Tutorial Problems on Polymer Dynamics
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Q1. Linear rheology - TTS
Explain the concept of time-temperature superposition. Why is it useful in experimental rheology? Under what circumstances would you expect it to work for a given material? For which of the following materials might you expect it to (possibly) work, and why?
a) A block copolymer
b) A melt of branched polystyrene molecules
c) A polybutadiene melt with side chains including hydrogen-bonding chemical groups.

Q2. Linear Oscillatory Rheology (for the mathematically-minded students)
If the dynamic modulus $G(t)=G_0e^{-t/\tau}$ 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.

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?

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!].

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).
(b) Give three relaxation mechanisms by which entangled linear polymers relax their stress.
(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.
(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.
(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.

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.

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?

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).

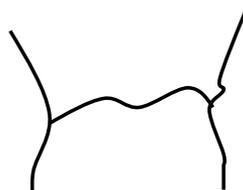   (d) the molecular weight of each melt.
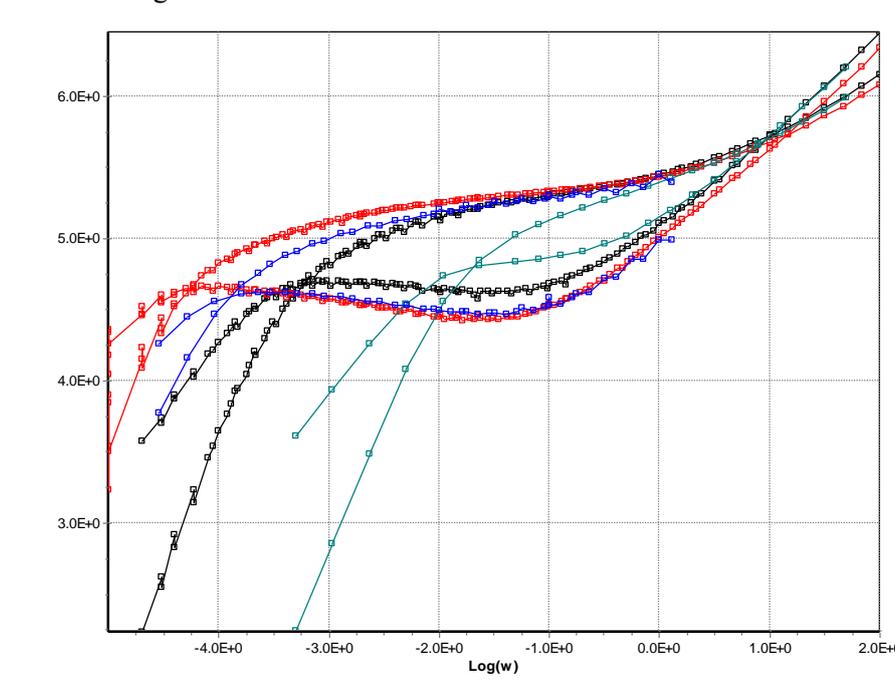
Q9   Branched polymers

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.
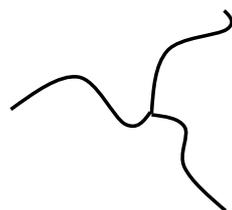
Symmetric star

Asymmetric star

H-polymer

Comb