

**Polymer Science 2025/26**

**Exercise 9**

1. In a relaxation test, a constant shear strain  $\gamma_0$  is applied and we monitor the stress  $\sigma(t) = G(t)\gamma_0$  as a function of time. The relaxation modulus according to the generalized Maxwell model is

$$G(t) = G_\infty + \sum_{i=1}^n G_i e^{-t/\tau_i} ,$$

where the parameters  $G_\infty$  and  $G_i$  are adjustable (within the limit of an infinite number of elements, the  $G_i$  can be replaced by a continuous function, the relaxation time spectrum, and the sum by an integral).

In the Rouse model for a dilute solution of  $N_m$  chains per unit volume, each chain contains  $n$  bonds, the expression for  $G(t)$  is

$$G(t) = N_m kT \sum_{p=1}^m e^{-t/\tau_p} \quad \tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 kT} , \quad p = 1, 2, \dots$$

Assume  $m \gg p$  and  $m \gg 1$ .

- i) Explain the meaning of  $m$ ,  $p$ ,  $\xi$  and  $R_s^2$ . Why is  $G_\infty = 0$  here?
- ii) If the monomeric friction coefficient is  $\xi_o = \xi m/n$ , show that

$$\tau_p \approx \frac{\xi_o n^2 a^2}{6\pi^2 p^2 kT}, \quad \text{for } m \gg 1, p$$

and therefore, that the longest Rouse time  $\tau_1$  scales as  $M^2$ .

- iii) Draw schematically the evolution of  $\sigma/N_m kT$  as a function of  $t/\tau_1$  for the contributions coming from  $p = 1$ , and add the decays for  $p = 2$  and  $p = 3$ . Discuss the contribution of the fast modes for  $t \geq \tau_1$ ?
- iv) The choice of  $m$  (number of beads/modes) is arbitrary. Is the Rouse model still reasonable when  $m \rightarrow n$  (i.e., when beads correspond to single bonds)?
- v) Suppose  $\tau_1 = \infty$  and  $\tau_p = 0$  for  $p > 1$ . Write the resulting expression for  $G(t)$ . Interpret your result.

2. The Rouse model does not describe dilute polymer solutions accurately because it neglects hydrodynamics interactions between beads (these are accounted for in the Zimm model). However, the Rouse model works well for chains in a polymer melt as long as entanglement effects are negligible (in this case, the other chains act as a highly viscous solvent).

- i) Rouse-like behavior can therefore be expected if the molar mass  $M$  is smaller than a certain critical molar value,  $M_c = 2M_e$ . What does  $M_e$  represent here? Using the concept of the entanglement network, explain how  $M_e$  can be determined experimentally from the rubbery plateau shear modulus.
- ii) The Rouse model can still describe fast relaxation modes (large  $p$ ) even when  $M \gg 2M_e$ , because these correspond to localized segmental motions that are not hindered by entanglements.

In contrast, slow modes involving the entire chain are blocked by entanglements. Assuming (as a simplification) that entanglements mainly affect the slowest relaxation mode  $\tau_1$ , what can we say about  $\tau_1$ , if the entanglements were permanent? What would represent in this limiting case?

- iii) In reality, entanglements are not permanent. The tube model describes the disentanglement process, in which a chain gradually escapes from its confining tube by reptation. This model implies that the chain can eventually recover its random coil conformation and relax all stresses.

Assuming that the diffusion coefficient along the tube scales as  $D \propto 1/M$ , explain where this scaling originates.

- iv) Knowing that the tube contour length (i.e. the total length the chain must diffuse to fully disentangle) is proportional to  $M$ , demonstrate that the disentanglement time  $\tau_d$  scales as  $M^3$ .
- v) Using Excel, Origin, or another plotting tool, plot on logarithmic axes:

$$G(t) = N_m kT \sum_{p=1}^m e^{-t/\tau_p}$$

for  $t$  ranging from 0.01 and  $10^5$  s, taking  $m = 5$ ,  $\tau_1 = 10^5$  s, and  $\tau_p = 40/p^2$ . Here, we simulate the effect of entanglements by assigning an arbitrarily large value to  $\tau_1$ . What feature of the resulting curve does this remind you of?

### Reading suggestion:

- Reader on the Rouse Model.

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