School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2025/26

Exercise 2

1. What is the root of the mean of the square of the distance between the ends (R_n) of a polyethylene chain with a molar mass of 140'000 g/mol?

2. Poly(*p*-benzamide) exhibits an unusually high chain stiffness, with a characteristic ratio of C_∞ = 325. Its chemical structure is shown on Slide 96. Explain this high value for C_∞ by considering possible restrictions on bond rotations and the role of *para*-linked aromatic rings.

3. Draw the chemical structure of bisphenol A polycarbonate.

   Although the structure contains aromatic rings that appear rigid, polycarbonate has a suprisingly low characteristic ratio, C_∞ = 2.2 (measured in dichloromethane). This is explained by the bond definition in the ideal chain model: each benzene ring is treated as only one effective catenary bond, instead of 5. As a result, the average bond length per repeat unit is estimated as (5 + 5 + 1 +1) / 4 = 3 times the length of a single C–C (or C–O) bond. What would the expected value of C_∞ if each individual bond in the aromatic rings were counted separately?

4. Some properties of ideal polymers are independent of chemical structure details. To treat any ideal polymer in a simple, unified way we can define an *equivalent freely jointed chain* that has the same mean-square end-to-end distance, R_n, and the same maximal end-to-end projection R_{max} as the real polymer. This equivalent chain is a straight chain N Kuhn segments of length b (the Kuhn length). Calculate the Kuhn length b of polypropylene. How many chemical repeat units make up one Kuhn segment? Calculate the molar mass M_0 of one Kuhn segment.

   Hint: For the calculation of R_{max} assume the all-*trans* conformation with a bond angle of θ = 68° for the backbone and the standard C–C bond length.

5. A hypothetical polymer chain consists of 100 repeated segments of length a = 3 Å. Its measured root-mean-square end-to-end distance is 100 Å. Does this chain behave as an ideal freely-jointed chain? Calculate the number of Kuhn segments in the chain and the Kuhn segment length.

Exam constraint: do not use a calculator for solving this question. You will not be allowed to use one in the exam either.

6. A polyethylene chain can be approximated as a freely rotating chain with fixed bond angle α between successive bonds and free torsional angle. The correlation between bond vectors $\vec{a}_i$ and $\vec{a}_i$ depends only on their separation along the chain:

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle = a|a|\cos^{|j-i|}\alpha \quad . \tag{1}$$

This correlation defines the persistence length, l_p, i.e. the distance along the chain over which this correlation decays.

By summing the projected components along the chain in the positive direction ($j = i, i+1, i+2, \ldots$) derive an expression for l_p in terms of bond length a and bond angle α. Calculate l_p for PE using realistic values for a and α.

Hint: You may need the geometric series:

$$\sum_{k=0}^{\infty} \cos^k \alpha = \frac{1}{1-\cos\alpha} \quad . \tag{2}$$

7. An ideal polymer chain is often referred to as a Gaussian chain (or Gaussian coil), because the end-to-end distance follows a Gaussian distribution. Which assumptions underlie the Gaussian approximation of polymer chains? Under what conditions does this approximation become valid? What are the main limitations of this approach?

Tip: consult the reading recommendation for support.

Reading suggestions:

- T. Sakai, *Physics of Polymer Gels*. First Edition. Wiley-VCH Verlag GmbH & Co. KGaA (**2020**).

(You can download this document from the Moodle-folder 'Reading Recommendation'.)

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