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

Polymer Science 2025/26

Exercise 10

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!

   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?

   iii) Why is the first Equation no longer valid when p approaches n? In what time interval can we therefore apply this model?

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?

   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?

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

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

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.

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.

Reading suggestion:

- Reader on the Tube Model.

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

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Dr. Daniel Görl
daniel.gorl@epfl.ch
lmom.epfl.ch

EPFL STI IMX LMOM
MXG 039, Station 12
CH-1015 Lausanne