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Polymer Science 2025/26

Exercise 10 – Solutions

1. Let us simulate the behavior of a freely jointed polymer that is slightly cross-linked.

i) It is assumed that the crosslinking points are separated along the chains by n_x bonds such that $n >> n_x >> m$ and that the positions of the crosslinking points are fixed by the macroscopic deformation. In this case, relaxations involving chain segments longer than n_x are blocked, leading to infinite relaxation times for these modes:

$$\begin{cases} \tau_p \approx \dfrac{\xi_o n^2 a^2}{6\pi^2 p^2 \mathrm{k}T}, & \text{for} \quad m \gg 1, \;\; p > p_x \\ \tau_p = \infty & \text{for} \quad p < p_x \end{cases}$$

Express p_x (the critical Rouse mode that becomes blocked by crosslinks) and the maximum unblocked relaxation time τ_x in terms of the number of bonds between crosslinks n_x!

Mode p involves motion over a wavelength corresponding to n/p bonds. Relaxation is blocked when the wavelength exceeds the crosslink spacing n_x. Thus:

$$\boldsymbol{p_x = \frac{n}{n_x}}$$

The longest unblocked relaxation time corresponds to mode p_x:

$$\boldsymbol{\tau_x = \frac{\xi_o n_x^2 a^2}{6\pi^2 \mathrm{k}T}}$$

ii) According to the phenomenological models (springs and dashpot) generalized for a linear viscoelastic material, the relaxation shear modulus is given by

$$\mathrm{G}(t) = G_\infty + \sum_1^n G_i e^{-t/\tau_i}$$

Show that the effective value of G_∞ is $N_x \mathrm{k}T$, where N_x is the number of crosslinking points per unit of volume. Have you seen this result before?

The unrelaxed modes are those with $p < p_x$, i.e. wavelengths larger than the crosslinking spacing. Their relaxation times are infinite, so their contribution to $G(t)$ does not decay. Because the modes larger than p_x have fully decayed at $t = \infty$, we obtain according to Rouse:

$$G_\infty = NkT \sum_{p=1}^{n/n_x} e^{-t/\infty} = NkT \sum_{p=1}^{n/n_x} 1 = \frac{nNkT}{n_x} = N_x kT$$

where $N_x = N(n/n_x)$ is the number of crosslinks per unit volume.

This is identical to the shear modulus of an ideal elastomer which you should recognize from the theory of rubber elasticity.

iii) Why is the first Equation no longer valid when p approaches n? In what time interval can we therefore apply this model?

The Rouse model assumes that each Rouse mode describes a Gaussian chain segment with n/p bonds. This requires $n/p \gg 1$. When $p \to n$, the wavelength becomes a single bond, Gaussian statistics break down, and the Rouse expression for τ_p no longer applies.

Because $\tau_p \propto 1/p^2$, the highest Rouse modes correspond to extremely short times (bond-vibration scale). These relaxations are not entropic and are therefore outside the range of applicability of the Rouse model.
Thus, the model is valid only for modes with $p \ll n$ whose segments remain Gaussian. In terms of time, this corresponds to the window

$$\tau_{p_{\max}} < t < \infty$$

i.e. between the relaxation time of the shortest still-Gaussian mode and the longest Rouse time, which is infinite in the present case.

2. In the case of an entangled but not crosslinked polymer, the behavior can be simulated very simply by posing $\tau_p = \tau_d$ if $p < p_e$.

i) What do τ_p and τ_d mean?

τ_d is the relaxation time of a given mode (internal segmental motion), τ_d is the disentanglement time (time required for the chain to escape its tube via reptation), and p_e is the critical mode number below which relaxation is blocked by the entanglement.

ii) In the tube model, the tube diameter, d_e, is given by

$$d_\mathrm{e} = \sqrt{n_\mathrm{e}}a = \sqrt{\frac{M_\mathrm{e}}{M_\mathrm{b}}}a$$

What do M_e and M_b mean?

M_e: entanglement molecular weight, which represents the molar mass of the polymer chain between two entanglement points.

M_b: molar mass per backbone bond.

iii) Show also that the length of the tube L can be expressed as:

$$L = \frac{M}{M_\mathrm{e}}\sqrt{\frac{M_\mathrm{e}}{M_\mathrm{b}}}a$$

The total polymer chain consists of M/M_e subchain segments separated by entanglement points. Each segment has a length d_e.

iv) According to Rouse's model, the diffusion coefficient of a chain inside the tube is

$$D_\mathrm{R} = \frac{\mathrm{k}TM_\mathrm{b}}{\xi_o M}$$

Schow that

$$\tau_\mathrm{e} = \frac{\xi_o a^2}{6\pi^2\mathrm{k}T}\left(\frac{M_\mathrm{e}}{M_\mathrm{b}}\right)^2 \quad \text{and} \quad \tau_\mathrm{d} = 6\pi^2\left(\frac{M}{M_\mathrm{e}}\right)^3\tau_\mathrm{e}$$

Tip: to find the relationship between τ_d and τ_e, start by using Fick's law to express τ_d, and then multiply and divide by τ_e.

We have already shown that

$$\tau_\mathrm{e} \approx \frac{\xi_o {n_x}^2 a^2}{6\pi^2\mathrm{k}T}$$

In analogy, we can now write using the expression from *ii)* with n_e being the number of bonds between entanglement points:

$$\tau_\mathrm{e} \approx \frac{\xi_o {n_\mathrm{e}}^2 a^2}{6\pi^2\mathrm{k}T} = \frac{\xi_o a^2}{6\pi^2\mathrm{k}T}\left(\frac{M_\mathrm{e}}{M_\mathrm{b}}\right)^2$$

with $n_\mathrm{e} = M_\mathrm{e}/M_\mathrm{b}$. For τ_d, we use Fick's law, the expression of the diffusion coefficient according to Rouse (see Slides), the expression for L from *iii*). For finding a relation to τ_e, let us then just multiply and divide by τ_e using the expression from above:

$$\tau_\mathrm{d} = \frac{L^2}{D_R} = \frac{\xi_o M}{\mathrm{k}T M_\mathrm{b}}\left(\frac{M}{M_\mathrm{e}}\sqrt{\frac{M_e}{M_\mathrm{b}}}\,a\right)^2 = \frac{\xi_o M}{\mathrm{k}T M_\mathrm{b}}\left(\frac{M}{M_\mathrm{e}}\sqrt{\frac{M_\mathrm{e}}{M_\mathrm{b}}}\,a\right)^2 \frac{6\pi^2 \mathrm{k}T\tau_\mathrm{e}}{\xi_o {n_\mathrm{e}}^2 a^2} = 6\pi^2\left(\frac{M}{M_\mathrm{e}}\right)^3 \tau_\mathrm{e}$$

v) Show schematically the behavior of an entangled chain by indicating τ_e and τ_d on a plot of shear modulus $\mathrm{G}(t)$ versus time t.

We must use the usual diagram of the elastic behavior of an amorphous polymer in the linear domain, i.e. G (or E) vs. log t, with the glassy regime, the glass transition, the rubbery plateau and the terminal zone, plus the right orders of magnitude. τ_e marks the beginning of the rubbery plateau, where entanglement effects start to dominate the polymer's mechanical response. τ_d marks the end of the rubbery plateau, where the chain has fully disentangled and begins to exhibit a liquid-like response (see Slide 306).

Reading suggestion:

- Reader on the Tube Model.

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