Polymer Processing
Quiz 2, 1/23/2000

In house paint it is desirable to have a fluid that spreads easily under shear, during painting, while having a high viscosity under low shear, such as after being applied to a wall under creeping flow due to gravity. The rheological properties desired in a house paint are close to the typical viscosity dependence of a high molecular weight polymer.

a) **-Sketch** the viscosity of a typical polymeric fluid (high molecular weight and an oligomeric fluid (low molecular weight) as a function of shear rate.
-Define the "Newtonian plateau viscosity" in this sketch.
-Give a constitutive equation that describes the flow behavior of a polymer at high rates of strain.
-What is responsible for the polymeric behavior in shear rate?

b) The *Deborah number*, De, for a given polymer in a given process is the ratio between the polymers relaxation time and the experimental time. The relaxation time is the time required for a polymer to relax to a random conformation from an elongated conformation, and the experimental time is often taken as the inverse of the rate of strain.
-Show in the sketch of "question a", where De << 1, De = 1, and De >> 1.
-For house paint show where creeping flow and painting (application) flow should fall (i.e. what is the desired De for each of these)?

c) You might consider the application of paint to a wall as crudely similar to parallel plate flow.
-Sketch parallel plate, laminar flow as shown in class (define a coordinate system).
-Show in this sketch the direction of motion of one plate and it's velocity, V_0.
-Show the velocity distribution across the gap between plates.
-Show the direction of force and the normal to the area that define *shear stress*.
-Show what part of this sketch defines the *rate of strain*.

d) The zero shear rate viscosity of linear chain molecules shows a transition in molecular weight at about 10,000 g/mole.
-Sketch the zero shear rate viscosity versus molecular weight showing this behavior.
-Write equations for the viscosity below and above this transition.
-What is responsible for this transition in behavior?
-Show on this plot where a good material for house paint would lie?

e) The temperature dependence of viscosity for a fluid such as water is described by the Arrhenius equation, $\log(\eta(T)/\eta_\infty) = T_a/T$, where T_a is called an activation temperature for flow. For a polymeric fluid $\log(a_T) = \log(\eta(T)/\eta_a) = T_a/(T-T_V) - C$, where T_V is called the Vogel temperature, C is a constant and a_T is the time/temperature shift factor.
-How do the two temperature dependencies differ? (Consider the limits in temperature of the two equations.)
-Is there any importance of this to paints?

Polymer Processing
Answers Quiz 2, 1/23/2000

a)

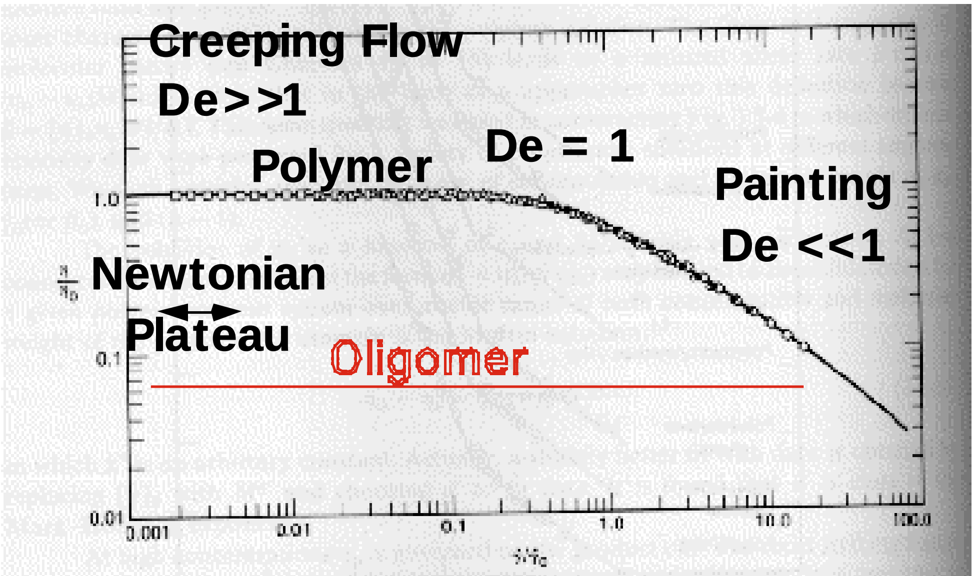
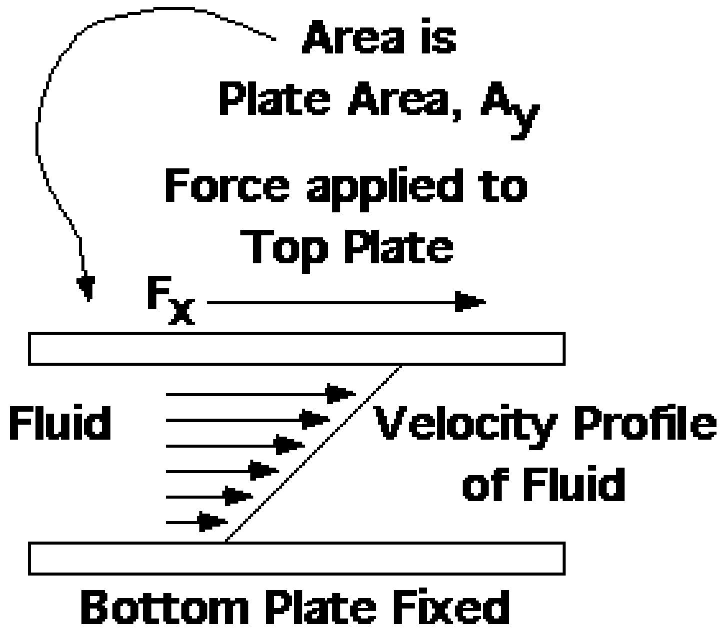


FIGURE 3.6-5. Composite plot of dimensionless viscosity η/η_0 versus dimensionless shear rate $\dot{\gamma}/\dot{\gamma}_0$ for several different concentrated polystyrene-*n*-butyl benzene solutions. Molecular weights varied from 1.6×10^5 to 2.4×10^6, concentrations from 0.255 to 0.55 g/cm^3, and temperatures from 303 to 333 K. [W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974).]

$\eta = m\,(dv_x/dy)^{P-1}$ at high rates of strain.

b) See figure above.

c)



$$\tau_{xy} = F_x / A_y$$

$$\gamma_{xy} = dx/dy \qquad \tau_{xy} = \eta \, \dot{\gamma}_{xy}$$

$$\dot{\gamma}_{xy} = dv_x/dy$$

d)

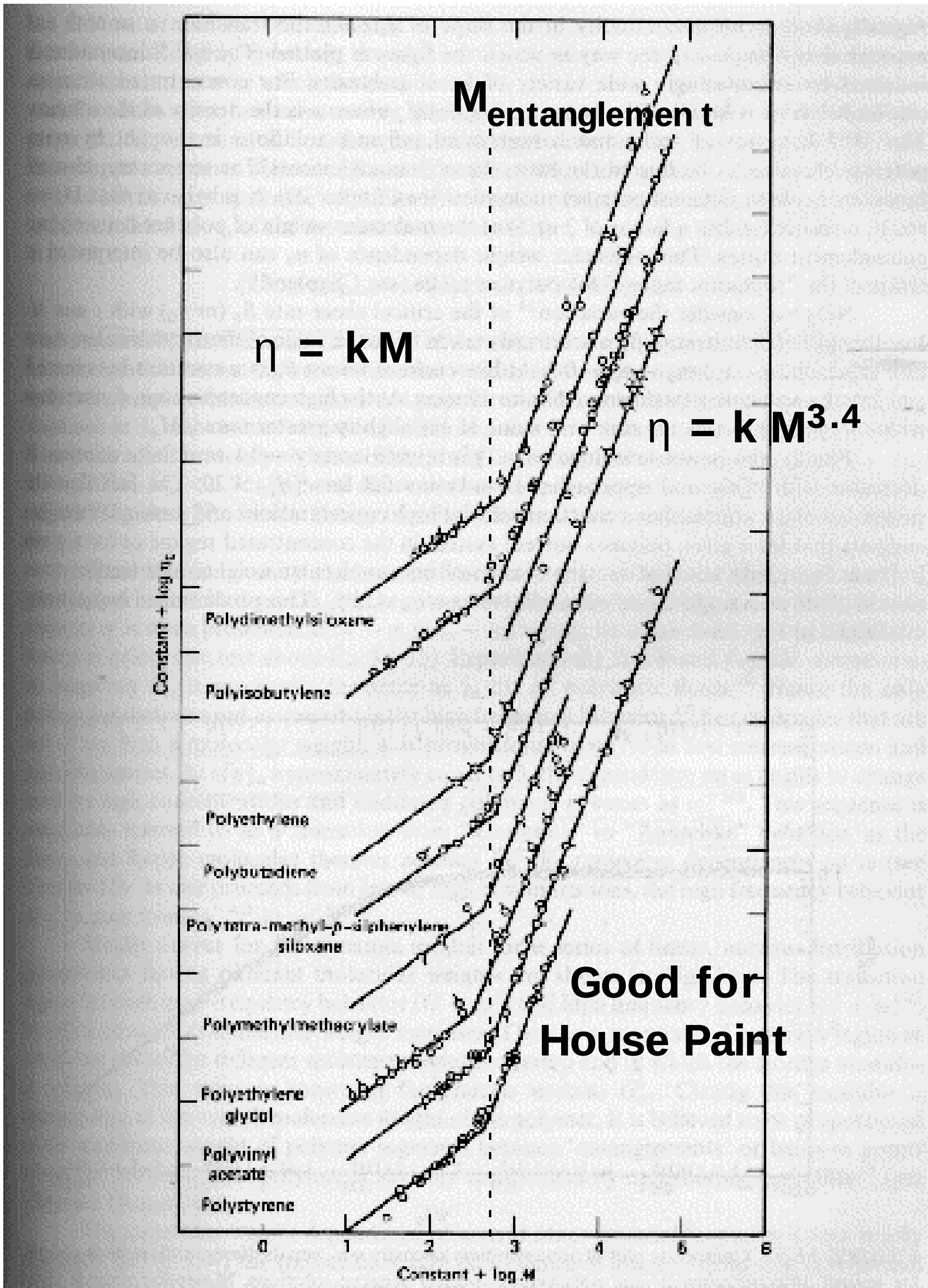


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261–357 (1968).]

d) See Notes:
Arrhenius for water:
$\eta/\eta_S = \exp(C/T)$

WLF

$\log(a_T) = C_1(\Delta T)/\{C_2+\Delta T\}$ or $\eta/\eta_S = \exp(C_1(\Delta T)/\{C_2+\Delta T\})$

$a_T = \eta/\eta_S$

-The two functions show similar behavior away from T_0.

e)

$$\nabla v = \begin{pmatrix} \frac{\partial v_1}{\partial x_1} & \frac{\partial v_2}{\partial x_1} & \frac{\partial v_3}{\partial x_1} \\ \frac{\partial v_1}{\partial x_2} & \frac{\partial v_2}{\partial x_2} & \frac{\partial v_3}{\partial x_2} \\ \frac{\partial v_1}{\partial x_3} & \frac{\partial v_2}{\partial x_3} & \frac{\partial v_3}{\partial x_3} \end{pmatrix}$$

Del v = 1/2(dγ/dt +del ω)

9 6 3 Components

del ω is the difference between **del v** and its transpose.

the rate of strain is the sum of **del v** and its transpose.