

Polymer Science 2025/26

Exercise 4

1. Let's try to better understand the theory of *free volume*!

At absolute zero ($T = 0$), each segment of a glassy amorphous polymer occupies a volume v_0 . As temperature increases, the molecules vibrate and the volume increases, characterized by the thermal expansion coefficient of the glass:

$$V_{\text{glass}} = \alpha_{\text{glass}} v_0 T \quad , \quad (1)$$

Note: For simplicity, we only consider the temperature-dependent contribution to the volume. The constant segment volume at $T = 0$ (v_0) is ignored, since it cancels when comparing glassy and liquid states.

According to the free volume theory, above a certain onset temperature T_0 , "holes" appear that are large enough to allow the displacement of chain segments. Conformational changes become possible and the system enters the liquid (or rubbery) state, characterized by the expansion coefficient α_{liquid} .

Because the glassy state is an out-of-equilibrium state, an average "free volume" v_{fm} is trapped in the glassy state. By definition, this is the excess volume compared to a hypothetically *equilibrated* glass.

- a) Show that

$$v_{\text{fm}} = v_0 (T - T_0) (\alpha_{\text{liquid}} - \alpha_{\text{glass}}) \quad . \quad (2)$$

We assume that the probability of finding a hole of size v_0 in a given time interval is proportional to $\exp(-v_0/v_{\text{fm}})$. Hence, the relaxation time and viscosity are

$$\tau = \tau_0 e^{\frac{v_0}{v_{\text{fm}}}}, \quad \eta = \eta_0 e^{\frac{v_0}{v_{\text{fm}}}} \quad . \quad (3,4)$$

- b) Express η in terms of T , T_0 and the thermal expansion coefficients. What happens to η when T tends towards T_0 ?
- c) If we cool at a given rate, conformational rearrangements eventually stop at a temperature $T > T_0$, when the viscosity becomes too high for relaxation on the

experimental timescale. This temperature is the *experimental glass transition temperature* T_g . Draw the evolution of the volume as a function of T for several constant cooling rates. Indicate T_g for each cooling rate.

- d) In DSC measurements, a characteristic enthalpy peak is often observed near the glass transition temperature during heating if the heating rate is faster than the cooling rate used in the prior cooling scan (see Slide 147). This enthalpy peak can also appear after physical ageing, i.e. densification of the glassy state when the material rests below T_g . Explain this behavior with the help of a schematic illustration showing the evolution of the specific volume (or enthalpy) as a function of temperature.
- e) An amorphous polymer is cooled relatively quickly from the rubbery state to a temperature well below T_g , and then reheated much more slowly. Schematically show the evolution of the specific volume as a function of the temperature under these conditions.
2. You saw that the glassy state out-of-equilibrium: no matter how slowly you cool, the free volume will not vanish at $T = T_0$. Therefore, some free volume is always trapped in the glass.

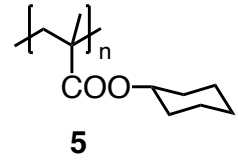
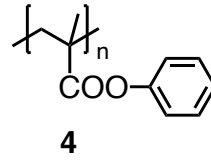
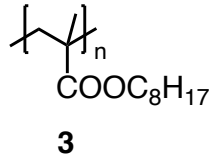
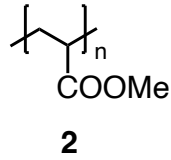
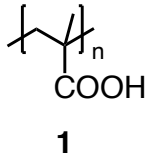
According to the free volume theory, polymer chain ends contribute an additional free volume θ . Explain, within this framework, how T_g varies with number-average molar mass M_n for a given cooling rate. In your answer, justify the empirical Fox–Flory law (see Slide 158) by expressing the total free volume v_{fm} , as a function of θ , and assuming that the glass transition occurs at the same critical free volume as in the hypothetical case of infinitely long chains without end groups.

Using the following data, determine the glass transition temperature $T_{g\infty}$ of the polymer at infinite molar mass:

T_g (K)	182	278	354	361	362	369.5	375.5
M_n (Da)	500	1'000	4'000	5'000	6'000	10'000	20'000

3. Show the qualitative shape of the elastic modulus $E(T)$ of an amorphous polymer as a function of temperature. Indicate the correct orders of magnitude of E in the different characteristic regimes. Also describe influence of the strain rate on the curve. Finally, sketch the corresponding $E(T)$ for a "small molecule".

4. Name each polymer below and order them by expected glass transition temperature T_g (highest \rightarrow lowest). Explain your ranking briefly.



5. You receive two samples of polystyrene. The supplier informs you that sample #1 can crystallize while #2 cannot. Is this possible? Explain your reasoning.