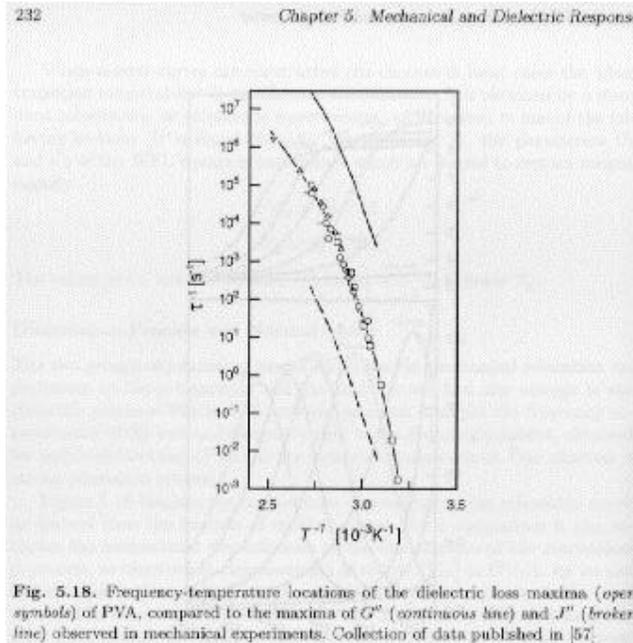


## Quiz 7 Polymer Physics 11/13/00

Two parameters describe the terminal regime of the time dependent behavior of polymers at low frequency or long times.

- a) **-Show** these two parameters in a sketch of  $\log J(t)$  versus  $\log(t)$ .  
**-Show** how this plot changes with molecular weight by plotting 3 such curves, one for very low molecular weight (below 10,000 g/mole) and two for fairly high molecular weight.  
**-What parameter** describes the transition point you observe?
- b) Both of the parameters you described in question "a" can be described by an integral relationship with  $G(t)$ .  
**-Give** these two relationships.  
**-How** can these two integral relationships be used to calculate the mean viscoelastic relaxation time  $\langle \tau \rangle$  from the two parameters?  
**-What** is the expected behavior of  $\langle \tau \rangle$  with respect to molecular weight. **Why?**
- c) Consider a high molecular weight polymer (100,000 g/mole polystyrene) in a dilute solution (so coils do not overlap).  
**-What is** the expected molecular weight dependence of the mean viscoelastic relaxation time?  
**-What is** the behavior for a melt of the same polystyrene?  
**-What is** the behavior for a low molecular weight polystyrene (1,000 g/mole) in a dilute solutions?

d) The following is a plot of  $\log \tau^{-1}$  versus  $1/T$  for  $J''$ ,  $G''$  and  $\epsilon''$ .

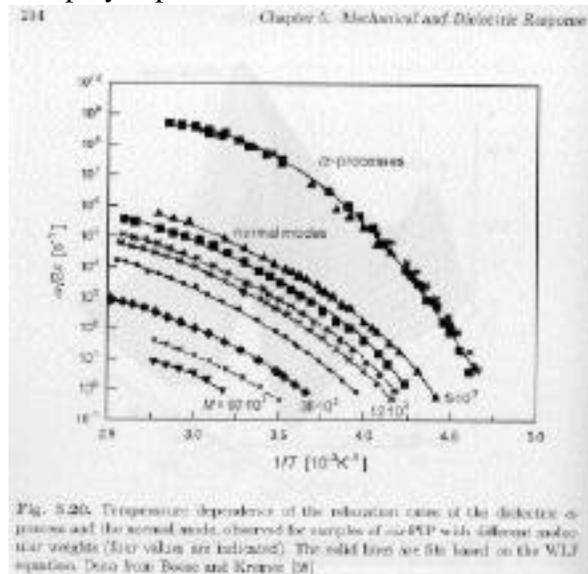


-From this plot is the Arrhenius function is followed?

-Give either the Arrhenius function or an appropriate function to describe this data.

-Why do the different measurements lead to different values of  $\tau$  in this plot?

e) The following plot shows  $\log(\tau^{-1})$  versus  $1/T$  for the dielectric loss peak for a series of molecular weights of polyisoprene. Both the  $\epsilon''$  and normal mode relaxations are shown.



-Is this difference between the  $\epsilon''$  and normal mode relaxations expected? Why?

-Is the normal mode measurement dependent on the use of dielectric relaxation rather than the loss compliance or modulus? Why?

## Answers Quiz 7 Polymer Physics 11/13/00

a)

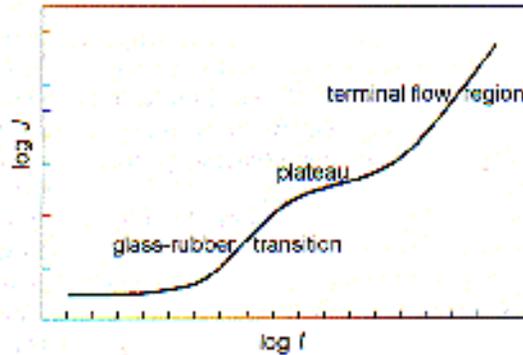


Fig. 5.12. General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 5.11

$J_e^0$  (recoverable compliance) occurs in the plateau region, the linear regime at long times follows  $J(t) = t/\eta_0$ .

As molecular weight increases, above the entanglement molecular weight, the length of the plateau region in time increases. Below the entanglement molecular weight the plateau doesn't exist. A kink in the curve yields  $J_e^0$  and this decays in value with decreasing molecular weight below the entanglement molecular weight.

The entanglement molecular weight determines the transition from  $J_e^0$  linear in molecular weight to  $J_e^0$  constant in molecular weight.

$$b) \quad \eta_0 = \int_0^\infty G(t)dt, \text{ and } J_e^0 = \int_0^\infty tG(t)dt$$

$$\frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt} = J_e^0$$

Below  $M_e$ , both  $J_e^0$  and  $\eta_0$  are linear in molecular weight so  $\langle \eta \rangle$  follows the square of the molecular weight. Above  $M_e$ ,  $J_e^0$  is constant and  $\eta_0$  follows the molecular weight to the 3.4 power so  $\langle \eta \rangle$  follows the molecular weight to the 3.4 power.

c) In dilute solution there are no entanglements and no plateau region so  $J_e^0$  should be linear in molecular weight and  $\eta_0$  is linear in molecular weight so  $\langle \eta \rangle$  follows the square of the molecular weight.

For a melt  $\langle \tau \rangle$  follows the molecular weight to the 3.4 power.

A low molecular weight oligomer in dilute solution follows the same law as the high polymer.

d) Arrhenius is not followed because plot is not a line.

WLF or Vogel/Fulcher equations are the appropriate functions:

$$\tau_0(T) = B \exp(T_A / \{T - T_v\}) \quad (\text{Vogel-Fulcher Fluid, i.e. polymers})$$

The relaxation times are different for compliance and modulus as was calculated in class.

If multiple relaxation times are considered the different measurements weight the different relaxation time distributions differently.

e) It is expected under the model that the  $\beta$ -transition reflects motion perpendicular the chain and the normal modes reflect motion in the chain direction.

The use of a dielectric relaxation is important since the polarizability is different in the different directions with respect to the chain axis. This may not be the case for the friction factor.