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Course Notes of Chapter 2

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1. Introduction: What is the “Size” of a Polymer Chain?

The remarkable properties of polymer materials are due to the large size of the constituting macromolecules, but how can we express this size? In the case of a simple aliphatic chain like polyethylene (PE), where all the catenary bonds are exclusively carbon-carbon single bonds, the enthalpically most stable conformation is a "zig-zag" conformation, with a fixed torsion angle $\varphi = 180°$ between the C-C bonds (Slide 68). This is the "**contour length**", equal to $n \times l$, in the case of a freely jointed chain, where n is the number of catenary bonds and l is the bond length. For large n, however, this zig-zag conformation is highly improbable: driven by entropy, ideal polymer chains preferably fold into random coil structures because of variations in the torsional angle. It is therefore more useful to consider the average size of this coil (the average size in time or over a very large number of chains). But which would be the best measurement for this size?

2. Polymer Chain Conformations

A chain can adopt different conformations due to low energetic barriers for the rotation around covalent single bonds. A long, stretched chain brought into contact with a solvent, for example, will quickly adopt a "random conformation". At a finite temperature, the solvent molecules will transfer their kinetic energy to the chain by literally hitting it. In a few picoseconds the zig-zag conformation will be completely lost, and the chain will form a "ball", which will continue to change shape passing from one random conformation to another at the picosecond time scale (therefore it is necessary to anchor the chains to a substrate to make an AFM image such as shown on Slide 12).

2.1 The mean square (root mean square) end-to-end distance of a freely jointed linear chain

The **end-to-end distance**, R_n, and the **radius of gyration**, R_g (by definition, the moment of inertia of a chain with mass M around its center of mass is equal to MR_g^2; R_g is therefore effectively the radius of the sphere occupied by the random coil.) are equivalent measures of the polymer chain size (Slides 70 and 74). **How can we express R_n and R_g in terms of the parameters n and l?**

To simplify the discussion of polymer chain conformations, we will first forget about torsional and bond angles and consider an ideal chain with free joints, where all catenary bonds are identical, and a given bond can take any orientation in relation to its neighbor bonds.

Let $\vec{R}_n$ be the vector which connects the two ends of a linear chain with n identical free joints in random conformation, going from the end associated with the first link 1 to that associated with the nth and last link.

Let $\vec{a}_i$ be the vector which represents the orientation and the length $|\vec{a}_i| = a$ of the ith link (which is between the i - 1st and the i + 1st link).

$$\vec{R}_n = \vec{a}_1 + \vec{a}_2 + \cdots \vec{a}_i + \cdots \vec{a}_n = \sum_1^n \vec{a}_n \qquad (1)$$

Since the orientation of $\vec{R}_n$ changes randomly, its average (in time or over a large number of identical chains) is 0. However, the square of the average distance between the two ends is a scalar quantity:

$$\begin{aligned}\langle \vec{R}_n^{\,2} \rangle &= \langle (\vec{a}_1 + \vec{a}_2 + \cdots \vec{a}_i + \cdots \vec{a}_n) \cdot (\vec{a}_1 + \vec{a}_2 + \cdots \vec{a}_i + \cdots \vec{a}_n) \rangle \qquad (2)\\ &= \langle \sum_{i=1}^n \vec{a}_i \cdot \vec{a}_i + \sum_{i\neq j}^n \vec{a}_i \cdot \vec{a}_j \rangle\\ &= na^2 + \langle \sum_{i\neq j}^n \vec{a}_i \cdot \vec{a}_j \rangle\\ &= na^2 + a^2 \langle \sum_{i\neq i}^n \cos\theta_{i,j} \rangle\end{aligned}$$

where $\theta_{i,j}$ is the angle between $\vec{a}_i$ and $\vec{a}_j$. It can take any value between 0 and 2π in a freely jointed chain. But the mean of $\cos\theta$ between 0 and 2π is 0. So,

$$\langle \vec{R}_n^{\,2} \rangle = na^2 \qquad (3),$$

and the "root mean square" (or the "geometric mean" or even the "quadratic mean"), which we simply call R_n is therefore

$$R_n = \sqrt{n}a \equiv \sqrt{n}l \qquad (4).$$

In other words, **the average square distance between the ends of a linear chain with identical free joints, and therefore the average "size" of the coil formed by this chain, is equal to the root of the number of bonds multiplied by the bond length**. This result, which must be engraved into the heart of any polymer scientist, is **a key result for the physical properties of polymers** which we will come back to a lot throughout our course. Moreover, because the distribution of R_n is governed by a Gaussian distribution function, an ideal polymer chain is often referred to as a **Gaussian chain**. Note that we often use l instead of a for the length of the bond in these equations. Sorry for the inconsistency, but this is just so…

Another way to specify the size of the coil is to use its radius of gyration, R_g. One can show "easily" (Slide 74) that

$$R_g = \frac{R_n}{\sqrt{6}} \qquad (5).$$

Indeed, this relation remains valid for large n regardless of the applied ideal chain model, and these two quantities thus intervene in the same way in the physical properties.

2.2 The "Rigidity" of a Chain

A real chain has fixed bond angles. Thus, the angle α will be 180° – 110° ≈ 70° for polyethylene (Slide 75). We can approach a little more towards a real chain with identical catenary bonds if we admit a constant value for α, but that the "**torsion angle**" ϕ, which is defined by the bonds $\vec{a}_{i-1}$ to $\vec{a}_{i+1}$, can take any value between 0 and 2π. We call this a "freely rotating chain". With this improved model, it can be "easily" shown again that

$$R_n = \sqrt{n\frac{1+\cos\alpha}{1-\cos\alpha}}a \equiv \sqrt{n\frac{1+\cos\alpha}{1-\cos\alpha}}l \qquad (6).$$

Note that for a reasonable choice of α (between 0 and 90 ° or π/2 therefore), the value of R_n given by Equation 6 will always be greater than that given by Equation 4.

More generally, whenever we restrict the freedom of bond movements, we tend to increase R_n, but we can always write it as

$$R_n = \sqrt{C_\infty n}a \qquad (7).$$

where C_∞**, which is normally greater than 1, is the "stiffness" of the chain. We see that the chain always behaves like a chain with free joints, and therefore this model has a certain generality.** Some examples of C_∞ are shown on Slide 78 for real polymers in solution. C_∞ varies considerably, even for vinyl-type chains (PE, PP, PS) containing only catenary C-C single bonds where α is *a priori* identical at approximately 70° in each case.

Slide 79 provides some explanations for these differences. Indeed, due to steric constraints on the torsion angle, ϕ tends to adopt values, for which the atoms that are not directly linked by the bond in question are placed as far away as possible (staggered conformations, see Slide 67). These values correspond to the *trans* position (most favorable in PE) and to the two gauche$^-$ and gauche$^+$ positions. This is the basis of the model with “hindered rotations” ("rotational isomeric states"), where a potential energy is assigned to each position, which makes it possible to calculate the probability of finding a given bond in these different conformations. Thus, in the presence of large side groups such as -CH_3 (PP) or, even more, a benzene group (PS), certain positions will be disfavored by increasing their potential energy. PS is therefore much more rigid than PP, which in turn is slightly more rigid than PE.

The angle α can also vary depending on the type of polymer. Consider, for example, a chain of benzenes linked by bonds in the *para* position. Here the angle α is effectively $\pi/2$. Why? What is the stiffness of the chain according to Equation 6? And what would R_n be? In fact, R_n must be equal to na in this case. The problem here is that the freely rotating chain model only works if the chain is long enough, i.e. if there are values of i and j sufficiently far apart for the correlation between $\bar{a}_i$ and $\bar{a}_j$ to tend towards 0. However, if $\alpha = \pi/2$, this is not possible, even if n is infinite.

In general, the chemical structures of polymers are much more complex than a simple chain of identical bonds and it is necessary to take the existence not only of the different bond lengths but also of the different bond angles into account, which leads to expressions for rather complicated R_n (see a book by Mattice and Suter (ETHZ): *Conformational theory of large molecules: the rotational isomeric state model in macromolecular systems*). Nevertheless, we can say qualitatively that **the presence of rigid catenary bonds will always increase the rigidity of a chain compared to a simple chain like PE (double bonds, conjugated systems, or bulky groups likely hinder the rotations of the catenary bonds, as well as specific intra-chain interactions such as hydrogen bonds)**. Unfortunately, the effective value of C_∞ also depends on the definition of the connection and therefore on its length. So, even though bisphenol A polycarbonate contains benzene units in its main chain and should *a priori* show a high rigidity, its C_∞ value is very low. Try Exercise 1.7 if you want to know why.

3. Real Polymer Chain Behavior

For real polymer chains, interactions and the own volume of polymer chain segments can no longer be disregarded. Because the monomer segments of a real chain have a finite volume, they cannot occupy the same spot in space. Real polymer chains may therefore be better mapped onto a **self-avoiding random walk**, where each monomer unit blocks the space for other monomer units and causes part of the volume to be **excluded volume**. The chain has therefore less conformational freedom and must expand in comparison to the random coil of an ideal chain (Slide 83).

Moreover, the monomer segments of a real chain display interactions among themselves and with their surrounding (solvent molecules, for instance). Those interactions can be attractive or repulsive, but we will focus our consideration on attractive monomer-monomer and attractive monomer-solvent interactions. In case of equal monomer-monomer and monomer-solvent interactions, the effective monomer-monomer interaction will be zero (monomeric units can't distinguish between other monomer units and solvent molecules), a scenario that can be described with the help of a hard-sphere potential. It is more common that the attraction between monomers is stronger than that between monomer and solvent due to the perfect structural match of two monomer units. The net monomer-monomer interactions are then attractive as long as they do not get too close to each other (Lennard-Jones potential).

We continue by calculating the probability of finding two monomeric units at a certain distance r using the Boltzmann distribution and its normalized form, the *Mayer f-function* (Slide 85), whose negative integral corresponds to the excluded volume. **The excluded volume quantifies the space that each chain segment blocks in its surrounding due to (*i*) its own volume, and (*ii*) the effective monomer-monomer interactions.** It allows us to classify solvents according to their quality as illustrated on Slide 86. As the monomer-monomer interactions become increasingly attractive over those with the environment, the excluded volume gets reduced and the solvent quality decreases. In the θ-state, the negative and positive contributions to the integral of the *Mayer f-function* cancel each other and the excluded volume becomes zero. It appears as if neither the hard-sphere repulsion nor the effective monomer-monomer attraction was present. **In the θ-state, the polymer chain therefore adopts their ideal random coil conformation and ideal chain models are applicable. This state is very important in the field of polymer physics and is omnipresent in polymer melts** (Slide 88).

4. Summary

Conformations: the trajectories of ideal chains follow a "random walk", with the end-to-end distance R_n and the radius of gyration, $R_g = R_n/\sqrt{6}$,, scaling as $n^{1/2}$ or $M^{1/2}$.

The expansion of the conformations of real chains with respect to the ideal freely jointed chain is expressed using C_∞, a measure of chain "stiffness":

$$R_n = \sqrt{C_\infty n}a$$

Ideal chain models are particularly applicable in the θ-state of solutions and in polymer melts.