Polymer Properties Quiz 13 April 22, 2016

Cheng, Lu, Liu and Wang present measurements and theory to explain stress relaxation and creep measurements for polymeric fluids after a step strain in shear and in tensile experiments ($\Delta\epsilon_{12}$ and $\Delta\epsilon_{11}$). (*Finite cohesion due to chain entanglement in polymer melts*, Cheng S, Lu Y, Liu G, and Wang S-Q, *Soft Matter* **12** 3340 (2016).) The behavior is governed by two relaxation times, τ_R and τ_d , the Rouse relaxation and the reptation relaxation time as shown in Figure 3 for tensile stress relaxation. Two relaxation processes are proposed, chain contour length relaxation that occurs on the Rouse time scale, and orientational relaxation that occurs on the reptation time scale.



Fig. 3 Linear stress relaxation behavior comparisons of shear and extension. The relaxation moduli show identical time dependence throughout the relaxation. Here the prescribed strains of $\gamma = 0.1$ and $\lambda = 1.2$ were applied in the arbitrary wave mode and were reached within 0.03 s.



Figure 6. Steady-state viscosity of PS rings, linear chains, and mixtures versus shear rate. Data obtained from Figure 5. Blue squares, red circles, black diamonds, and green triangles correspond to PS-84k linear, PS-84k ring, their mixture with $\phi_{\rm L}$ = 85%, and PS-185k linear, respectively.

a) Cheng gives two measures of
$$\tau_{\rm R}$$
, $\tau_{R\eta} = \frac{6M\eta}{\pi^2 \rho RT} \left(\frac{M_c}{M}\right)^{2.5}$ and $\tau_{R\omega} = \left(\frac{aM}{1.111\rho RT}\right)^2$ using the

zero shear viscosity η , the density ρ , the entanglement molecular weight M_c and the parameter a, $G' = a\omega^{1/2}$ at high frequencies (from class $a = \eta^{1/2}$). In class we obtained $\tau_R = ((\zeta_R/a_R^2) R_0^4)/(3kT\pi^2) = ((\zeta_R/a_R^2) N_0^2)/(3kT\pi^2)$. Explain the relationship between these three expressions as best you can (I don't think you can fully explain these). In class we

three expressions as best you can (I don't think you can fully explain these). In class we found that $G' \sim (\tau_R \omega)^{1/2}$, and for the plateau modulus $G' \sim RT/M$.

- b) Roughly, how is the expression G' = $a\omega^{1/2}$ obtained, where $a = \eta$? (See equations below)
- c) The reptation time that Cheng calculates is 2578 s while the Rouse time is about 13 s. Why is the reptation time about 200 times the Rouse time? ($M/M_c =$ about 200)
- d) Figure 3 shows two superimposed curves one for a tensile step strain and the other for a shear step strain. Explain what is the difference between these two measurements. Would you expect a difference in response between the two?
- e) Figure 6 is from *Linear and Nonlinear Shear Rheology of a Marginally Entangled Ring Polymer* Yan Z-C, Costanzo S, Jeong Y, Chang T, Vlassopoulos D *Macromolecules* **49** 1444 (2016). They find that ring polymers display Rouse behavior rather than reptation seen in linear chains since the viscosity is lower (bottom curve compared to the second lowest curve for linear chains of the same molecular weight.) Explain why this might be the case. What is the difference in Rouse relaxation time for linear and ring chains? Can this explain the observed result?

Integral from the beginning of the course:

$$G(\alpha) = \int_{-\infty}^{\infty} \exp(-\alpha x^{2}) dx$$

$$(G(\alpha))^{2} - \int_{-\infty}^{\infty} \exp(-\alpha x^{2}) dx \int_{-\infty}^{\infty} \exp(-\alpha y^{2}) dy - \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(-\alpha (y^{2} + x^{2})) dy$$
Then Cartesian coordinates are replaced with circular coordinates, r and θ ,
$$(G(\alpha))^{2} = \int_{0}^{\infty} r dr \int_{0}^{2\pi} d\theta \exp(-\alpha r^{2}) = 2\pi \int_{0}^{\infty} r dr \exp(-\alpha r^{2})$$

$$= \frac{-2\pi}{2\alpha} \int_{0}^{\infty} -2\alpha r dr \exp(-\alpha r^{2}) = \frac{-\pi}{\alpha} \left[\exp(-\alpha r^{2}) \right]_{0}^{\infty} = \frac{\pi}{\alpha}$$
Modulus integral for Rouse model:

$$G(t) = \rho_c kT \sum exp(-2t/\tau_m)$$

$$G(t) \approx \int_{m=1}^{N_R-1} dm \exp\left(-2m^2 t/\tau_R\right) \approx \int_{m=1}^{\infty} dm \exp\left(-2m^2 t/\tau_R\right)$$

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a) The friction factor is related to the melt viscosity so one might expect a linear dependence on viscosity. The relaxation time should also be inverse to kT or RT. Reptation occurs within a tube of size M_c (see Larson definition of tube model terms on web page). Inside of this tube we observe Rouse relaxation. So the number of Rouse units is M/M_c . The molecular weight dependence in the first expression is confusing. a_R^2 is proportional to the number Kuhn units in a Rouse unit so M/M_c . The inverse of this yields $(M_c/M)^2$. The relaxation time is also proportional to M^2 but this dependence is missing from the first expression of Cheng.

The second expression is arrived at using G' ~ $(\tau_R \omega)^{1/2}$ and G' ~ RT/M for the plateau modulus so G' ~ $(RT/M)(\tau_R \omega)^{1/2}$. G' is also given by G' ~ $\eta \omega^{1/2}$. Equating the two expressions and solving for $\tau_{R \sim} (\eta M/RT)^2$. So it has nothing to do with the derivation in class. It is based on the storage modulus definition. This seems to be an extremely weak equation since there are no entanglements in a Rouse chain and therefore no storage modulus and the second expression doesn't hold, G' ~ RT/M. Yet he gets the same answer... It makes you wonder.

These derivations are from *Stress Overshoot of Polymer Soltuions at High Rates of Shear*, Osaki K, Inoue T, Isomura T *J. Polym. Sci, Polym. Phys.* **38** 1917 (2000).

b) The fluctuation dissipation theorem is used $\langle \sigma_{zx}(0) \sigma_{zx}(t) \rangle = kT G(t)/v$ Then the stress correlation function is calculated based on extension of the Rouse chain which involves the integral of an exponential relaxation. Since the relaxation time depends on the mode squared and you sum or integrate all modes you end up with a Gaussian and the prefactor is the square root of tau/time. This yields $G(t) \sim t^{-1/2}$ or $G'(\omega) \sim \omega^{-1/2}$.

c) τ_d is the time for the chain to reptate from the tube. This involves a longer time than simple Rouse relaxation. Cheng states that $\tau_d = Z\tau_R = 13.5$ s for this case, where Z is the number of tube segments of length a, $Z = Nb^2/a^2$.

d) Tensile experiment is pulling the sample, similar to a mechanical testing arrangement. Shear involves slipping two plates with the sample between. If there is a base response function and you have measured it in the creep experiments then the two curves should be identical. They are pretty close to identical in the data. This is a verification of the methods used by this group.

e) One explanation is that it is more difficult for ring polymers to entangle. However, theoretically the cyclic Rouse relaxation time is $\frac{1}{4}$ of that for a linear chain as calculated in class. So the cyclic should have a much shorter relaxation time as is observed. This could fully explain the observed lower viscosity. Observed cyclic zero shear rate viscosity is about 30 kPa s. The linear of the same molecular weight is about 105 kPa s so a ratio of 3.5, close to 4.