Materials for Devices: Problem Set 4

14. (i) Given that the C−C bond length is 0.154 nm and the C−H bond length is 0.114 nm, estimate the length and width of a linear polyethylene molecule consisting of 1,000 carbon atoms (the tetrahedral bond angle is 109.5°).

(ii) What is the molecular weight of this molecule?

(iii) What is the end-to-end distance assuming a completely flexible chain made up of C−C segments which can twist and rotate completely independently?

(iv) What is the end-to-end distance using the more reasonable assumption that the Kuhn length is made of 3.5 C−C segments?

(v) If this chain were scaled up to the dimensions of a piece of string (e.g. about 2 mm wide), how long would it be? In a scaled-up polymer model, if this piece of string represents a linear polyethylene molecule, what would be the average end-to-end distance in the model?

Solution

(i) The hydrogen-hydrogen separation gives one width $L_{\mathrm{H-H}}$, which can be estimated from the group H−C−H of three atoms with two sides of length $L_{\mathrm{C-H}} = 0.114\,\mathrm{nm}$ and an angle $\alpha = 109.5°$. From basic trigonometry, we get:

$$L_{\mathrm{H-H}} = 2L_{\mathrm{C-H}} \sin\left(\frac{\alpha}{2}\right) = 2 \times 0.114 \times \sin\left(\frac{109.5}{2}\right) = 0.186\,\mathrm{nm}.$$

The hydrogen-hydrogen separation H−C−C−H projected along a direction perpendicular to the chain length gives the perpendicular width $L_{\mathrm{H-C-C-H}}$. This is given by the projection of two separate C−H bonds and one C−C on the perpendicular direction which is at an angle of $\frac{1}{2}\alpha = \frac{1}{2} \times 109.5 = 54.75°$ from the perpendicular. We get:

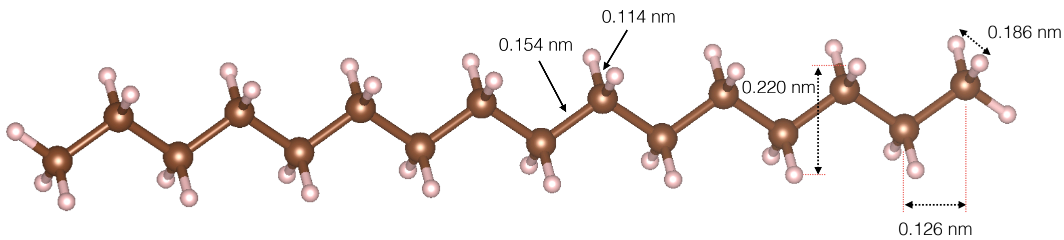
$$\begin{aligned} L_{\mathrm{H-C-C-H}} &= 2 \times L_{\mathrm{C-H}} \cos\left(\frac{\alpha}{2}\right) + L_{\mathrm{C-C}} \cos\left(\frac{\alpha}{2}\right) \\ &= 2 \times 0.114 \cos(54.75) + 0.154 \cos(54.75) = 0.220\,\mathrm{nm}. \end{aligned}$$

The C−C bond distance projected along the length of the chain, which we call $L_{\mathrm{C-C\,proj}}$, can be estimated from the group C−C−C of three atoms with two sides of length $L_{\mathrm{C-C}} = 0.154\,\mathrm{nm}$ and an angle $\alpha = 109.5°$. From basic trigonometry, we get:

$$L_{\mathrm{C-C\,proj}} = \frac{1}{2} \times 2L_{\mathrm{C-C}} \sin\left(\frac{\alpha}{2}\right) = 2 \times 0.154 \times \sin\left(\frac{109.5}{2}\right) = 0.126\,\mathrm{nm}.$$

The full molecule has 999 such bonds, so we get a total length of $999 \times 0.126 = 125.9\,\mathrm{nm}$.

A schematic diagram of the various lengths in the polyethylene chain is depicted in the Figure below:



(ii) In the centre of the molecule we have two hydrogen atoms for every carbon atom. Additionally, the carbon atoms at the ends have an additional hydrogen each. Using relative atomic masses from webelements, which for each elements includes the average isotopic mass using natural abundances, we obtain:

$$\begin{aligned}1000 \times M(\mathrm{C}) + 2000 \times M(\mathrm{H}) + 2 \times M(\mathrm{H}) &= (1000 \times 12.011 + 2002 \times 1.008) \times M_\mathrm{u} \\ &= 14029.016 \times M_\mathrm{u}.\end{aligned}$$

This is equivalent to about $14\,\mathrm{kg\,mol^{-1}}$.

(iii) The end-to-end distance is defined as $\sqrt{\langle \mathbf{R}_n^2 \rangle} = l\sqrt{n}$, where l is the length of each segment and n is the number of segments. In our case, $l = 0.154\,\mathrm{nm}$ is equal to the C−C distance and $n = 999$. Therefore:

$$\sqrt{\langle \mathbf{R}_n^2 \rangle} = l\sqrt{n} = 0.154 \times \sqrt{999} = 4.867\,\mathrm{nm}.$$

(iv) In this case, $n = \frac{999}{3.5} = 285.4$ and $l = 3.5 \times 0.154 = 0.539\,\mathrm{nm}$, and we get:

$$\sqrt{\langle \mathbf{R}_n^2 \rangle} = l\sqrt{n} = 0.539 \times \sqrt{285.4} = 9.1\,\mathrm{nm}.$$

Note that the end-to-end distance has increased because the chain is more rigid so it can pack less effectively.

(v) The cross-section of the molecule is $0.186\,\mathrm{nm} \times 0.221\,\mathrm{nm}$, so we can take a width of about $0.2\,\mathrm{nm}$. Scaling $0.2\,\mathrm{nm}$ ($2 \times 10^{-10}\,\mathrm{m}$) to $2\,\mathrm{mm}$ ($2 \times 10^{-3}\,\mathrm{m}$) gives a scaling factor of 10^7. Therefore, the original length of the molecule of $0.126\,\mathrm{nm}$ becomes (using metres):

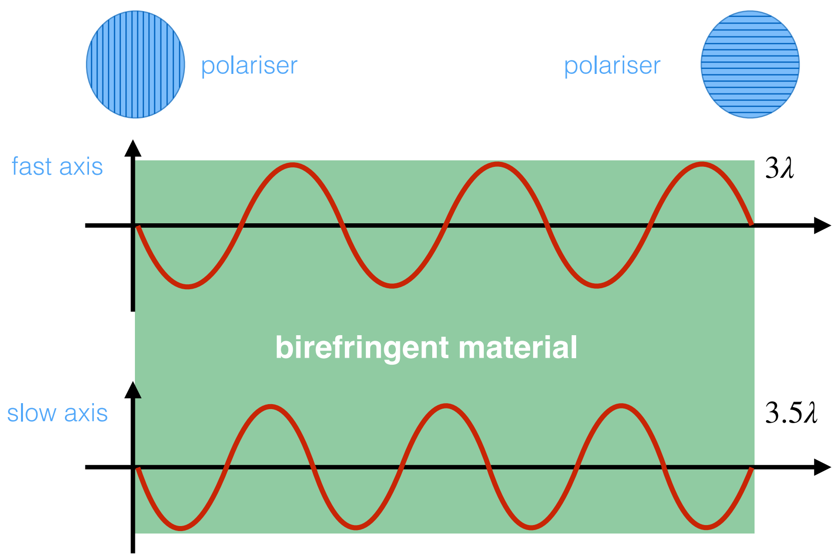
$$126 \times 10^{-9} \times 10^7 = 1.26\,\mathrm{m}.$$

Using the same scaling factor of 10^7, the end-to-end distance of $4.9\,\mathrm{nm}$ for flexible C−C bonds becomes $4.9\,\mathrm{cm}$, and the end-to-end distance of $9.1\,\mathrm{nm}$ for a Kuhn length of 3.5 C−C segments becomes $9.1\,\mathrm{cm}$.

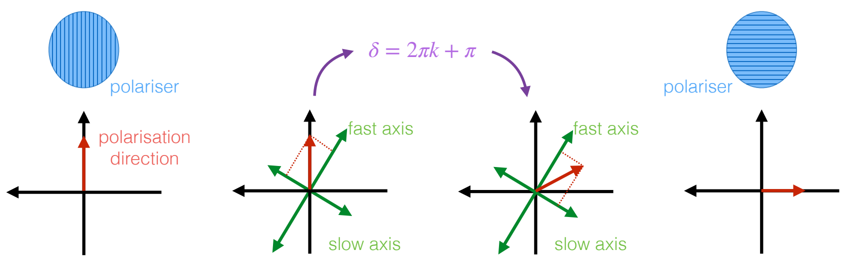
15. Consider a birefringent material placed between crossed polarisers. Let the optical path difference be OPD $= k\lambda + \frac{\lambda}{2}$ for positive integer k, or equivalently the phase difference is $\delta = 2\pi k + \pi$. Discuss whether light is transmitted in this setup.

Solution

A schematic of the setup is depicted in the Figure below:

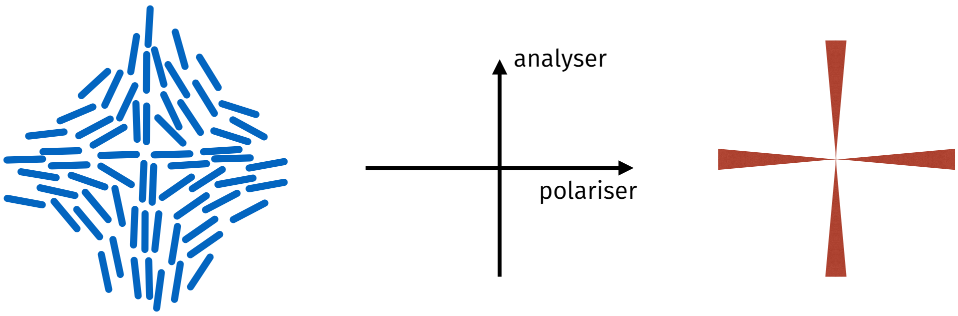


The transit of ligth through this setup is depicted in the Figure below:

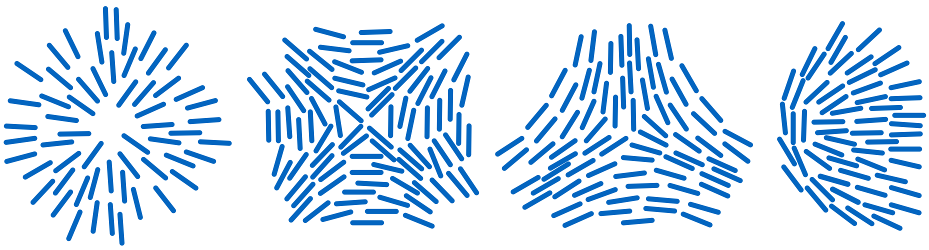


Light enters the material through the first polariser, so its polarisation direction is initially vertical (left diagram above). Inside the birefringent material, the light polarisation will in general not be aligned with the permitted vibration directions, so we can separate the oscillating electric field into its components along the fast and slow axes (middle-left diagram above). At the end of the birefringent material, the relative phase difference of the two light components has changed by a factor of π (middle-right diagram above). This means that the light polarisation now has a component parallel to the seconod polariser, so that overall light will be transmitted through the second polariser (right diagram above).

16. A nematic liquid crystal, which hosts different director orientation patterns in different regions, is observed between crossed polarisers. The following Figure depicts a the orientation of the rod-like molecules in a particular sample (left) together with its appearance (right) when the crossed polarisers are oriented as shown (centre):

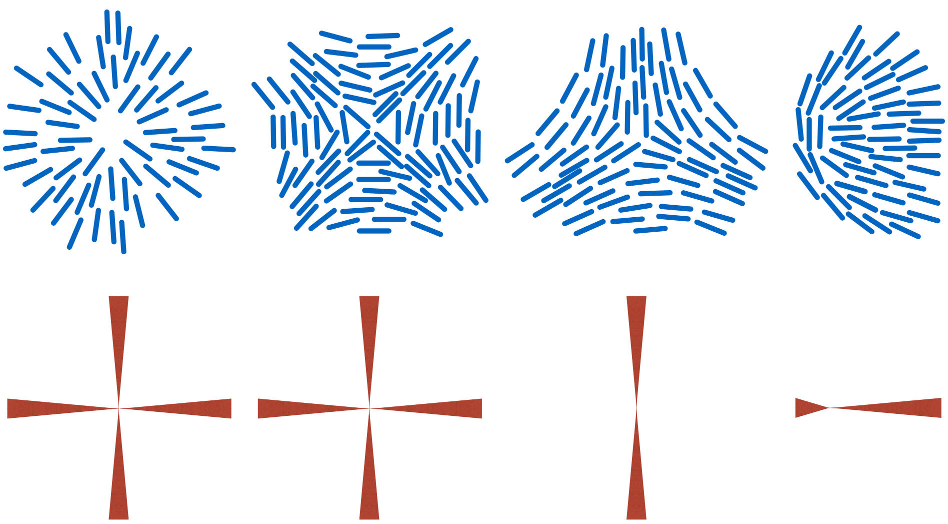


Sketch the patterns that would be observed for the following samples if the crossed polarisers remain in the same orientation as above:



Solution

The observed patterns are sketched below the corresponding liquid crystal configuration:



17. A wedge of quartz with a birefringence of 0.009 and an angle of $1°$ is cut with a permitted vibration direction along its length.

(i) Describe and explain what will be observed when the wedge is viewed between crossed polars, with its length at $45°$ to the polariser/analyser, when using sodium light of wavelength $\lambda = 590\,\mathrm{nm}$. What is the distance between dark bands?

(ii) Describe and explain what happens if the wedge is then rotated so that its length lies parallel with (a) the polariser, and (b) the analyser.

The quartz wedge is next viewed in white light, and a uniform nematic liquid crystal sample is added to the light path, that is, the quartz wedge is placed on top of the liquid crystal sample and viewed between crossed polars. The long axes of the liquid crystal molecules in this sample, known to correspond to the slow vibration direction of the sample, are oriented parallel to the length of the wedge.

(iii) A black band is observed on the wedge, 13.6 mm from its tip. Does the length of the wedge correspond to the fast or the slow vibration direction in the quartz sample?

(iv) What colour would the liquid crystal sample show if the wedge were removed?

(v) The liquid crystal sample is measured to have a thickness of 0.05 mm. What is its birefringence?

Solution

(i) Remember that the phase difference is:

$$\delta = 2\pi \frac{l\Delta n}{\lambda}, \tag{1}$$

for sample thickness l, birefringence Δn, and wavelength of light λ. Black bands will appear when the phase difference is an integer multiple of 2π, so that we require $l\Delta n = k\lambda$ for non-negative integer k. This gives the following general condition for the width of the quartz wedge to give dark bands:

$$l = \frac{k\lambda}{\Delta n}. \tag{2}$$

In terms of the length d along the wedge, standard trigonometry yields:

$$d = \frac{l}{\tan(1°)} = \frac{k\lambda}{0.017455\Delta n}. \tag{3}$$

For $k = 0$, we have $l = 0$, which corresponds to $d = 0$, the very tip of the wedge. The next dark band will appear when $k = 1$, which gives $l = 65.6\,\mathrm{nm}$ or $d = 3.8\,\mathrm{mm}$. For subsequent dark bands we get d values of 7.5 mm, 11.3 mm, 15.0 mm, and so on.

(ii) When the length of the wedge lies parallel to the polariser, light passing into the quartz sample has its polarisation direction parallel to the permitted vibration direction along the length of the wedge. In this case there is no rotation of the light, so that no light will be transmitted through the second polariser (analyser). When the length of the wedge lies parallel to the analyser, light passing into the quartz sample again has its polarisation direction along a permitted vibration direction, but this time perpendicular to the length of the wedge. Again, there will be no rotation of the light and no light will be transmitted through the analyser.

(iii) A black band corresponds to a vanishing phase difference for light passing through both specimens, which occurs when the phase difference in quartz and the liquid crystal are equal and opposite. If the slow direction in the liquid crystal is parallel to the length of the wedge, this means that the wedge must have its fast direction along its length.

(iv) A length of 13.6 mm along the wedge corresponds to a thickness of 0.237 mm, which gives an optical path difference of $0.237 \times 0.009 = 2140\,\text{nm}$. Therefore, the liquid crystal sample on its own will appear as a uniform fourth order pink colour from the Michel-Levy chart.

(v) For an optical path difference of 2140 nm and a thickness of 0.05 mm, the birefringence Δn is 0.043.