Morphology of complex materials: Quiz 8 081124

1. The Rouse model describes the relationship between the zero shear viscosity and the molecular weight of a polymer.
   a. How does the dependence of viscosity on molecular weight change with increasing *M*? Does the Rouse model account for this change?
   b. Draw a plot showing the behavior in (a). Mark the region of Rouse model and Reptation model.
   c. What is the reason for this change in behavior? Explain
   d. Draw a plot of log(shear storage modulus) vs. log (frequency) for a polymer say, polyethylene, with Mwts of 10^3, 10^4 and 10^5 g/mole. Explain the change in behavior as seen from this plot.
   e. Do entanglements affect the glass transition temperature of polyethylene? Explain.

2. The tube model is used to describe a monodisperse linear polymer melt beyond its critical molecular weight of entanglement (M_c).
   a. What are the 3 major mechanisms for relaxation in the tube model?
   b. What is primitive path, as described in the Reptation model?
   c. What dependence of viscosity on *M* is obtained from the Reptation model? What power law dependence is actually seen in real polymers (beyond M_c)?
   d. Can you give a few reasons for the change from the predicted theoretical dependence in question (c)?
   e. Compare the dependence of viscosity, relaxation time and diffusion coefficient on *M* for Rouse model and the Reptation model. (Just a table is sufficient)

3. Packing model is a widely used model to relate the structural properties of a polymer with its physical properties.
   a. Write the equation for the volume occupied by one polymer chain (V_c) used in this model.
   b. What does the pervaded volume refer to? Write an equation for V_{sp}.
   c. Write the equation describing the packing length. What is the dependence of entanglement molecular weight M_e on packing length p?
   d. How is M_e related to the plateau modulus of a polymer? Derive the relationship from rubber elasticity.
   e. Can you list the dynamic hierarchy in polymer melts as understood from the discussions in class?

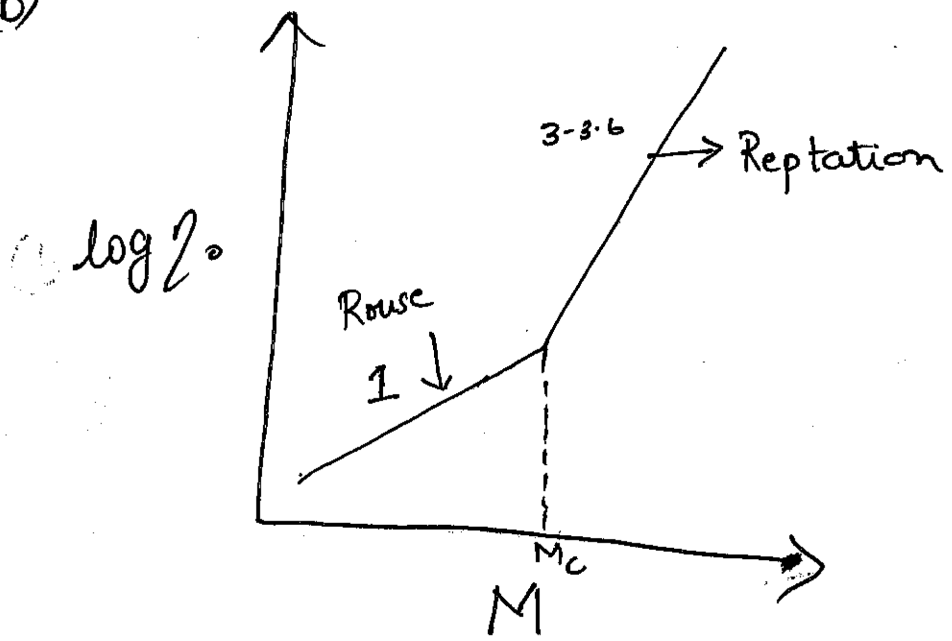
QUIZ 8 ANSWERS 081124

1) a) Below a certain molecular weight, referred to as the critical molecular weight for entanglement (M_c), $\eta_0 \propto M$

Beyond M_c $\eta_0 \propto M^x$ ($3 \leq x \leq 3$-

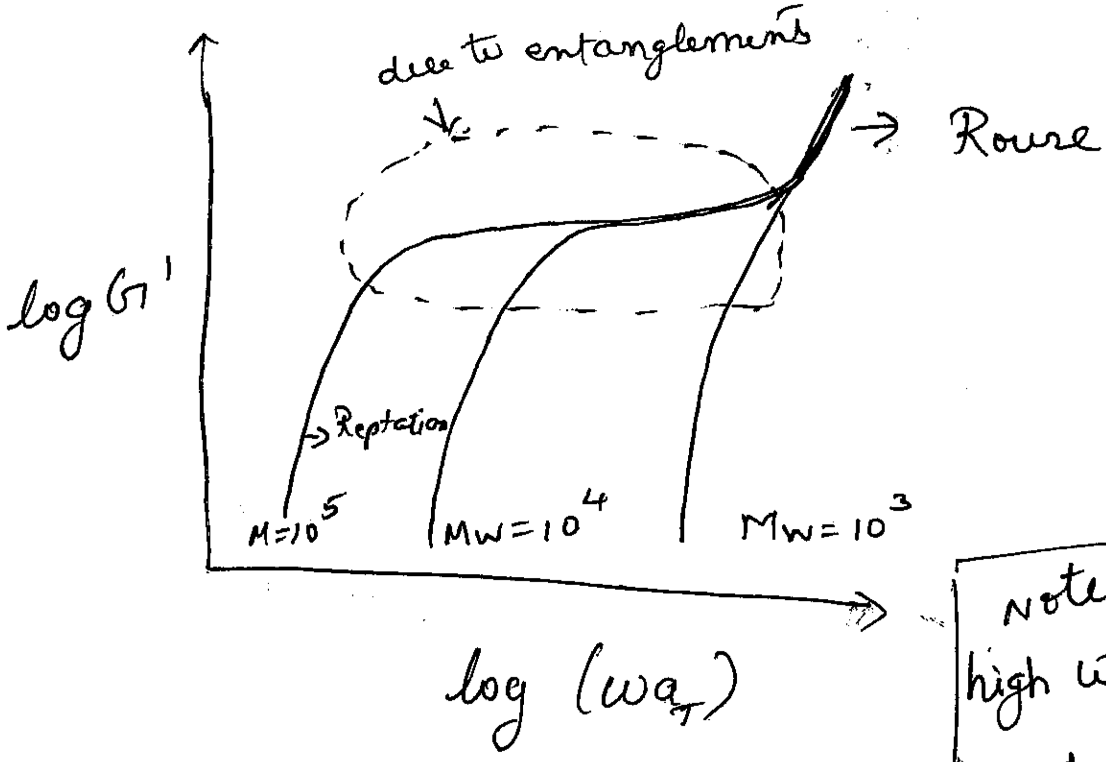
The Rouse model only describes the dependance below M_c.

(b)



(c) As molecular weight increases polymer chains interpenetrate each other forming entanglements. This constrains the motion of the chains. Hence an increased dependance of η on M-wt.

(d)



Note
high ω ~ low relaxa
tim
and vice versa

As M.wt increases beyond Mc, entanglement come into the picture. This causes a plateau-like region to appear for the high~~t~~ M.wt polymers. Higher the MWt, wider is the plateau region.

(e) No. Since glass transition temp is based on local chain motion. Entanglem affect properties that related to the entire chain.

(2) (a) (i) Reptation

(ii) Primitive path fluctuation

(iii) Constrain release. (Multiple reptation)

(b) The path of the reptation test tube is termed as the primitive path

(c) $\eta \propto M^3$

In real polymer, the exponent varies from 3 to 3.6.

The deviation could occur due to various reasons

(i) Non linear chains

(ii) Polydispersity

(iii) Reptation model is assuming a single test chain reptating among stationary chains, which is not the real case

(d)

	Rouse $\propto M^x$ $x=$	Reptation $\propto M^x$ $x=$
τ	1	3
η	2	3
D	-1	-2

(3) (a)

$$V_c = \frac{M}{\rho N_A}$$

(b) Pervaded volume refers to the smallest sphere that can completely contain a molecule /chain

$$V_{sp} \propto \langle R_g^2 \rangle_0^{3/2}$$

(c) $$p = \frac{M}{\langle R^2\rangle_0 \, \rho N_A} = \frac{V_c}{\langle R^2\rangle_0}$$

$$\langle R^2\rangle_0 = 6\langle R_g^2\rangle_0$$

Then from V_c, V_{sp}, we get

$$M_e \propto p^3$$

(d) The equilibrium shear modulus in rubber elasticity theory is described by

$$G_e = \nu RT$$

where G_e is equilibrium shear modulus

ν is molar density of network stands

Replacing G_e with plateau modulus G_N^0

and ν with ν_e molar density of entangled networks

$$G_N^0 = \nu_e RT = \frac{\rho}{M_e} RT$$

(e) Heirarchy ↓ Size / Mass

(i) Rouse Unit

(ii) Packing length

(iii) Persistence / Kuhn length

(iv) Tube dia

(v) Primitive path length of a single tube
(or)
Contour length of ~~entire~~ polymer chains

(vi) Me / Mc

(vii) Rg / M.wt of polymer