Tutorial Problems on Polymer Dynamics – solution outlines
Daniel Read

NOTE: all page numbers refer to the notes with one slide per page, i.e. with 90 pages in total.

Q1. Linear rheology - TTS
Explain the concept of time-temperature superposition. Why is it useful in experimental rheology?
TTS works on the principle that if you increase temperature, then the molecular motion speeds up (and hence, so does the relaxation of the material as measured in rheology). For thermorheologically simple materials, the shape of the relaxation spectrum does not change, and the temperature change accelerates all relaxations by the same factor. Hence linear rheology measured at different temperatures can be superposed by shifting the data along the log frequency axis. This allows an effectively wider range of frequencies to be probed.

Under what circumstances would you expect it to work for a given material?
The material needs to be thermorheologically simple, which requires all relaxation processes to shift in the same way with temperature – i.e. all must depend on the same underlying motion, i.e. a single processs.

For which of the following materials might you expect it to (possibly) work, and why?
a) A block copolymer
No – there are two different monomers, so likely two different temperature dependencies to the motion of each monomer type.

b) A melt of branched polystyrene molecules
Probably yes – there is only one monomer type, and all motion of the molecules depends on local monomer motion.

c) A polybutadiene melt with side chains including hydrogen-bonding chemical groups.
No – the sticky groups will have different temperature dependence to the monomers.

Q2. Linear Oscillatory Rheology (for the mathematically-minded students)
If the dynamic modulus $G(t)=G_0 e^{-t/\tau}$ is a pure single exponential, show that under an oscillatory linear strain $\gamma(t)=\gamma_0\sin\omega t$ the stress developed is of the form $\sigma(t)=\gamma_0 G'(\omega)\sin\omega t +\gamma_0 G''(\omega)\cos\omega t$ with the forms for $G^*(\omega)$ given in the notes
[Hint: write the continuous harmonic deformation as a series of infinitesimal deformations in linear superposition].

Q3. The Rouse model was originally developed as a model for the dynamics of dilute polymer solutions. Soon it was found that it had a major deficiency. It did not account for the effect of so-called intra-chain hydrodynamic interactions. Explain what these interactions are.

Here, please refer to page 38 of the notes for the answer.

How does the diffusion coefficient of the centre-of-mass of a polymer molecule scale with molecular weight in unentangled polymer melts and in dilute polymer solutions?

For polymer melts, diffusion constant is inversely proportional to molecular weight (see page 30 of notes). For dilute polymer solution, see page 35. Diffusion constant is inversely proportional to radius, with radius proportional to molecular weight to the power of ½ (theta solvent) or 3/5 (good solvent).

Q4. Starting from an appropriate expressions for the diffusion constant and end-to-end length of a (sub)chain of *n* monomers, obtain the scaling expression of the relaxation time of the subchain for (i) the Rouse model and (ii) the Zimm model. Hence obtain an expression for $G(t)$ in the form $G(t) = At^{-\alpha}$ for the two models. Predict how the intrinsic viscosity scales with molecular weight for the two models.
[Hint: the full derivation for $G(t)$ is given in the notes for Rouse – you need to adapt it for Zimm; but the derivation of intrinsic viscosity is given in the notes for Zimm but not Rouse!].

In the notes, see page 34 for tau(n) and n(t) for the Rouse model, and page 39 for the Zimm model. To obtain G(t), use the method on page 35, i.e. G(t) ~ 1/n(t). For the intrinsic viscosity, use the method on page 43, i.e. start from the equation top left, with viscisity given by equation top right. For G use the equation given, but use the appropriate relaxation time (tau) for the whole chain, as indicated in the two models.

Q5. Phenomenology and Experimental Review
(a) Plot a suitable graph and describe the main features of the general relationship between the viscosity of polymer melt and its molecular weight (for all reasonably monodisperse melts).
See graph on page 44 of the notes… should have two regions, with slope of 1 (unentangled) and 3.4 (entangled).

(b) Give three relaxation mechanisms by which entangled linear polymers relax their stress.
Options include reptation, contour length fluctuation, constraint release, local Rouse motion.

(c) For each regime of behaviour in the graph of (a), sketch a suitable graph and describe the behaviour of the stress relaxation modulus *G(t)*. Explain in qualitative terms the physics that gives rise to the behaviour in each case.
The graphs you are looking for are on pages 36 right (unentangled regime) and 49 top-right (entangled regime), and you should explain the appearance of the plateau and the power-law Rouse relaxation behaviour.

(d) A polystyrene melt with M_w=100 000 has a terminal relaxation time of 0.1s. Estimate the relaxation time of a polystyrene melt with M_w=250 000 at the same temperature.
Here you are expected to use the 3.4 power law. So, the relaxation time can be estimated as:
$$0.1 \times \left(\frac{250000}{100000}\right)^{3.4} = 2.3s.$$

(e) If the entanglement molecular weight of polystyrene is 13 500 (for a polymer of this length the Rouse and reptation times are equal), estimate the ratio τ_{rept}/τ_{Rouse} for the melt with M_w=250 000.
The ratio is roughly $3Z = 3\frac{M}{M_e} = 3 \times \frac{250000}{13500} = 56$.

Q6 Assuming that an entangled linear chain diffused a distance of order its end-to-end vector during one reptation time, derive a scaling expression for the 3D diffusion constant as a function of chain length from the pure reptation model.

Here, you should be using $D = R^2/\text{tau}$, with $R^2 = Nb^2$ (end to end vector of a random walk) and relaxation time tau as given on page 48.

Q7. You want to reduce the viscosity of a liquid containing some polymers. Briefly discuss several strategies to do this. Can you do it whilst keeping the same terminal relaxation time? Can you do it whilst keeping the polymer loading (i.e. amount of polymer in the liquid) constant? How will your considerations change if the liquid is a dilute polymer solution, entangled linear melt, or entangled branched melt?

This is an open-ended question, but consider that viscosity is modulus times relaxation time. Usually relaxation time is increased by increasing concentration of entangled melts, or by decreasing temperature, or (always) by increasing the molecular weight. The relevant modulus is either the entanglement modulus (Ge)

for entangled melts, which is independent of molecular weight, but which increases with increasing concentration in semidilute polymer solutions. For dilute polymer solutions, the modulus is increased by increasing concentration, but is inversely proportional to molecular weight (it is kT per chain per unit volume).

Q8. The plot below shows the linear rheology of a series of linear polystyrene polymer melts time-temperature shifted to 130C (the axes are the logarithm of angular frequency in s^{-1} and logarithm of modulus in Pa). Based on these plots and on material from the lectures, *estimate* (NB we are expecting only rough estimates):

(a) the entanglement time τ_e and the plateau modulus G_e (and hence the entanglement molecular weight M_e.

(b) the reptation time for each melt.

(c) the number of entanglements per chain for each melt (you could use either $\tau_d = 3Z^3\tau_e$ or – better - iterate the Likhtman-McLeish formula).

(d) the molecular weight of each melt.
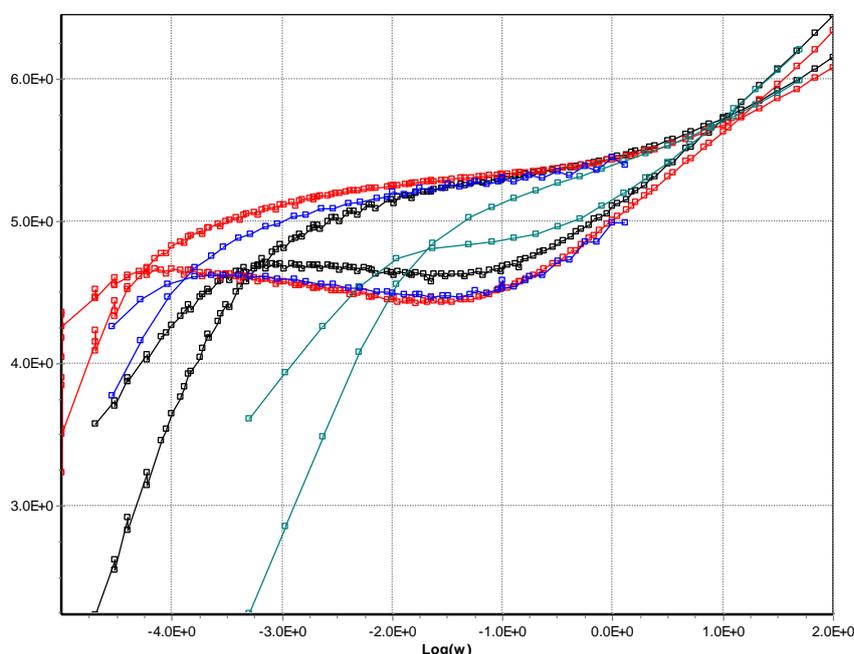

For this question in part (a) and (b) you are supposed to extract times and modulus as indicated in the graph below. Me can be obtained from G_e=rho*R*T/M_e where rho is the density. Be careful to use SI units!! In part (c) you are told what to do, and in part (d) just use M=Z*M_e.
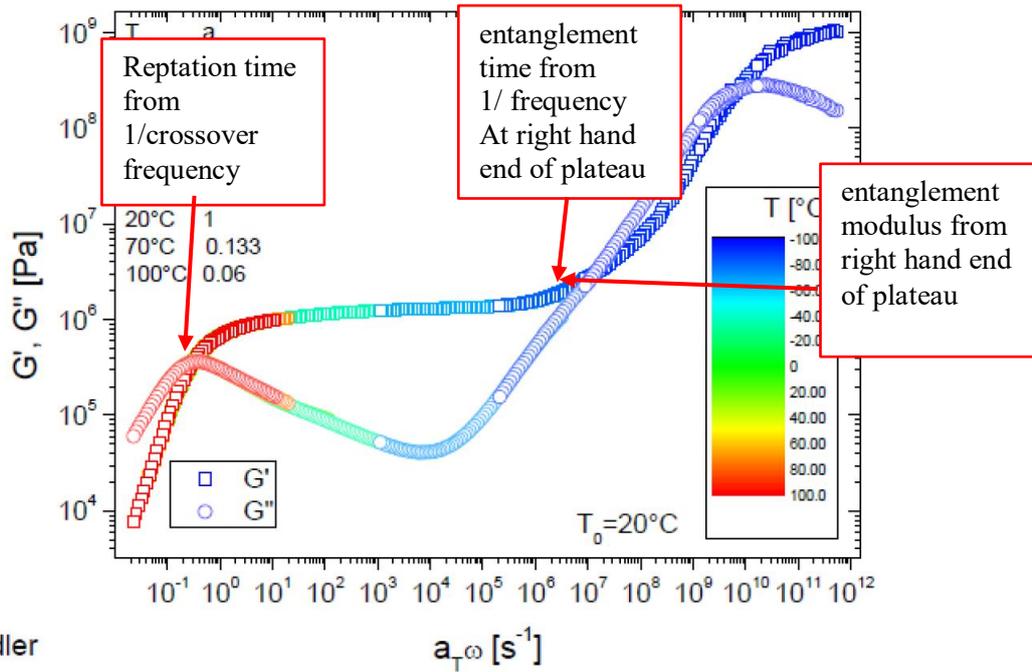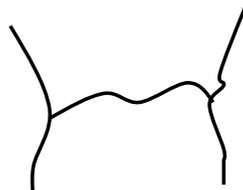
Q9 Branched polymers

a) What is the main relaxation mechanism by which entangled star polymers relax their stress?

b) Use your imagination: describe qualitatively how you might expect the following branched entangled polymer chains to move within the tube model.
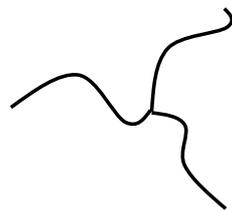
Symmetric star

Asymmetric star

H-polymer

Comb