

Polymer Science 2025/26

Exercise 2 – Solutions

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?

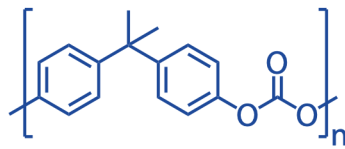
Use the magic formula for $\langle R_n^2 \rangle$, which you hopefully already know by heart. The molar mass of a CH_2 group is 14 g/mol, $n = 140,000/14 = 10,000$, $R_n = (6.7 \times 10,000)^{1/2} \times 0.152 \text{ nm} = 38.83 \text{ nm}$

2. Poly(*p*-benzamide) exhibits an unusually high chain stiffness, with a characteristic ratio of $C_\infty = 325$. 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.

For the chemical structure, see Slide 96. Rotation around the C-N bond of the amide group is strongly restricted due to its partial double-bond character (formulate the resonance structure to rationalize this). The only bonds that, in principle, allow free rotation are those connecting the *para*-linked benzene rings. However, such rotations do not alter the overall linear geometry of the chain, and they are themselves hindered by conjugation between the aromatic rings and the amide groups, which favors a coplanar arrangement. The combination of these factors turns the backbone into a semi-rigid rod over many repeat units with a very large C_∞ .

3. Draw the chemical structure of bisphenol A polycarbonate.

Although the structure contains aromatic rings that appear rigid, polycarbonate has a surprisingly low characteristic ratio, $C_\infty = 2.2$ (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?



Let the average effective bond length be l . In the simplified bond definition (benzene treated as one bond) each repeat unit contains 4 effective bonds of length $\approx 3l$. If instead we count all covalent bonds, the repeat unit contains 12 individual bonds of length l . Since the value of $\langle R_n^2 \rangle$ must be independent of how we define the bonds, we can relate the characteristic ratios by scaling with the bond count and effective bond length:

$$2.2 \cdot n_1 \cdot l_1^2 = C_{\infty}(\text{new}) \cdot n_2 \cdot l_2^2$$

$C_{\infty}(\text{new})$ is therefore equal to $4 \times 2.2 \times 9/12 = 6.6$, which is more in line with the expectation for an aromatic-containing polymer backbone. Note: the experimentally reported $C_{\infty} = 2.2$ is an artifact of the effective-bond definition. The purpose of this exercise is to highlight how bond definitions affect stiffness values.

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 $\theta = 68^\circ$ for the backbone and the standard C-C bond length.

$$b = \frac{\langle R_n^2 \rangle}{R_{\max}} = \frac{C_{\infty} \cdot n \cdot l^2}{R_{\max}}, \quad \text{with } R_{\max} = nl \cos(\theta/2)$$

$$b = \frac{C_{\infty} \cdot n \cdot l^2}{nl \cos(\theta/2)} = \frac{C_{\infty} \cdot l}{\cos(\theta/2)} = \frac{6.8 \cdot 1.54 \text{ \AA}}{\cos(34^\circ)} \approx 12.6 \text{ \AA}$$

$$N = \frac{C_{\infty} \cdot n \cdot l^2}{b^2} = \frac{R_{\max}^2}{C_{\infty} \cdot n \cdot l^2} = \frac{n^2 l^2 \cos^2(\theta/2)}{C_{\infty} \cdot n \cdot l^2} = \frac{n \cos^2(\theta/2)}{C_{\infty}}$$

$$\frac{n}{N} = \frac{C_{\infty}}{\cos^2(34^\circ)} \approx \frac{6.8}{0.6873} \approx 9.9$$

This corresponds to ca. 5 repeat units per Kuhn segment.

$$M_b = 5 \cdot 42.08 \frac{\text{g}}{\text{mol}} \approx 210 \frac{\text{g}}{\text{mol}} .$$

5. A hypothetical polymer chain consists of 100 repeated segments of length $a = 3 \text{ \AA}$. Its measured root-mean-square end-to-end distance is 100 \AA . 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.

The expected RMS end-to-end distance for an ideal freely jointed chain of this length is $an^{1/2} = 30 \text{ \AA}$. The “real” RMS (= 100 \AA) of this chain is greater than this number, therefore it does not behave as an ideal chain.

Flory’s characteristic ratio:

$$C_\infty = \frac{\langle R_{\text{real}}^2 \rangle}{na^2} = \frac{100^2 \cdot \text{\AA}^2}{100 \cdot 3^2 \cdot \text{\AA}^2} \approx 11.1 \text{ \AA}$$

The number of Kuhn segments:

$$N = \frac{na}{b} = \frac{na \cdot R_{\text{max}}}{na^2 \cdot C_\infty} = \frac{n}{C_\infty} = 9$$

The length of a Kuhn segment:

$$b = a \cdot C_\infty = 33.3 \text{ \AA}$$

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}_j depends only on their separation along the chain:

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

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 ($j = i, i + 1, i + 2, \dots$) 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:

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

$$l_p = a(1 + \cos \alpha + \cos^2 \alpha + \cos^3 \alpha + \dots) = a \frac{1}{1 - \cos \alpha} .$$

with $a = 0.154 \text{ nm}$ and $\alpha = 70^\circ$, one gets

$$l_p \approx \frac{1.54 \text{ \AA}}{1 - 0.34} \approx 2.34 \text{ \AA} .$$

The persistence length of polyethylene is only slightly larger than a single bond length. This means correlations between bond directions decay very rapidly along the chain, and polyethylene behaves as an extremely flexible polymer at the local (bond-scale) level.

This result is a direct consequence of the freely rotating chain model: torsional angles are completely free and the only correlation comes from the fixed bond angle. The model therefore predicts a flexible chain at the local scale.

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.

The Gaussian approximation is only valid for large n , and, as we will see later, will fail if the polymer chain segment length of interest becomes short. We will also note soon that the Gaussian distribution does not accurately describe the situation of large end-to-end distances (it even predicts a finite probability for end-to-end distances that are larger than the contour length, which is physically not plausible). Limitations that arise from that and workarounds will be discussed in Chapter 4.1.

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'.)