080407 Quiz 1 Introduction to Polymers
(*Please answer each question even if you guess*)

This week we explored the definition of a polymer in terms of properties.

1) The flow of polymer melts and concentrated polymer solutions display features that are distinct from low molecular weight materials.
a) Sketch a plot of log of shear viscosity versus log of molecular weight showing shear thinning behavior for a polymer.
b) Sketch a plot of log of the viscosity at low shear rate (from part "a" for instance) versus log of the molecular weight for oligomers and polymers indicating the transition from oligomer to polymer.
c) Give an example of the first normal stress difference observed in polymer flow (that is stress generated at a right angle to the direction of flow).
d) Give a short explanation based on the structure of a polymer melt that can explain the observed behavior in parts a, b and c.
e) At higher temperatures polymers under shear act as if they were subjected to a lower shear rate, that is, they behave more Newtonian at higher temperatures. Explain why you think high temperatures would be associated with a reduction in the feature you describe in part d.

2) Paul Flory stated that *"...perhaps the most significant structural characteristic of a long polymer chain… (is) its capacity to assume an enormous array of configurations."*
a) Explain how butane (4 carbon chain) can assume 3 isomeric conformations (configurations) using a Newman projection and a plot of molecular energy versus rotation angle.
b) For a polymer chain explain how the environmental energy, kT, controls molecular motion through an energy plot similar to that of part a.
c) If you fix a reference frame at one end of a polymer chain what function would describe the probability p(R) for the other end of the chain to be a distance R from the first end of the chain? (Write a function and sketch p(R) versus R.)
d) Compare this function with the Boltzman probability, $p(R) = \exp(-E_{chain}/kT)$ to obtain an expression for the energy of a polymer chain, E_{chain}.
e) How do you think E_{chain} might be related to the isomeric states for the polymer chain similar to the states for butane in part a? (This is the subject of Paul Flory's second book, *The Statistical Mechanics of Chain Molecules* for which he won the Nobel Prize.)

3) Metals and ceramics are purely elastic materials since at low strains they return exactly to their original shape with no loss of energy, that is they act as Hookean springs, $dF = k_{spr}\, dR$, where k_{spr} is a spring constant (similar to a modulus). Low molecular weight liquids, like water, are purely viscous materials since at low strains they show no return to their original shape. A change in force leads to a proportional change in velocity as governed by the friction factor f (similar to a viscosity), $dF = f\, du$, where u is the velocity.
a) How are these viscoelastic properties of importance to the production of a nylon fiber in a fiber spinning process?

b) Explain how the rubber ball displayed both viscous and elastic features as it warmed from -196 ºC (liquid nitrogen) to room temperature. Describe the glassy, and rubbery states as well as the behavior at T_g.

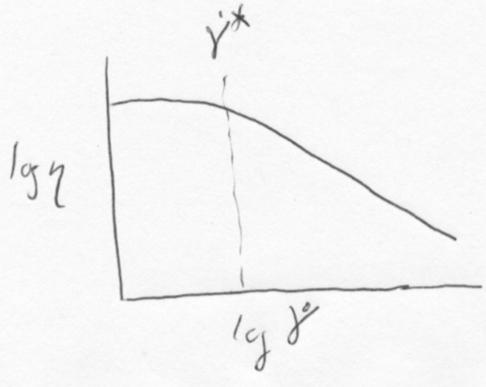
c) How does this temperature dependence of viscoelastic response relate to the energy plot of question 2 a?

d) Temperature is one way to change the viscoelastic behavior of polymers. Describe two other ways that the vicoelastic properties can be manipulated.

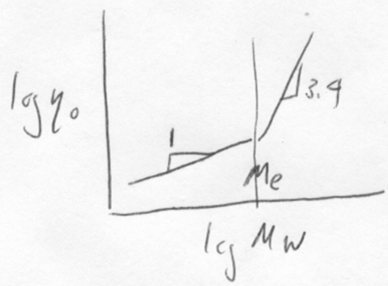
e) A rubber seal is functional only well above the glass transition temperature (> 50ºC above T_g) where it displays rubber-like elasticity. What kinds of problems would you consider for a rocket engine seal subject to vibrations at 50,000 Hz during liftoff on an exceptionally cold morning?

ANSWERS 080407 Quiz 1 Introduction to Polymers

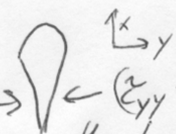
1) a)



b)



c) A bubble in a polymer melt is shaped like a tear. This is due to normal stresses



$\rightarrow$ $\leftarrow (\tau_{yy}-\tau_{xx}) = \Psi_1$

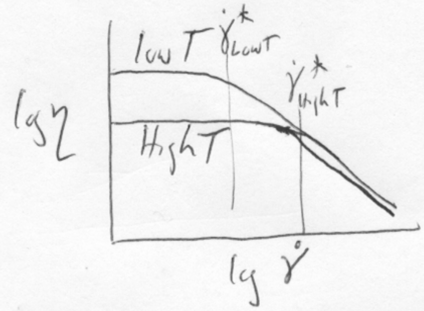
squeezing the bubble.

d) The polymer chains spring back displaying some Hookean characteristic leading to a normal force in the fluid in part c. In part b the short chains are not entangled. In part a the chains display a characteristic time τ.

~~e) The elasticity is related to a time constant~~

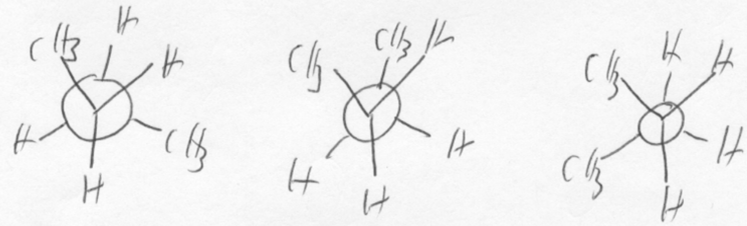
Rate of strain $\dot\gamma$ has units of 1/time. At the transition from the plateau to the power-law fluid the imposed strain rate $\dot\gamma^* \approx \frac{1}{\tau}$ where τ is the characteristic time for the polymer.

e) At high T the chain relaxes faster so τ is smaller & the transition in "a" occurs at a higher $\dot{\gamma}^* \sim \frac{1}{\tau}$



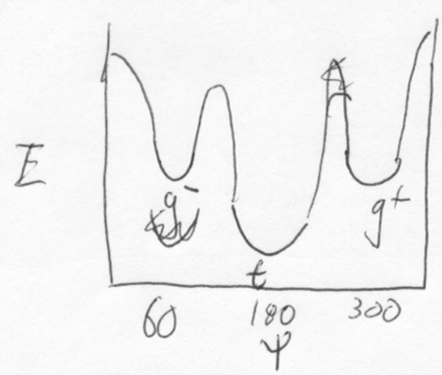
$\dot{\gamma}^* = f(T)$

2) a)



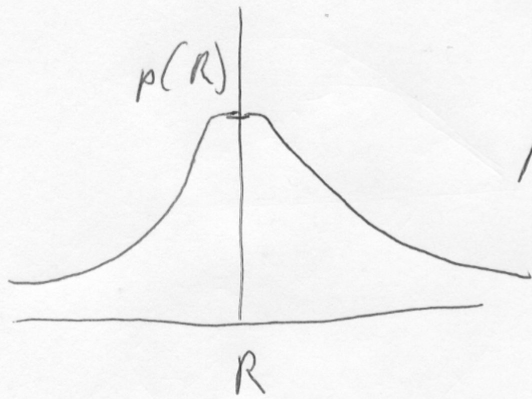
trans gauche + gauche −

Ψ 180



b.) As temperature increases the KT energy overcomes the barrier energy allowing easy rotational function of the chain. This means the chain has overall more motion.

c)



$$p(R) = K \exp\left(\frac{-3R^2}{2Ne^2}\right)$$

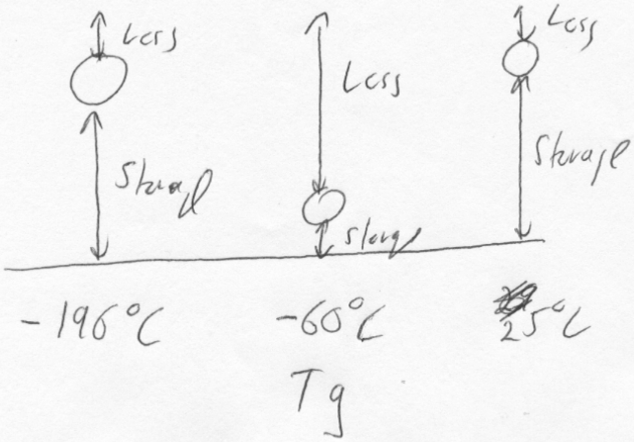
d)

$$\Delta E_{chain} = \frac{3KT\,R^2}{2Nl^2}$$

e) Echain is calculated by considering all possible bond rotations that can lead to a given end-to-end separation distance R. As bonds rotate the chain energy changes.

3) a) The formation of a fiber requires melt strength, that is, the melt must display both viscous & elastic properties.

b.)

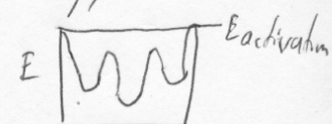


The bounce is composed of motion lost to heat through viscous flow & bounce retained through anelastic response. (see above). At low temperature the ball is glassy & we observe some small loss but mostly bounce. Near Tg the material absorbs all energy & the response is mostly loss. Above T_g the rubber displays rubber-like elasticity.

c) At low T the chain is well below the energy barrier

so $kT \ll E_{activation}$

So Chain can not easily move.



At Tg $kT_g \sim E_{act}$ So Chain Absorbs All Energy

Above Tg $kT \gg E_{activation}$ So Chain freely Moves.

d) ① Happy & Sad Ball's show that chemistry can change Viscoelastic behavior

② Speed of impact of the ball or shear rate in polymer rheology effects the behavior.

e) Low Temperature + very short times i.e. high frequency could make the seal act like a glass & cause failure of the engine seal.