Quiz 1 Polymer Physics
January 17, 2020

Shear measurements can be used to describe many features that define a high polymer. Figure 11.14 shows the dependence of log shear viscosity versus log rate of strain for polystyrene of different molecular weights from G. R. Strobl, Chapter 5 "The Physics of Polymers, 2'nd Ed." Springer, NY, (1997) (http://www.eng.uc.edu/~beaucag/Classes/Physics/DynChapter4html/Chapter4.html). Figure 4 is from *Viscoelastic properties of dendrimers in the melt from nonequlibrium molecular dynamics* J. T. Bosko, B. D. Todd, R. J. Sadus, J. Chem. Phys. 121 12050-12059 (2004) and shows the calculated log viscosity versus log shear rate from simulations of dendrimers of generation 1 to 4 (top) and linear polymers of variable molecular weight (bottom) from computer simulations.

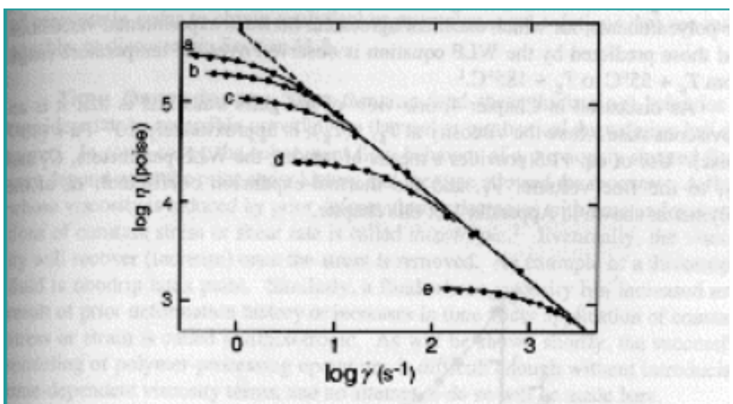


Figure 11.14. Effect of increasing molecular weight on the dependence of polymer viscosity on $\dot{\gamma}$ for polystyrene (M_c = 31,200) at 183°C. Molecular weights are (a) 242,000; (b) 217,000; (c) 179,000; (d) 117,000; and (e) 48,500. [Adapted from R. A. Stratton, *J. Colloid Interface Sci.*, **22**, 517 (1966), with permission of the publisher.]

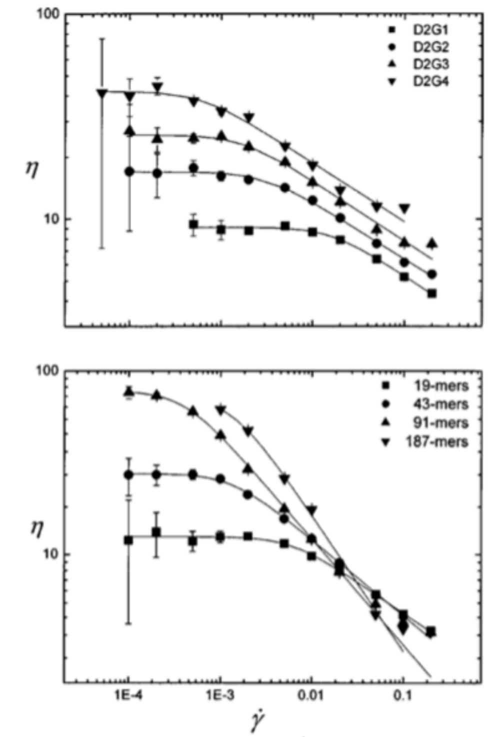
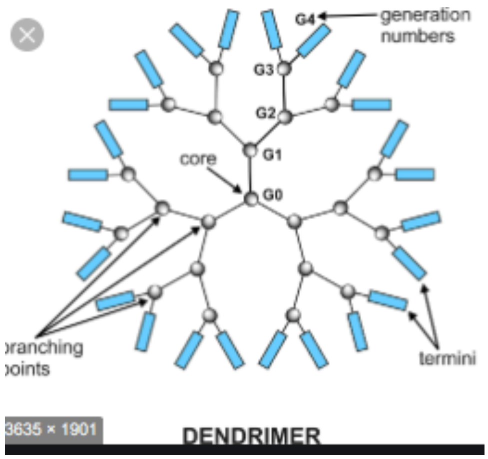


FIG. 4. Comparison of shear viscosity vs strain rate for dendrimers and linear chains of equivalent molecular weight (i.e., same number of beads in the molecule). Solid lines represent fitting with the Carreau–Yasuda (Ref. 3) model: $\eta = \eta_0/[1+(\lambda\dot{\gamma})^2]^p$ Parameters obtained from this fit are in agreement with results presented in the text.

a) Draw a sketch of deck-of-cards flow and define the shear stress, shear strain rate, and shear viscosity.
b) How can the viscoelastic relaxation time be determined from Figure 11.14?
c) If you were reviewing the paper by Bosko (figure to right) what comment would you make concerning Figure 4 (bottom for linear chains) in comparison to Figure 11.14?
d) A dendrimer is a branched polymer that starts from a center point with star architecture at the center (arms coming out like a spider) and splitting of the arms for each generation,

that is generation 0 is the star (spider), generation 1 has one set of bifurcating branches, generation 2 has branches on branches etc. hence G1 to G4 in Figure 4a. Figure 10 below is from Bosko's simulations for a G4 dendrimer under shear.



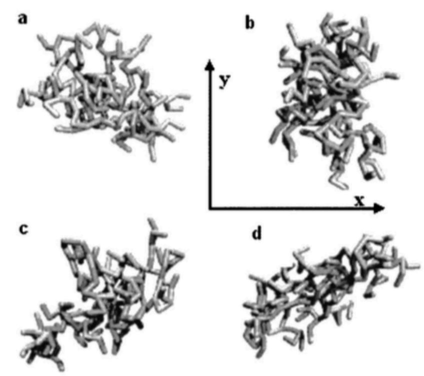


FIG. 10. Configuration of a single dendrimer D2G4 in the melt under shear at strain rate (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1.

The viscosity plots in figure 4a for the dendrimers differ from the linear chains in that the relaxation time is smaller (larger shear rate) and the curves do not overlap or intersect in the power-law regime. Try to explain these two features.

e) Sketch a plot of Newtonian zero shear viscosity versus molecular weight through the entanglement molecular weight. Comment on the molecular weights used in this study (19 to 187 mer units). Do you expect to see the curves shown in Figure 4 for chains of 19 units?

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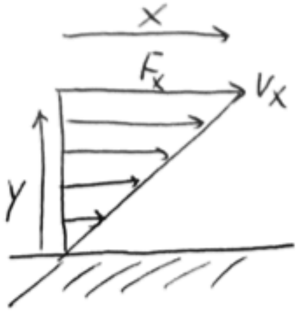
a)



$$\tau_{xy} = \frac{F_x}{A_y} \qquad \gamma_{xy} = \frac{dx}{dy}$$

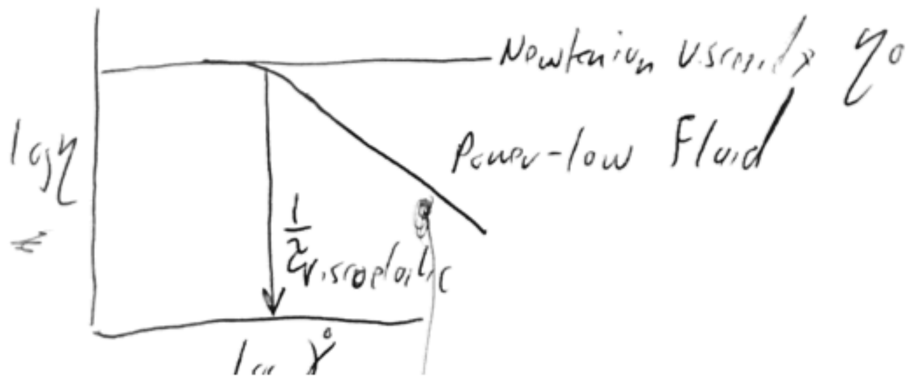
$$\dot{\gamma}_{xy} = \frac{d(dx/dy)}{dt} = \frac{dv_x}{dy}$$

A_x is the y-z plane

$$v_x = \frac{dx}{dt}$$

$$\tau_{xy} = \eta\,\dot{\gamma}_{xy}$$

b)



c) Figure 4b seems to be a mess compared to the experimental data on first glance. The power-law slope should be a constant with slope of about one. The slope varies and has a value of about 1/3. The Newtonian plateau should rise with molecular weight. That works for the first few but the last is not consistent. The relaxation time increases for the first three but drops for the longest chain. This isn't correct.

d) The power-laws differ because the lateral size of the dendrimers is different so the profile of an extended chain is larger for higher generation dendrimers making a larger viscosity power-law prefactor.

The relaxation time is smaller than linear chains because they structures have a smaller short circuit path through the structure (minimum path) so a short chain segment (or an arm) can relax faster than a larger linear polymer chain despite having the same molecular weight.

e) It would seem that the molecular weight is well below the entanglement molecular weight for all of the polymers studied, especially for a 19 mer unit dendrimer. This makes the curves shown in figure 4 suspect.

MW	gamma Linear (unitless)	gamma Dendrimer (Unitless)
19	5^{e}-3	0.014
43	1.8^{e}-3	3e-3
91	4.2 e-4	1.8e-3
187	9^{e}-4	9.23-4

MW	PS gamma(s^{-1})
48.5	1000
117	32
179	4
217	1.6
242	1

MW	Tau Linear (unitless)	Tau Dendrimer (Unitless)
19	200	71.4
43	556	333
91	2380	556
187	1110	1080

MW	PS tau (s)
48.5	0.001
117	0.0312
179	0.25
217	0.635
242	1