of preformed polymer **"blocks"** or by **sequential polymerization**



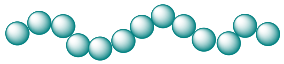
Star-like



Comb-like

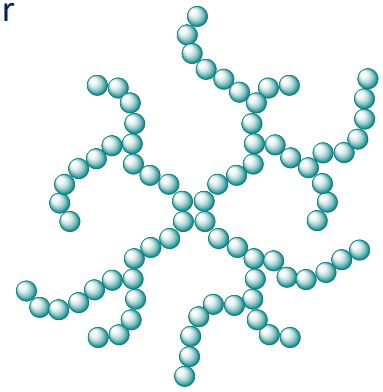


Cyclic



Linear

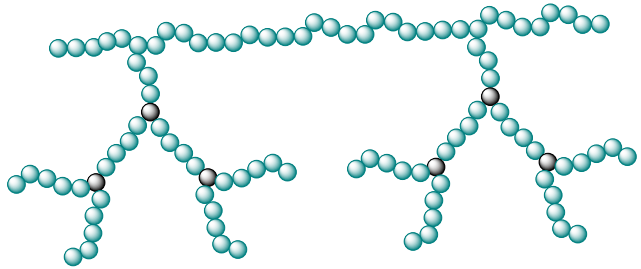
Architecture



(Hyper)branched

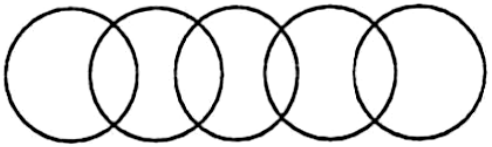
or dendrimers

Dendronized chain

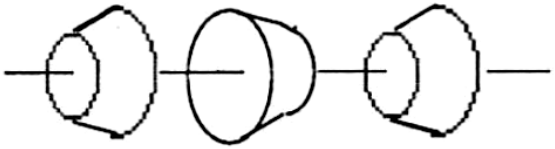


1. Constitution

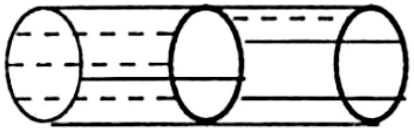
Higher constitution dimensions



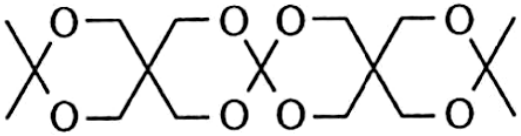
Polycatenane



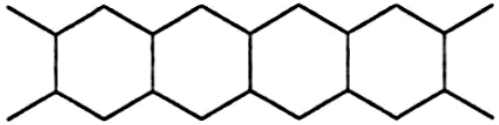
Polyrotaxane



Polymer tube



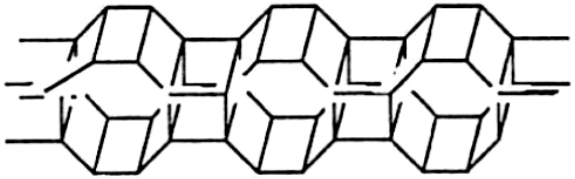
Spiro chain



Ladder polymer

Double helix

Spheroidal protein



Double ladder

Spherical molecule

Phyllo polymers- usually called layer or parquet polymers, form two-dimensional lattices- **Graphene**

Higher constitution dimensions

COMMUNICATIONS CHEMISTRY

ARTICLE

https://doi.org/10.1038/s42004-019-0180-x OPEN

One-pot synthesis of cyclodextrin-based radial poly [n]catenanes

Taishi Higashi[1,2,3], Kentaro Morita[2], Xia Song[3], Jingling Zhu[3], Atsushi Tamura[4], Nobuhiko Yui[4], Keiichi Motoyama[2], Hidetoshi Arima[5] & Jun Li[3]

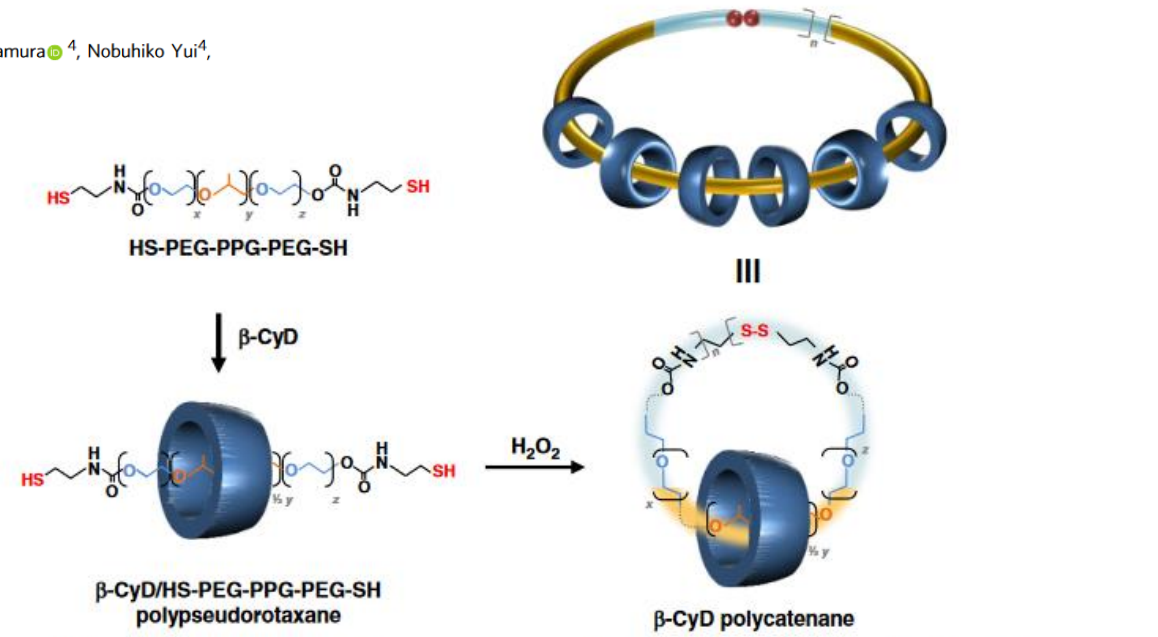


Fig. 1 Preparation of a β-CyD-based polycatenane. To remove the remaining polypseudorotaxane and free HS-PEG-PPG-PEG-SH and β-CyD, the crude product was dissolved in DMSO and washed with water and acetone

Commun Chem **2,** 78 (2019). https://doi.org/10.1038/s42004-019-0180-x

Higher constitution dimensions

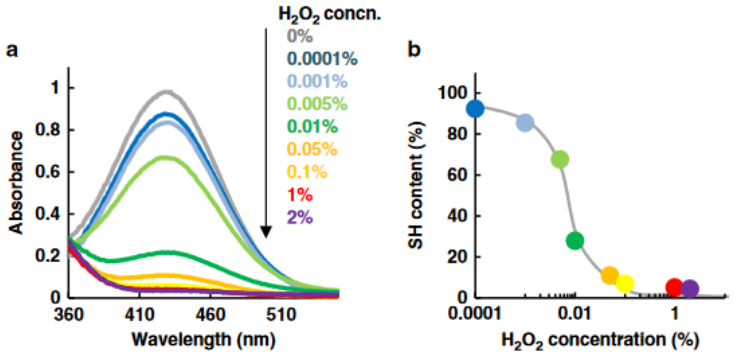


Fig. 2 Thiol-group content in the reaction suspensions. **a** Absorbance of 2-nitro-5-thiobenzoic acid and **b** thiol-group content in suspensions obtained by treating the prepared polycatenane with H_2O_2 solutions of varying concentration

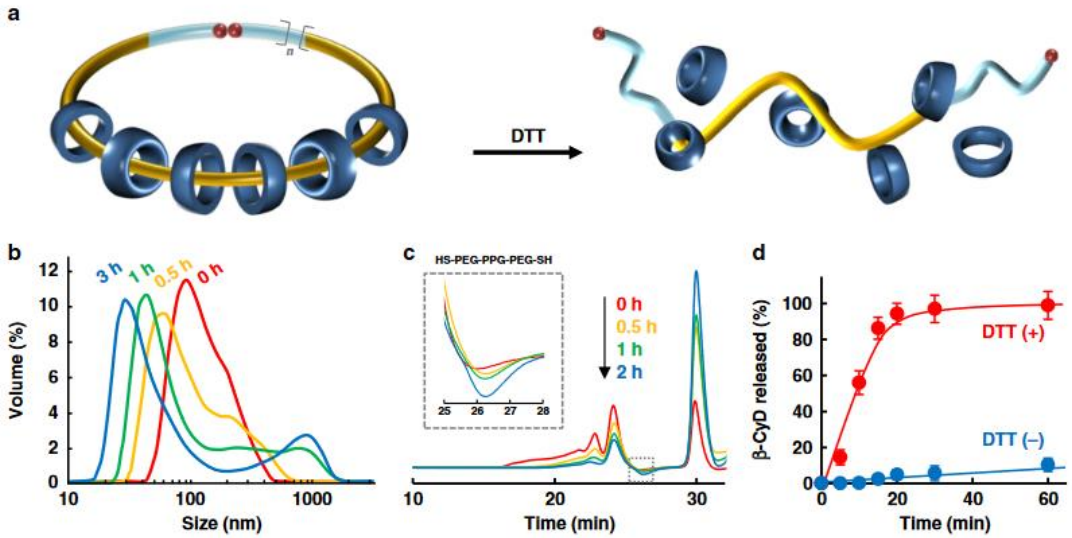


Fig. 4 Release of β-CyD from the polycatenane. **a** Schematic release of β-CyD from a polycatenane upon reduction. **b** Particle size distributions of β-CyD polycatenanes in the presence of DTT. **c** GPC profiles of β-CyD-based polycatenanes after treatment with DTT. **d** β-CyD-release profiles from polycatenanes in the absence/presence of DTT. Each data point corresponds to the mean ± standard error of three experiments

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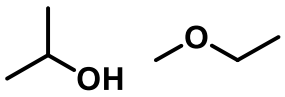
2. Chemical configuration. Basic Terms

Isomers

Same molecular formula- different compounds

Constitutional

Same formula, different connectivity

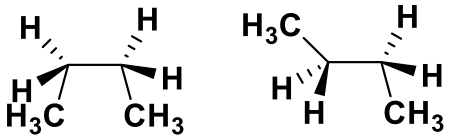


Stereoisomers

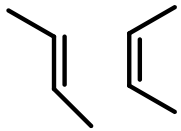
Same formula, same connectivity, different arrangement

Configurational

Conformational



Geometric



Trans/cis

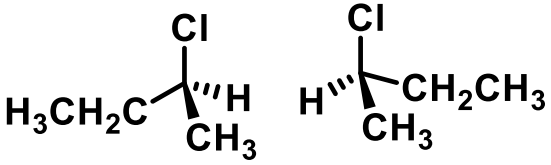
Optical

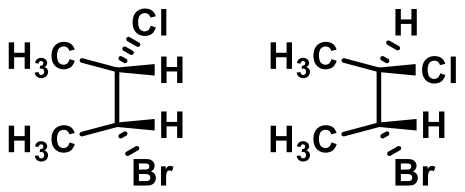
Enantiomers

mirror images

Diastereomers

not mirror images





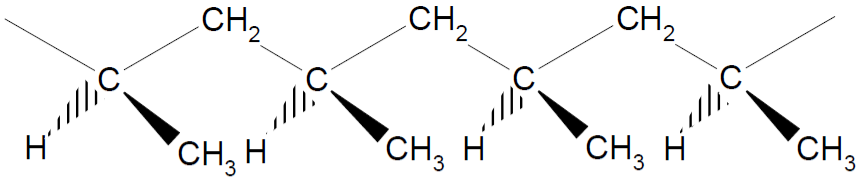
2. Chemical configuration Statistics

Configurational isomers- a large energy barrier (Isotactic/Syndiotactic or cis/trans)

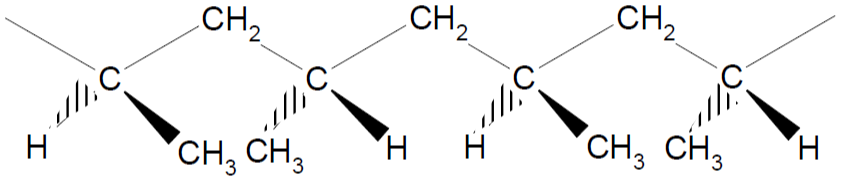
Conformational isomers- a low energy barrier, they are interconverted rapidly into each other

Configurational statistics (1940s)

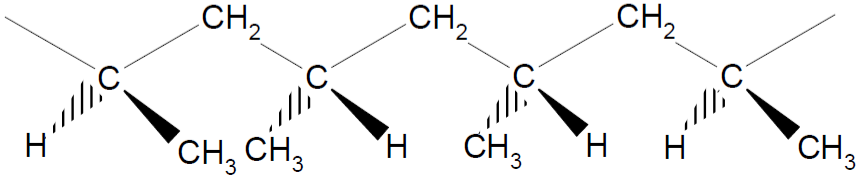
Isotactic



Syndiotactic



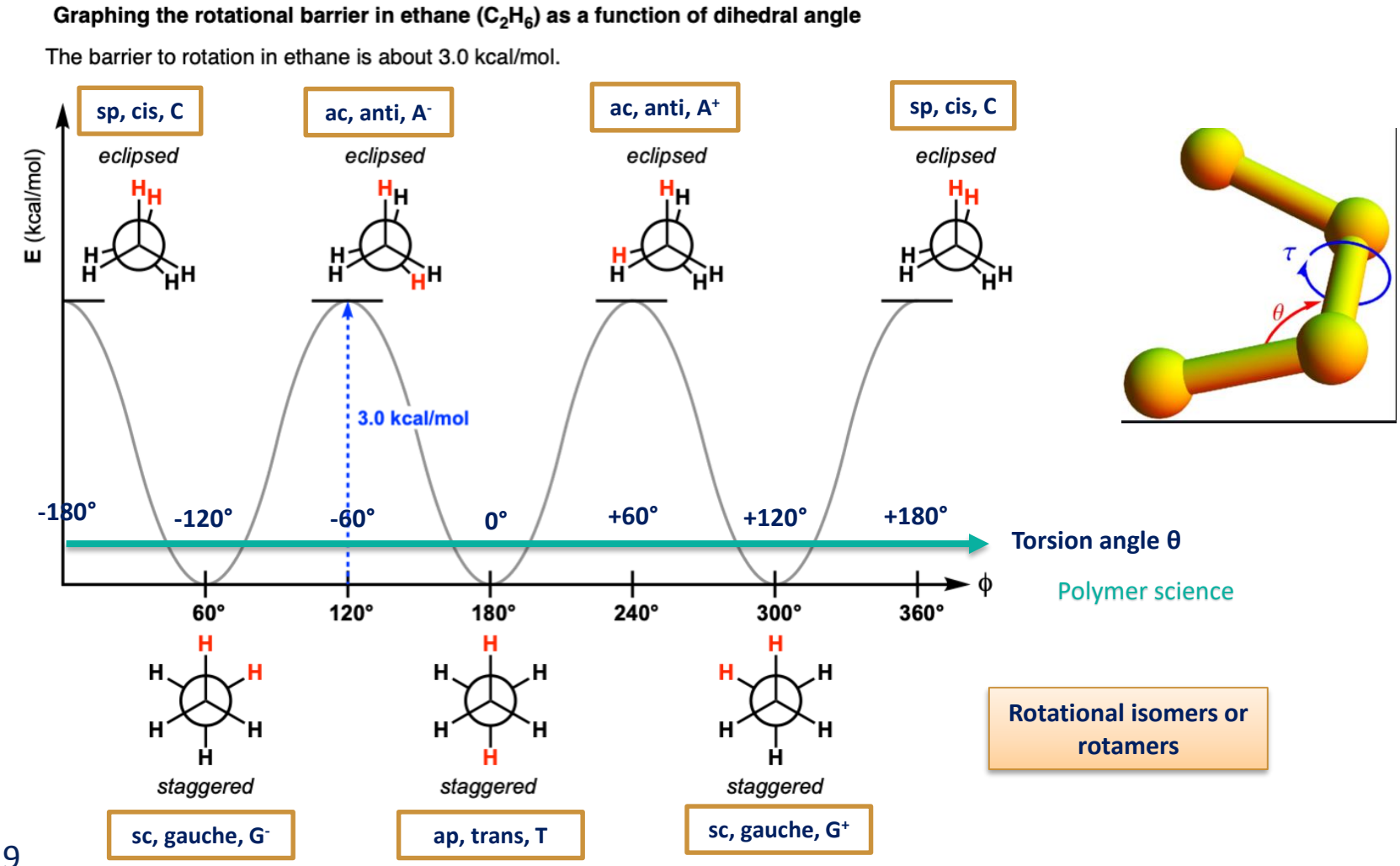
Atactic



3. Microconformations

Local Conformations

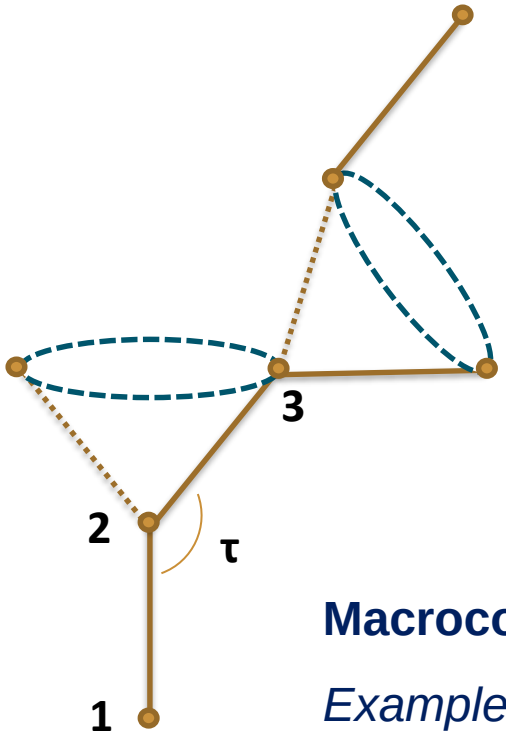
Torsion angle θ (conformational angle, rotational angle, dihedral angle)



Polymer science

Rotational isomers or rotamers

3. Microconformations



- **Prefered positions** are **microconformations**
- **Repeating sequences of microconformations** defining the **macroconformation**
- Very slow changes in crystalline state
- Very fast changes in dilute solution
- **Persistence** of prefered conformation

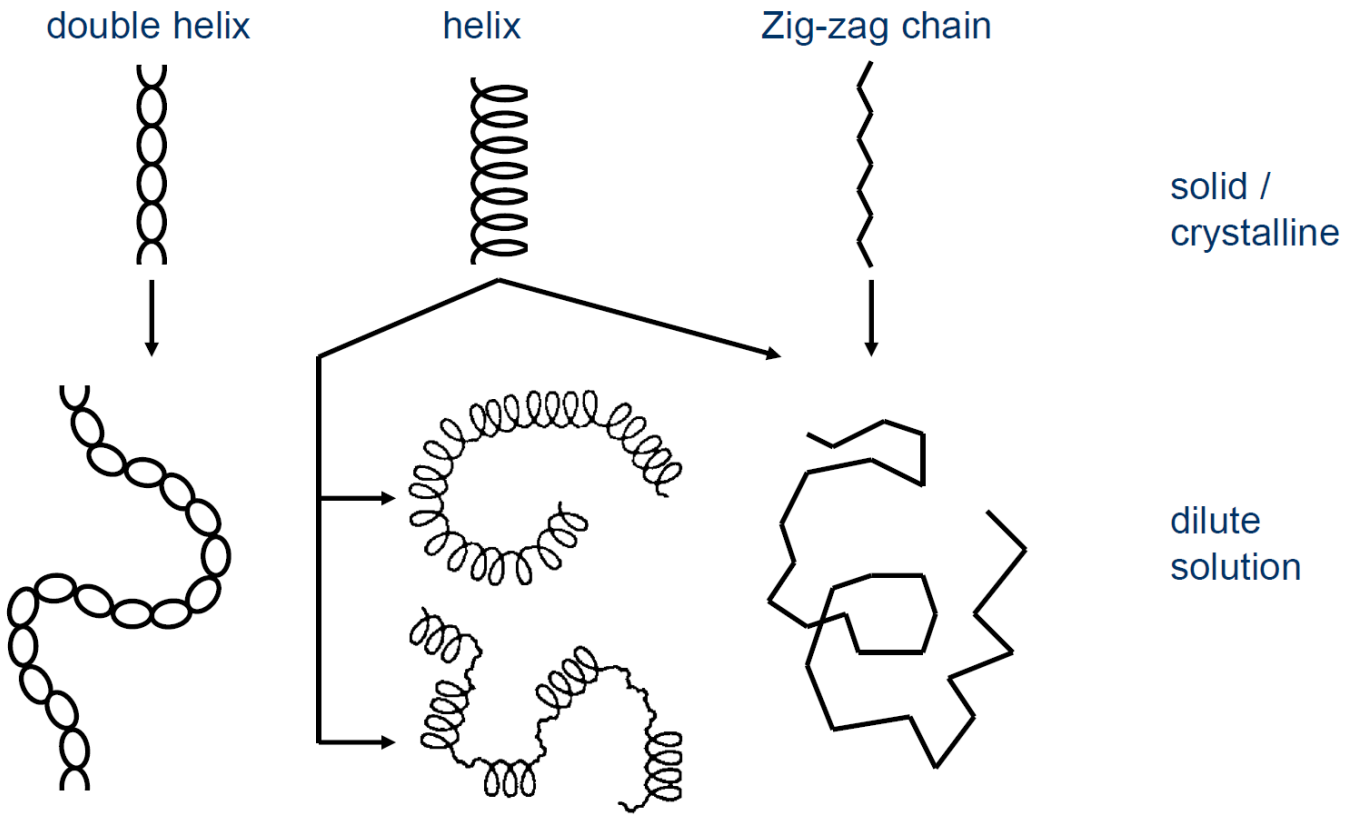
Macroconformations:

Examples: spheroidal proteins, rod like nucleic acids, stabilised by internal interactions constitution

Chemistry (configuration/constitution) → **Microscopic properties** → **Macroscopic properties**

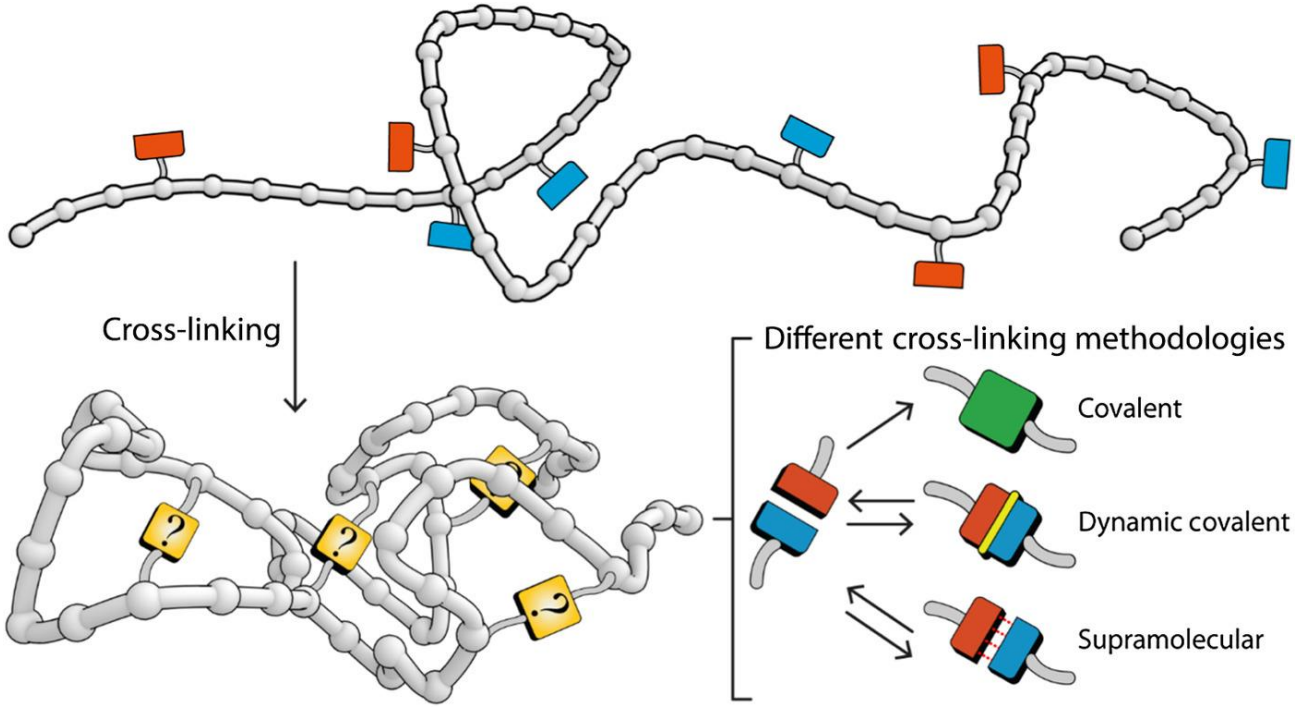
4. Macroconformations

The shape of an isolated macromolecule is determinated by its molecular conformation (= macroconformation) which in turn depends on the type, proportion, and sequence of microconformations within the molecule.



4. Macroconformations

Nature has unparalleled control over the conformation and dynamics of its folded macromolecular structures. Nature's ability to arrange amino acids into a precise spatial organization by way of folding allows proteins to fulfill specific functions in an extremely efficient manner. Chemists and materials scientists have used the delicate structure–function relationships observed in proteins to elucidate nature's design principles.



4. Macroconformations

The ideal chain

No correlation between polymer monomers separated by long distances along the polymer.

- Short range correlations between neighboring monomers are not excluded
- Ideal chain models do not take interactions caused by conformations in space into account
- Ideal chains allow the polymer to cross itself

Modeling a polymer

Imagining a blown up picture of a section of the polymer in a certain conformation, could look like this:

a) **Conformations:**

Torsion angle **θ**

Bond angle **τ**

b) **Bond vectors:**

Starting from one end we use vectors r_i to represent the bonds

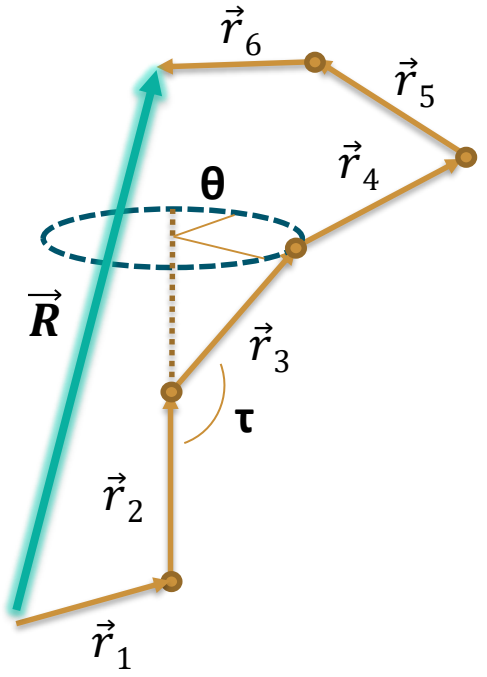
c) **End-to-end vector:**

The sum of all bond vectors

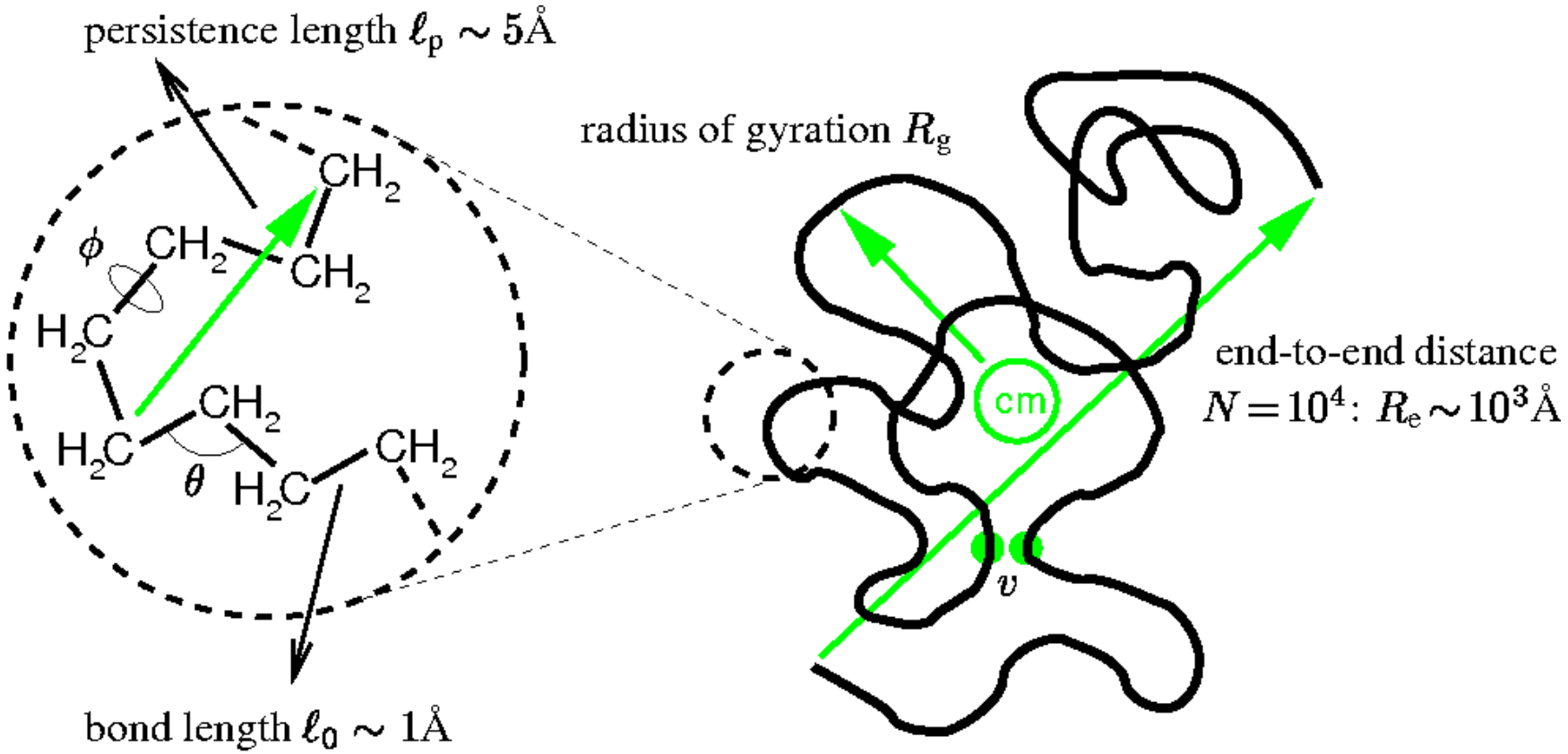
The ensamble average of $\langle \vec{R}_n \rangle = 0$ due to isotropy $\quad \vec{R}_n = \sum_{i=1}^{n} \vec{r}_i$

d) **Mean square end-to-end distance:**

Simplest non-zero average $\quad \langle R^2 \rangle = \langle \vec{R}_n * \vec{R}_n \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i * \vec{r}_j \rangle$

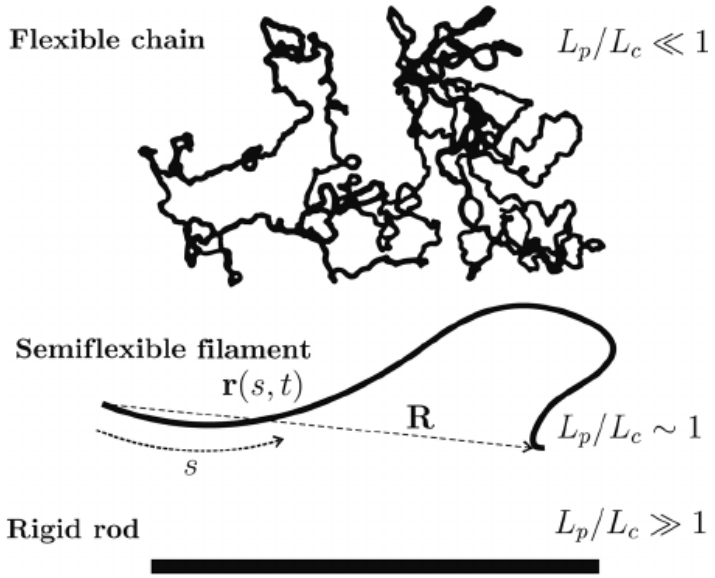


4. Macroconformations

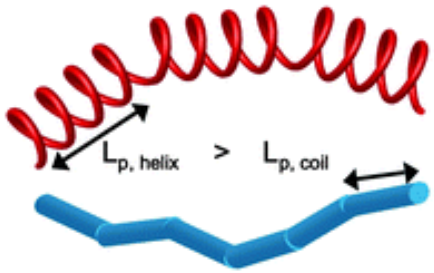


4. Macroconformations

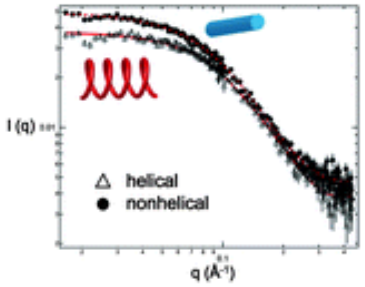
Single chain



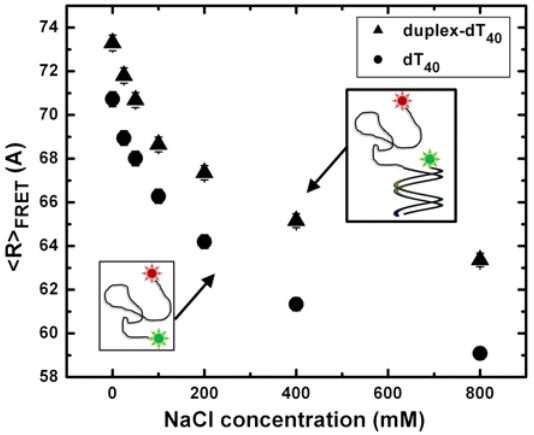
Helical chain



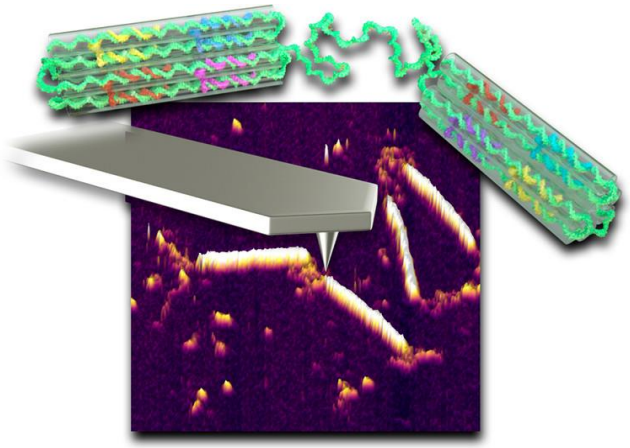
SANS



Ionic strength-dependent persistence lengths of single-stranded RNA and DNA



Measuring the Conformation and Persistence Length of Single-Stranded DNA Using a DNA Origami Structure

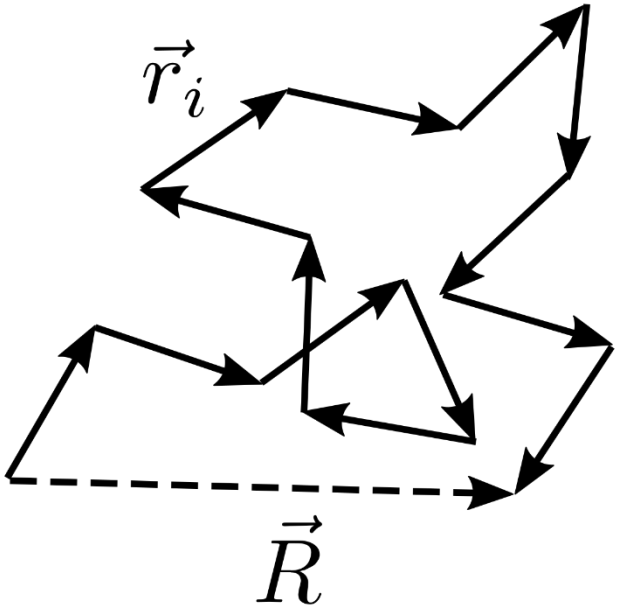


Nano Lett. **2018**, 18, 11, 6703–6709

4. Macroconformations

Freely jointed chain — Kuhn 1934

The **end-to-end distance** is the **distance** between the first particle and the last particle of one molecular chain. It has no physical meaning for cyclic or branched molecules.



It can be only determinated experimentally for chains with specially marked end groups (fluorescent groups).

Undisturbed dimension (θ state)

No correlation between the directions of different bond vectors. θ and τ are free to rotate. All bond vectors have: l_s (segment lenght) and n_s (number of segments), R (end-to-end distance)

$$\langle \vec{R}^2 \rangle = \langle \vec{R}_n * \vec{R}_n \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i * \vec{r}_j \rangle$$

$$\langle \vec{r}_i * \vec{r}_j \rangle = \langle l_s l_s con\tau_{ij} \rangle \rightarrow \langle \vec{R}^2 \rangle = l_s^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle con\tau_{ij} \rangle$$

No correlation between different bond vectors, i≠j

$$\langle \vec{r}_i * \vec{r}_j \rangle = \langle \vec{r}_i \rangle * \langle \vec{r}_j \rangle = 0$$

$$\langle R^2 \rangle = n_s l_s^2$$

Maximum R- the most probable end-to-end distance Kuhn segment

$$L_k = R_{max} = n_s l_s$$

$M \sim n_s \qquad \langle R^2 \rangle \sim M$

4. Macroconformations

Freely rotating chain and characteristic ratio (C_∞)

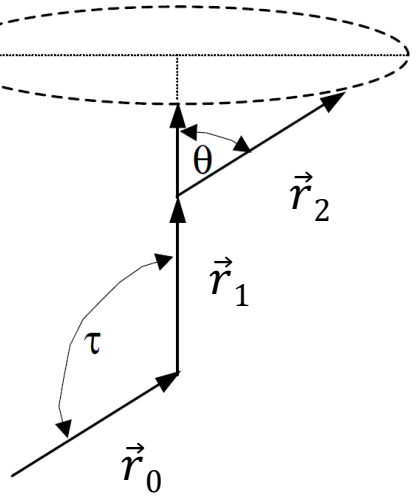
Bond angle τ is fixed. Torsion angle θ still free to rotate.

$$\langle \vec{R}^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i * \vec{r}_j \rangle \quad ==> \langle \vec{r}_i * \vec{r}_j \rangle = ?$$

Ex: What is the correlation between vector $\vec{r}_3$ *and* $\vec{r}_0$?

Due to the free rotation around the torque angle, only the perperdicular component of r_3 is paased down.

$$\langle \vec{r}_3 * \vec{r}_0 \rangle = l_{cc} \langle con\tau \rangle^2 * l_{cc} \langle con\tau \rangle = l_{cc}{}^2 \langle con\tau \rangle^3$$



The general expession becomes:

$$\langle \vec{r}_i * \vec{r}_j \rangle = lcc^2 \langle con\tau \rangle^{|i-j|}$$

$$\langle R^2 \rangle_{0f} = n_{cc} l_{cc}{}^2 \frac{1 - cos\tau}{1 + cos\tau}$$

Restricted rotation

$$\langle R^2 \rangle_{0r} = n_{cc} l_{cc}{}^2 \frac{1-cos\tau}{1+cos\tau} \frac{1+cos\theta}{1-cos\theta}$$

$$\frac{\langle R^2 \rangle_{0r}}{\langle R^2 \rangle_{0f}} = \frac{1+cos\theta}{1-cos\theta} = \frac{1+cos\ 70{,}5}{1-cos 70{,}5} \approx 2$$

$$\frac{\langle R^2 \rangle_{0r}}{\langle R^2 \rangle_{0f}} = \sigma^2$$ **σ restriction parameter**

C_∞ is called Flory's characteristic ratio, and can be seen as a measure of the stiffness of the polymer in a given ideal chain model.

$$\langle R^2 \rangle = n_{cc} l_{cc}{}^2 C_\infty$$

4. Macroconformations

Freely rotating chain and characteristic ratio

Polymer	Solvent	T (°C)	C_∞	l_s/l_{CC}	σ
at-Polystyrol	cyclohexane	34	10.2	12	2.3
at-Polypropylen	diphenylether	153	5.3	6.5	1.61
Polyisobutylen	benzene	24	6.6	8.0	1.80
at-Polymethylmethacrylat	different	4 - 70	6.9	8.4	2.08
at-Polymethylmethacrylat	butyl chloride	35	7.2	8.8	1.74
Polysimethylsiloxan	2-butanone	20	6.2	-	1.39
Polyvinylchlorid	benzyl alcohole	155	9.2		2.08
Polyethylen	diphenyl methane	142	6.7	8.2	

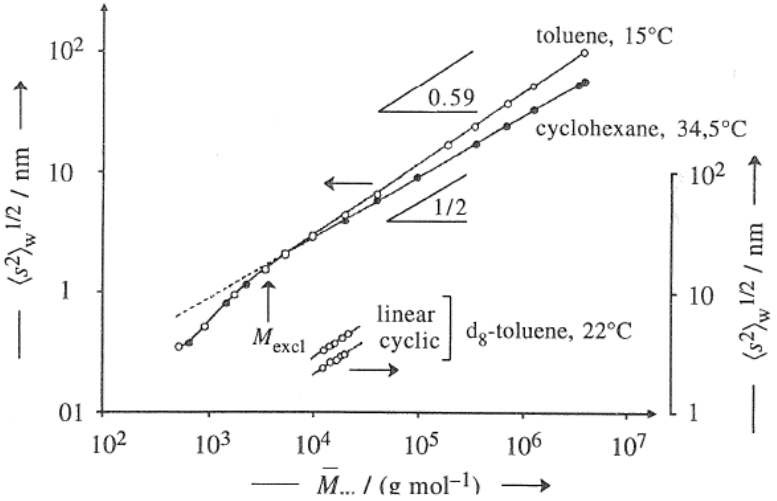
$l_{C\text{-}C}$ = length of C-C bond

4. Macroconformations

Scaling of the Radius of Gyration

$\langle s^2 \rangle$ scattering methods deliver the average square of the **radius of gyration**

$\langle R^2 \rangle$ not easy to determine; problems in case of branching —**end-to-end distance**



S center of mass; s_i distance center of mass-segment; r_{ij} distance segment-segment

$$\langle s^2 \rangle_0 = \frac{1}{2n^2} \sum_i \sum_j r_{ij}^2 = \frac{1}{n+1} \sum_i s_i^2$$

For n > > 10 $\langle s^2 \rangle_0 = \frac{\langle R^2 \rangle_0}{6}$ Θ state

$$\langle s^2 \rangle = \frac{\langle R^2 \rangle_0}{(2+\varepsilon)(3+\varepsilon)}$$

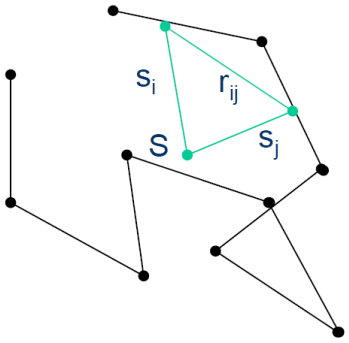
$$\langle s^2 \rangle \sim M^{2\nu}$$

$\varepsilon = 2n - 1$, *depends on the quality of the solvent*

$$\langle s^2 \rangle^{1/2} \sim M^{\nu}$$

$$\langle s^2 \rangle = R_g$$

Radius of Gyration



Unperturbed chain ➔ $\nu = 0.5$

1. Polymer chain is collapsed onto itself and is very dense object ➔ $\nu = 0.33$

2. Polymer chain is in a solution and the polymer prefers the solution to itself, thermodinamically good solvent ➔ $\nu = 0.60$

3. Polymer chain is rod-like ➔ $\nu = 1.00$

4. Macroconformations

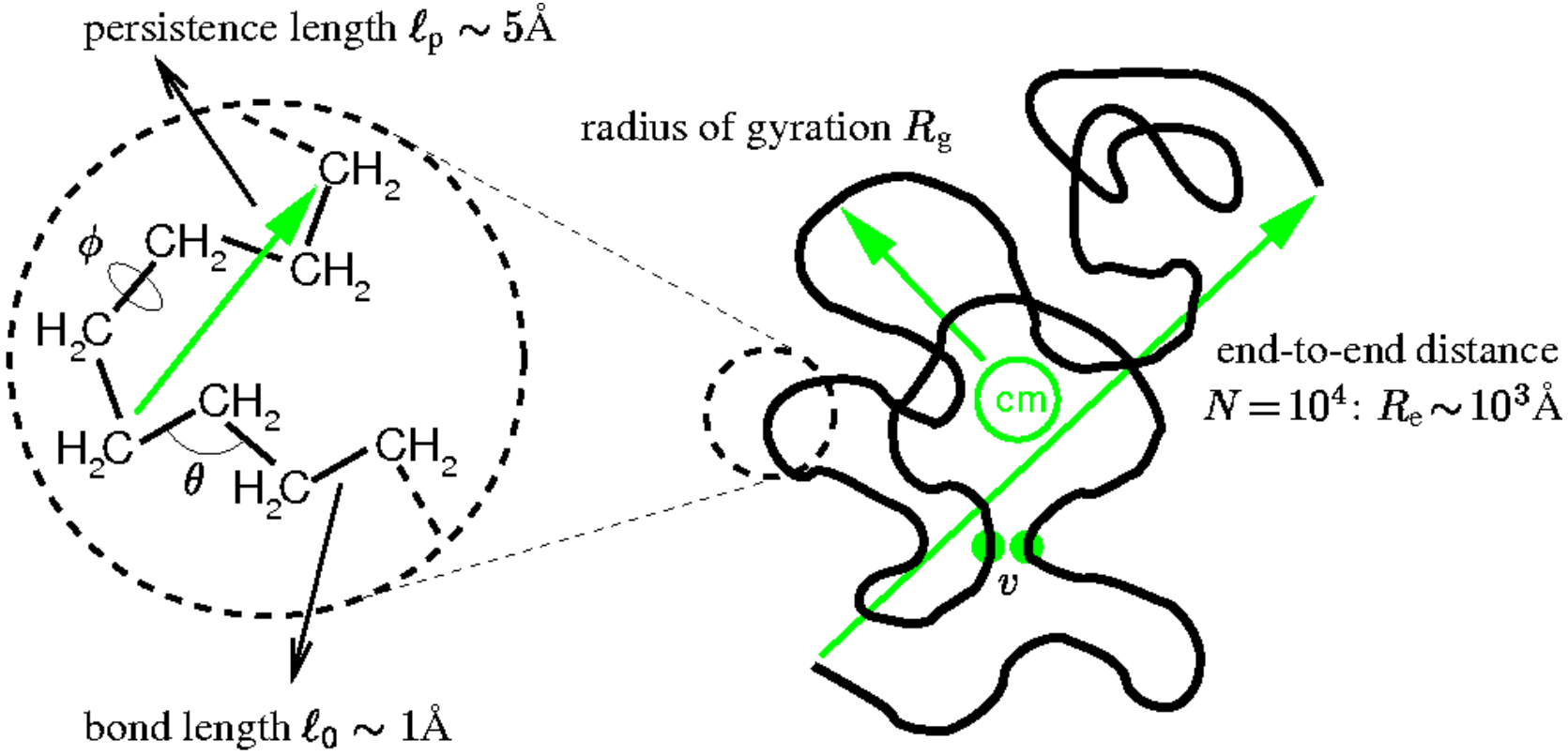
Radius of gyration and molar mass

Shape of macromolecule	Characteristic dimension – radius of gyration	Characteristic dimension – molecular weight
unperturbed coil	$\langle h^2 \rangle_o = 6 \langle r^2 \rangle_o$	$\langle h^2 \rangle_o \sim M$
random coil, good solvent	$\langle h^2 \rangle = (2 + \varepsilon)(3 + \varepsilon) \langle r^2 \rangle$	$\langle h^2 \rangle \sim M^{1+\varepsilon}$
thin rod, length L	$\langle L^2 \rangle = 12 \langle r^2 \rangle$	$L \sim M$
hard sphere, radius R *)	$\langle R^2 \rangle = (5/3) \langle r^2 \rangle$	$R \sim M^{1/3}$
disc, radius R	$\langle R^2 \rangle = 2 \langle r^2 \rangle$	$R \sim M^{1/2}$

$\langle R^2 \rangle_0 = 6 \langle s^2 \rangle_0$ $\langle R^2 \rangle_0 \sim M$

end-to-end distance radius of gyration

4. Macroconformations



➔ Conformational analysis and estimation of the persistence length of DNA using **atomic force microscopy** in solution DOI: 10.1039/c0sm01160f

➔ Flexibility of single-stranded DNA measured by single-molecule FRET https://doi.org/10.1016/j.bpc.2014.08.004

4. Macroconformations

The dynamics of solvation dictates the conformation of polyethylene oxide in aqueous, isobutyric acid and binary solutions

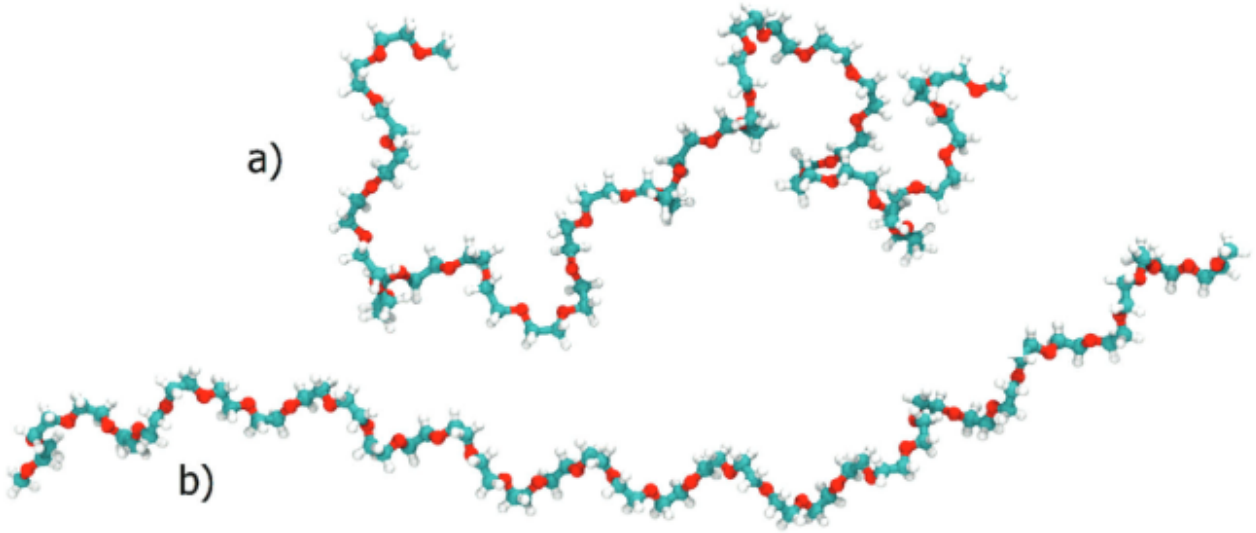


Fig. 1 Simulation snapshots of typical PEO (n = 36) conformation in (a) water and (b) isobutyric acid. Solvent is not shown. Carbons, oxygens and hydrogens are shown in cyan, red and white, correspondingly.

Table 1 The average end-to-end distance, R_{end}, radius of gyration, R_g, aspect ratio, R_{end}/R_g, and asphericity (eqn (1)) for PEO in different solvents

Solvent	R_{end} (nm)	R_g (nm)	R_{end}/R_g	Asphericity (nm^2)
Hexane	1.61 ± 0.6	0.75 ± 0.08	2.15 ± 0.78	0.21 ± 0.13
Benzene	3.08 ± 1.3	1.30 ± 0.30	2.32 ± 0.71	1.18 ± 0.87
Water	3.42 ± 1.0	1.35 ± 0.19	2.50 ± 0.51	1.31 ± 0.62
Isobutyric acid	5.95 ± 0.46	2.07 ± 0.08	2.87 ± 0.22	3.50 ± 0.70

DOI: 10.1039/c7cp00526a

4. Macroconformations

Size, shape, and structure. Gyration tensor and measures of asphericity

SIZE: How large or how long is the polymer chain?

SHAPE: What does the polymer chain look like?

STRUCTURE: How order/disorder the system is?

Isotropic system: no differences in dimension $R_g^2 = R_x^2 + R_y^2 + R_z^2$

Anisotropy system ➔ no differences in dimension, **gyration tensor**
Desviation form the ideal sphere

ASPHERICITY VALUE $$< A > = 1/2 \frac{\Sigma < (R_{gi}^2 - R_{gj}^2) >}{(< \Sigma R_{gi}^2 >)^2}$$

Higher A, higher anisotropy

$< A > = 0$ **Perfect sphere** $R_{g1} = R_{g2} = R_{g3}$

$< A > = 1$ **Perfect rod** $R_{g1} = R_g$ $R_{g2} = R_{g3} \sim 0$

4. Macroconformations

Size, shape, and structure. Gyration tensor and measures of asphericity

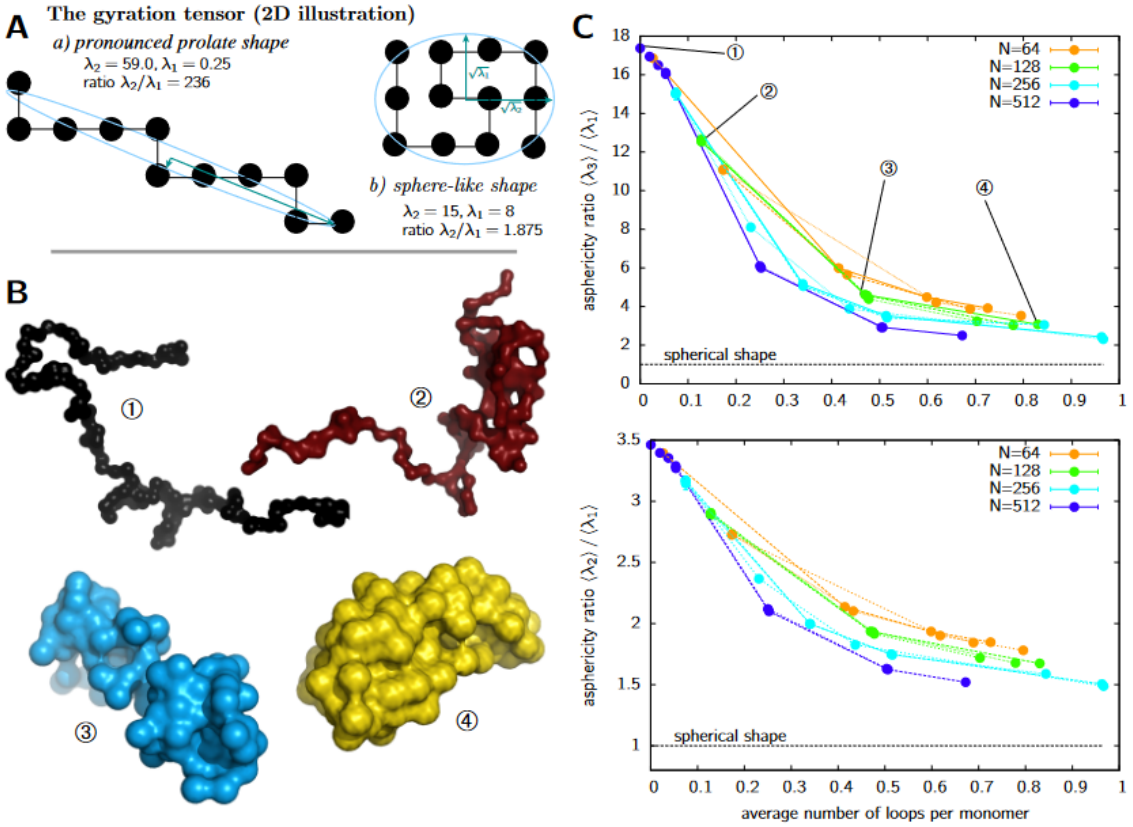
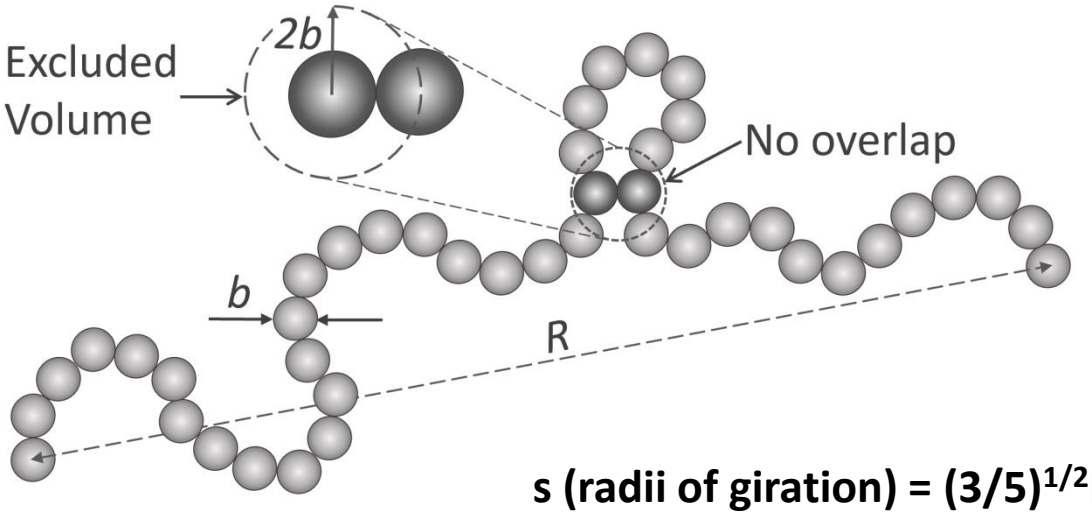


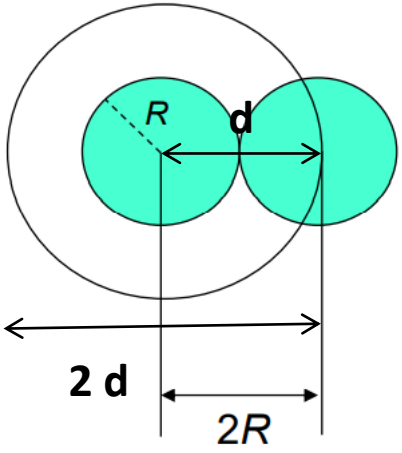
Figure 6: **Elongated shape of the chromatin model polymers. A.** Illustration of the gyration tensor. The gyration ellipsoid is shown for an elongated and a compact polymer conformations in two dimensions. The ratio λ_2/λ_1 is large for the elongated polymer, indicating strong devations from a sphere-like shape. **B.** Example conformations for a chain of length $N = 128$ and loop lifetime τ_1 (see eq. **??**) for different looping probabilities. The shown conformations are one sample of the ensemble of conformations belonging to the data point marked in figure C. **C.** The ratios between the gyration tensor's main axes. The upper graph shows the ratio between the largest and smallest main axis, the lower graph the ratio between the second largest and smallest main axis. The data is shown for chain length up to $N = 512$, different lifetimes of the loops ($\tau = \tau_1$ solid line, $\tau = \tau_2$ dotted line, $\tau = \tau_3$ dashed line) and different looping probabilities p.

doi: 10.3389/fgene.2013.00113

4. Macroconformations

Volume excluded – hard sphere





s (radii of giration) = $(3/5)^{1/2}$R

$$V_e = \frac{4}{3}\pi\ (2R)^3$$

u (excluded volume) = $4\pi d^3/3 = 32\pi R^3/3 = 8V$

Collects all interactions on an inter- and intramolecular level

5. Example questions

- Define end-to-end distance, radius of gyration and persistence length

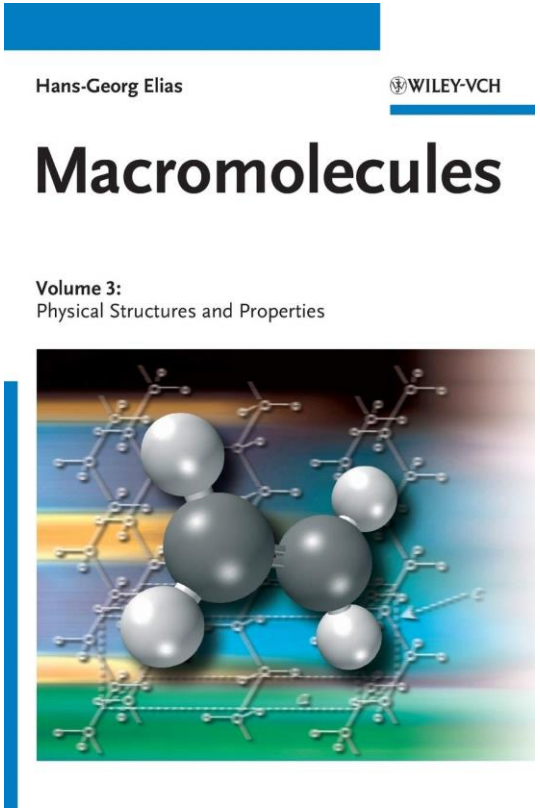
- Polystyrene with molar mass 5×10^5 g/mol has $\langle h^2 \rangle_o = 300$ nm^2, calculate $\langle h^2 \rangle_o$ for a PS with molar mass of 1×10^6 g/mol; calculate $\langle r^2 \rangle_o$ for both molar masses

- How can you measure $\langle r^2 \rangle_o$?

- How can you measure persistence length?

6. Recommended Books

Macromolecules
Volume 3: Physical Structures and Properties
Hans-Georg Elias
Wiley-VCH GmbH & Co. KGaA, Weihnheim 2008



Polymer Solutions
An introduction to physical properties
Iwao Teraoka
Wiley-Interscience 2002