# Polymer Properties
## Quiz 4
February 8, 2017

Unidad,…,Richter, and Fetters [*Macro.* **48** 6638 (2015)] draw connections between the packing length, p, and certain rheological transitions they have found in polymer melts. Unidad describes three regimes seen in Figure 1 below: 1. Rouse behavior for $M < M_c$; 2) Reptation with constraint release and contour fluctuations between M_c and M_r; and pure reptation behavior for high molecular weights $M > M_r$.
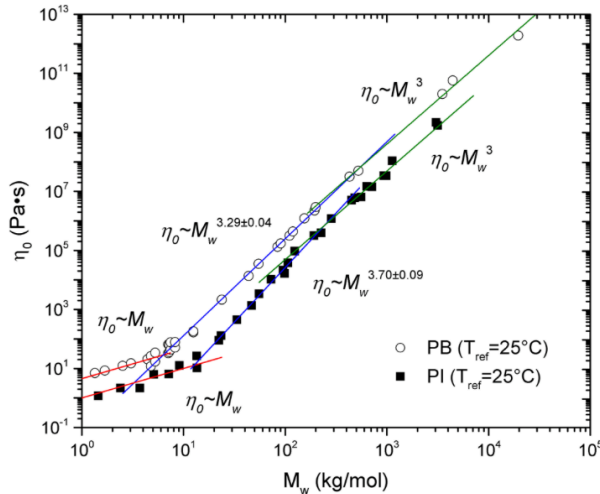
Figure 1. Experimental data for the zero-shear viscosity as a function of molecular weight of polybutadiene (PB) and polyisoprene (PI) melts. Data are obtained from various sources[9,11,12] and show the three scaling regimes. Lines show the different power law fits for each regime.
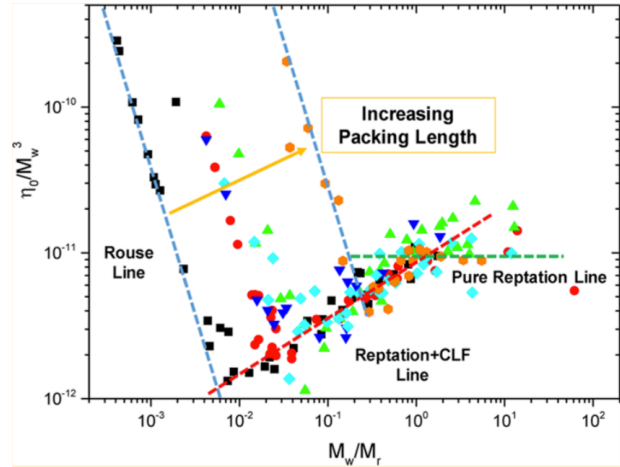
Figure 3. Normalized zero-shear viscosity data as a function of the molecular weight normalized with M_r for various polymers. Curves are shifted vertically to make the pure reptation regime (0 slope) coincide.

$$\eta_0/M_w^3 \quad vs \quad M_w/M_r$$

a) Why does Unidad choose a log log plot for Figure 1? What are the power-law relationships for the three regimes?

b) The traditional entanglement molecular weight, M_e, is determined by the plateau modulus, $G_0 = \rho RT/M_e$. Unidad relates M_c and M_r from Figures 1 and 3 with this M_e using, $M_c = M_e[p*/p]^{0.65}$ and $M_r = M_e[p*/p]^{3.9}$, where p is the packing length, and p* is a constant of about 12 Å which may be an upper limit to packing length.
From these equations explain the behavior in Figure 3.

c) Unidad defines packing length as, $p = M_w/(\rho N_A <R^2>_0)$
From this relationship, how is packing length related to the Kuhn length, l_k? For a chain of 100,000 g/mole with a density of 1 g/cm^3, $N_A = 6.022 \times 10^{23}$/mole, and with $n_k = 100$ what is the value of l_k that corresponds with $p = p* \sim 12$ Å. Comment on what type of chain would have such a Kuhn length (for instance what is C_∞ for $l_{bond} = 1.5$Å).

d) Unidad describes the tube diameter, a, as "the end-to-end distance of an entanglement strand" citing Doi and Edwards. Explain this definition of the tube diameter.

e) Doi and Edwards (*The theory of polymer dynamics* (1986)) show that polymers with the same $Z = M/M_e$ have dynamics (rheology) that can be rescaled to a universal curve using the relaxation time of an entanglement, τ_e, and the tube diameter, a, or the equivalent, M_e. Explain what this means.

ANSWERS: Polymer Properties
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1)

a) log-log plot is the traditional way to highlight power-law relationships. It is a linearization of the power law,

$\eta_0 = kM^P$

$\log \eta_0 = \log k + P \log M$

There are three power-laws, so three lines in this plot, with slope 1, 3.4, and 3.

For the Rouse Regime $\eta_0 = kM^1$, For the transition regime $\eta_0 = kM^{3.4}$, For the Reptation Regime $\eta_0 = kM^3$.

b) The low molecular weight points reflect Rouse behavior, the abrupt change in slopw occurs at $M_w = M_c$, at high molecular weight there is a second transition at M_r for pure reptation. For larger packing length M_c and M_r decrease. The curves are shifted so that the M_r values coincide. This shifts the curves to the right for larger p.

c) $<R^2> = n_k l_k^2$. So $p \sim 1/ l_k^2$

  From the equation we can solve for l_k,

$l_k = (M_w/(\rho N_A n_k p))^{1/2} = (1e5 \text{ g/mole}/(1 \text{ g/cm}^3 \ 6.022e23/\text{mole} \ 100 \ 12\text{Å} \ 1e\text{-}8 \text{ cm/Å}))^{1/2}$ 1e8 Å/cm

$l_k^* \sim 12\text{Å}$

$C_\infty^* = 12\text{Å}/1.5\text{Å} = 8$

This is similar to polystyrene, nothing special, it is a normal polymer. This result is rather odd since you would expect a strange Kuhn length and characteristic ratio for a polymer with $p = p^*$. Polymers with $p = p^*$ should have no transition regime so the tube renewal and contour length fluctuations that modify reptation do not exist.

d) The tube is composed of entanglements that constrain the chain. The size of this "mesh" is the linear distance between entanglements which is $<R^2>^{1/2} = n_{k,e} l_k^2$.

e) The tube makes a freely jointed like walk in space, so the Kuhn model can be used to describe the tube. This becomes useful in calculations since you can then use the random walk equation to describe the tube. The Kuhn length of the tube is a, this is a gross assumption. Since the tube is somewhat of a construction, the Kuhn step length can be defined in any way that they can dream up. The tube diameter is a convenient size that can be easily calculated. It is an ad hoc assumption of the reptation model.

e) According to figure 3 in the question, the viscosity $/M_w^3$ follows power law, so we can write it as

$Eq.1 \rightarrow \log\left(\eta_o / M_w^3\right) = k \log\left(\frac{M_w}{M_r}\right)$ where $M_r = M_e \cdot \left(\frac{P^*}{P}\right)^{3.9}$

On the other hand $\tau_e \sim M_w^3$

so we can write the equation (1) in the form

$$\log\left(\frac{\eta_o}{\tau_e}\right) = k \log\left[\frac{M_w}{M_e \cdot \left(\frac{P^*}{P}\right)^{3.9}}\right] =$$

$$= k \log\left[\frac{M_w}{M_e}\right] - \underbrace{3.9 \, k \log\left(P^*/P\right)}_{k'} = k \log\left(\frac{M_w}{M_e}\right) + k'$$

$\Rightarrow$ so we have $\log\left(\frac{\eta_o}{\tau_e}\right) = k \log\left(\frac{M_w}{M_e}\right) + k'$

for all polymers.

This means that if two polymers have the same $Z = M/M_e$, then their $\log\left(\eta_o/\tau_e\right)$, which is a measure of dynamics (rheology), can be rescaled to the same curve.