Polymer Properties
Quiz 4
February12, 2016

1) 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 $M > M_r$.

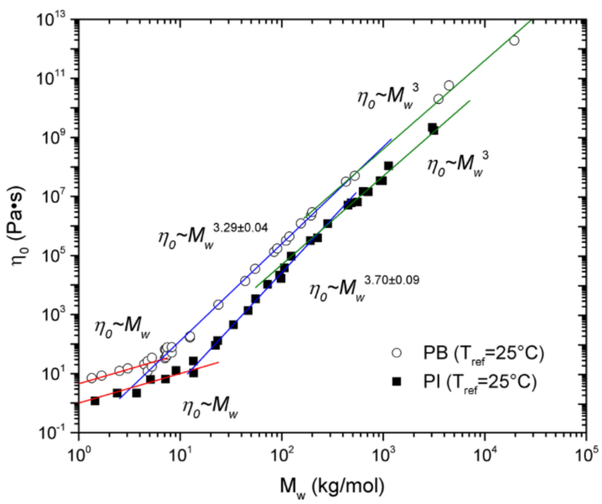

Figure 1. Experimental data for the zero-shear viscosity as a function of molecular weight of polybutadiene (PB) and polyisoprene (PI) melts. Data are obtained from various sources[9,11,12] and show the three scaling regimes. Lines show the different power law fits for each regime.

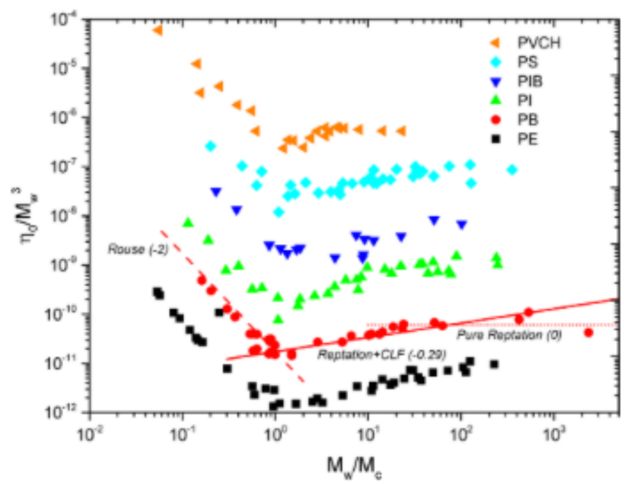

Figure 2. Reduced absolute zero-shear viscosity data as a function of the molecular weight normalized with respect to M_c and with an arbitrary vertical shift for each polymer data set at a polymer-specific reference temperature. Examples of the power law fits are shown for the PB data set.

a) Why does Unidad choose a log log plot for Figure 1?
b) What are the power-law relationships for the three regimes?
c) Unidad also relates M_c and M_r with the traditional M_e that is determined by the plateau modulus,
$G_0 = \rho RT/M_e$.
$M_c = M_e[p^*/p]^{0.65}$ and
$M_r = M_e[p^*/p]^{3.9}$.
From the equation for G_0 explain what M_e is using the chain spring constant you derived in a previous quiz. (p is the packing length, p* is a constant of about 12 Å which may be an upper limit to packing length.)
d) Unidad defines packing length as,
$p = M_w/(\rho N_A \langle R^2 \rangle_0)$
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, $N_A = 6.022\times10^{23}$/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).
e) Unidad made Figure 2 to enhance the transition behavior of Figure 1 in the context of M_c. Explain why he chose the axies in Figure 2 and what is the meaning of $M_w/M_c = 1$

2) Unidad,…,Richter, and Fetters [*Macro.* **48** 6638 (2015)] describes the tube diameter, a, as "the end-to-end distance of an entanglement strand" citing Doi and Edwards.

a) Explain this definition of the tube diameter
b) Unidad also describes the tube diameter as "the step length of the tube" also attributed to Doi and Edwards. Explain this definition of a.
c) How can the tube diameter be used to calculate the number of entanglements per chain, $Z = M/M_e$?
d) Doi and Edwards (*The theory of polymer dynamics* (1986)) show that polymers with the same Z 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.
e) Can the theory of Doi and Edwards (using Z and a) predict the behavior seen in Figure 1?

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.

b) For the Rouse Regime $\eta_0 = kM^1$

For the transition regime $\eta_0 = kM^{3.4}$

For the Reptation Regime $\eta_0 = kM^3$

c) Me is the molecular weight of the chain between entanglements. We previously found, $k_{spr} = 3kT/n_k l_k^2$. Modulus is like spring constant divided by cross sectional area times length, $F = k_{spr}\, x$ and $G = \tau/\gamma = F/A\ /\ x/L = F/x\ \ L/A = k_{spr}\, L/A$. etc.

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

From the equation we can solve for l_k,

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

$l_k^* \sim 12Å$

$C_\infty^* = 12Å/1.5Å = 8$

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. Makes you wonder about the approach… It is good to be skeptical even when they show perfect log-log plots as proof…

f) He chose log-log to highlight the power-law dependencies like in Figure 1. He reduces the zero shear rate viscosity by M^3 to remove the expected behavior from reptation. The highest q part of the curve should be flat, this is where he anticipates reptation to show up. The Rouse regime is now a steep power-law decay of -2 slope so that it becomes clear when it approaches the more constant and positive slope transition regime with a weak slope of 0.4. The x-axis shows M/Mc so when this has a value of 1 we observe the transition from Rouse behavior to transition behavior. The curves all show similar slope in the different regimes.

2)

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

b) 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 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.
c) M_e is ~ $(a/l_k)^2$, following a Kuhn model for the tube.
d) So you would plot viscosity/ τ_e and M/M_e to find a universal plot.
e) The Doi Edwards theory ignores the transitions seen in Figure 1. It does not predict a transition zone.