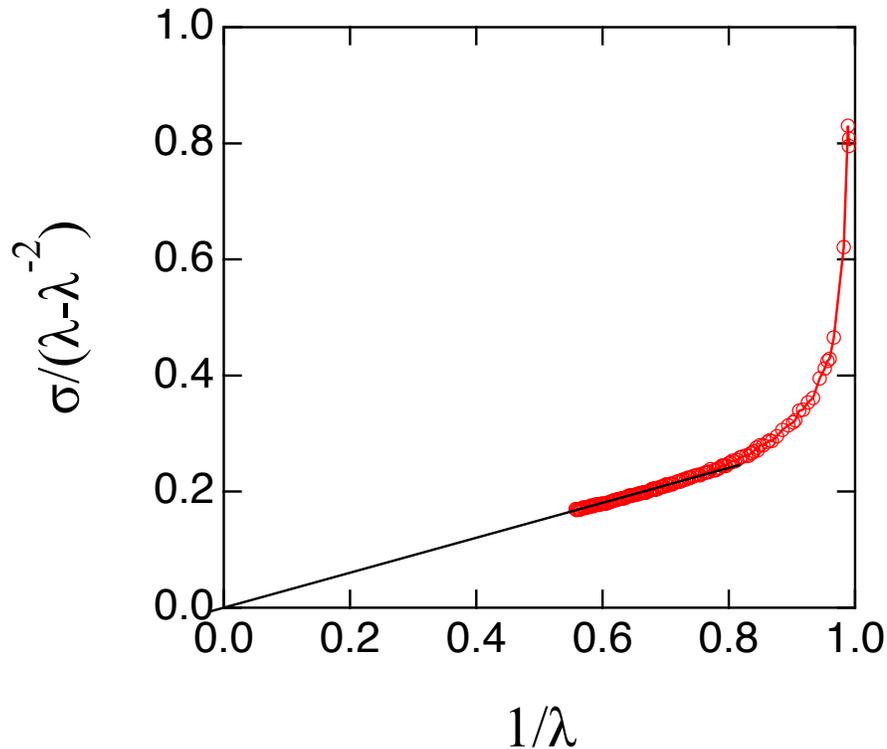


Polymer Physics
Quiz 2
January 22, 2021

Wang Y; Wang W; Hong K; Do C; Chen W-R *Quantitative examination of a fundamental assumption in small-angle neutron scattering studies of deformed polymer melts* Polymer **204** 122698 (2020) discuss the suitability of assuming a Gaussian chain as a structural basis for deformed polymer samples, and the appropriateness of assuming that deuterated chains in a melt of hydrogenous chains deform identically to the hydrogenous chains.

- a) Figure 3 of Wang shows five scattering curves from undeformed polystyrene samples with a small number of deuterated chains where the deuterated chains are observed. Explain the shape of the scattering curves in Figure 3, identify the power-law scaling regime, estimate the slope and indicate why the curve tails over at low- q .
- b) Figure 4 shows the stress strain plot for the same samples shown in figures 2 and 3. The sample is stretched in the melt and then is quenched below the glass transition at a strain of 0.8 for study of oriented samples in Figure 5.
- For a Hookean elastic, $\sigma = E \epsilon$ yields a straight line in a stress-strain plot like figure 4, while the data in figure 4 is not linear and therefore non-Hookean. Hookean elastic materials, like copper, deform at low strains due to reversible elastic stretching of atomic bonds in the crystal. Hookean elastic materials are compressible meaning that tensile loading in the x-direction yields strain in the x direction but leaves the y and z directions unstrained. Materials like Jell-O, human skin, rubbers are not Hookean elastics. These materials display a modulus increasing with the cross-link density and with temperature, $C_1 = \rho_x RT$ where ρ_x is the crosslink density. These materials are ideally incompressible and because of their incompressibility they follow the Mooney-Rivlin equation, $\sigma/(\lambda - \lambda^{-2}) = 2C_1 + 2C_2/\lambda$ rather than Hooke's Law where C_1 is a modulus due to crosslinks between chains. λ is the elongation ratio, $L/L_0 = \lambda = \epsilon + 1$. The data of Wang for polystyrene melts is digitized and replotted in a Mooney-Rivlin plot below. The linear part follows the Mooney-Rivlin equation. Explain the high and low strain behavior. Why is the modulus $C_1 = 0$? Why are the low elongation points higher than expected? (You might think about this in terms of the relaxation time and the distance of relaxation for the chain at low elongations.) From this plot, do you think that quenching the material to a glass at the highest elongation will result in orientation of the chains?



Mooney-Rivlin plot of Wang's data as digitized from Figure 4. $\lambda = L/L_0 = \varepsilon + 1$ is the elongation ratio.

- c) Figure 2 of Wang shows the linear viscoelastic spectra for the polymers. Explain all of the features in these curves especially specifying where the material is a fluid and where it is rubbery and how this can be determined. What happens at the highest frequency?
- d) The entanglement molecular weight, M_e , is determined in Figure 2 from the rubbery plateau modulus using $G_0' = \rho_e RT$ where ρ_e is the entanglement density (number of entanglements per volume). The equation is similar to the definition of the Mooney-Rivlin modulus, C_1 . The entanglement molecular weight is the molecular weight between entanglements of the chains along one chain so $\rho_e = \rho/M_e$. Explain the similarity between the equations for G_0' and C_1 .
- e) We know from our simple simulations in class that most polymer chains will have asymmetry that could be oriented under tensile or shear strain, that is, it is not necessary for the chain to deform in order to display orientation under strain in Figure 5. Figure 5 shows the 2d scattering pattern from deformed chains (the undeformed chains would show isotropic scattering patterns with no orientation). Comment on how you might distinguish between orientation of asymmetric chains and deformation of chains in the experiments conducted by Wang.

ANSWERS:
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- a) Explain the shape of the scattering curves in Figure 3, identify the power-law scaling regime, estimate the slope and indicate why the curve tails over at low- q .

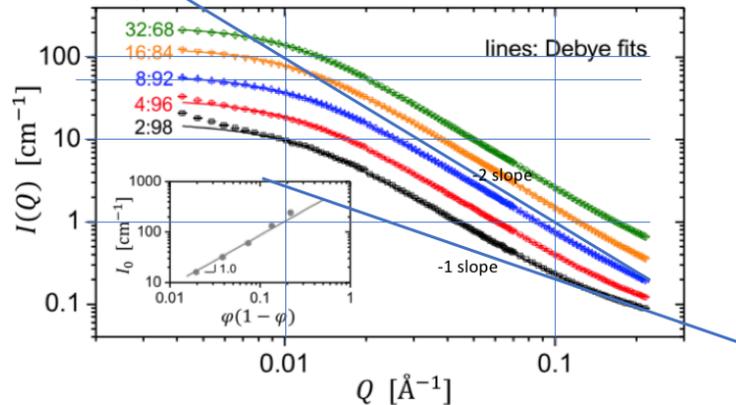


Fig. 3. Small-angle neutron scattering spectra of the isotropic, undeformed polystyrene samples of different h/d ratios. Solid lines: Fits by the Debye function [Eq. (8)]. Inset: Zero-angle scattering intensity I_0 as a function of $\phi(1 - \phi)$. ϕ : Volume fraction of the hydrogenous polymer.

At low- q the intensity is constant, this is for sizes much larger than the coil and the material blurs into a uniform field. Near the knee the coil becomes visible as a spot with a radius of gyration. This is followed by a power-law decay of -2 indicating a Gaussian chain of dimension 2 since $\text{Mass} \sim \text{Size}^2$, $R^2 = nl^2$. At the highest q for the black curve a region of power-law decay -1 indicates linear structure, the persistence length is about $2\pi/q$ for the transition between -2 and -1 slopes.

- b) Explain the high and low strain behavior.

Why is the modulus $C_1 = 0$?

Why are the low elongation points higher than expected? (You might think about this in terms of the relaxation time and the distance of relaxation for the chain at low elongations.)

From this plot, do you think that quenching the material to a glass at the highest elongation will result in orientation of the chains?

At high-strain, low $1/\lambda$, the melt follows the Mooney-Rivlin equation but the modulus, $C_1 = \rho_x RT$, is zero. This means that there are no crosslinks. This is consistent with a polymer melt.

At low strain, high $1/\lambda$, the reduced stress is larger than expected from the Mooney-Rivlin approach. Possible explanation: The sample is being strained at a fixed rate, $d\lambda/dt$, and there is a relaxation time to the motion of the chains, τ . The relaxation time for the chains is reached at some time $t^* = \tau/(d\lambda/dt)$ which corresponds to an extension ratio $\lambda^* = t^* d\lambda/dt$. Prior to this value of λ^* the material is stiffer than it is after the chains can relax and flow.

If the chains were extending due to the presence of entanglements we would expect to see two signatures that are visible in the Sombatsompop paper for the dry sample in Figure 1, below. (Sombatsompop N, *Practical Use of the Mooney-Rivlin Equation for Determination of the Crosslinking of Swollen NR Vulcanisates* J. Sci. Soc. Thailand **24** 199-204 (1998).) In Sombatsompop's dry sample the polymer chains are drawn out and reach extension which leads to an increase in the stress at high strain. This is not seen in the Wang samples. Further, the impact of crosslinks (entanglements for Wang) leads to a non-zero intercept at $1/\lambda = 0$. These two signatures indicate that there is a retractive force on the chains and that this leads to deformation of the chains. The value of 0 for the intercept means that the entanglements have had time to fully relax and there is no retractive force on the individual chains. One premise of Wang's paper is disproven by this plot, it seems that the chains do not mechanically stretch in his experiment.

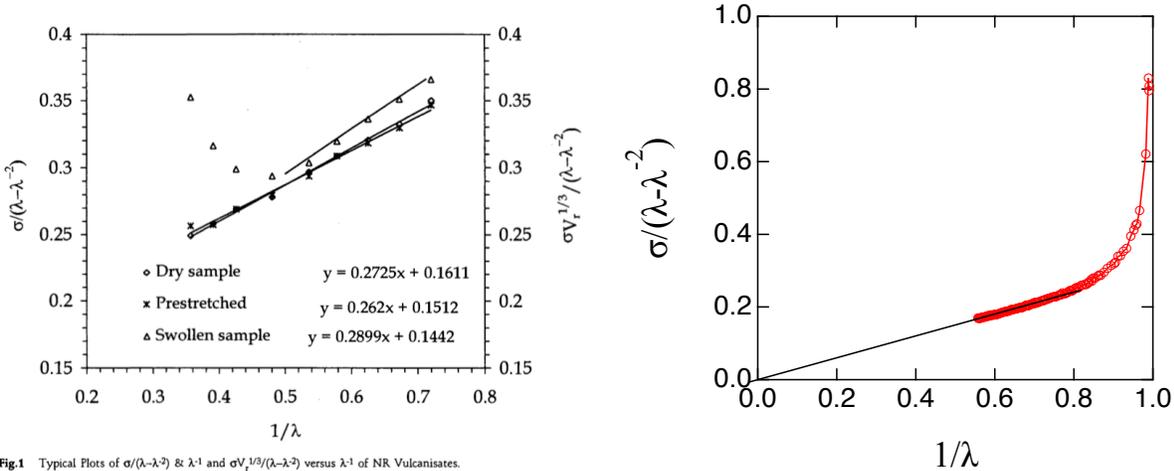


Fig.1 Typical Plots of $\sigma/(\lambda-1)^2$ & λ^{-1} and $\sigma\lambda^{1/2}/(\lambda-1)^2$ versus λ^{-1} of NR Vulcanisates.

c) Figure 2 of Wang shows the linear viscoelastic spectra for the polymers. Explain all of the features in these curves especially specifying where the material is a fluid and where it is rubbery and how this can be determined. What happens at the highest frequency?

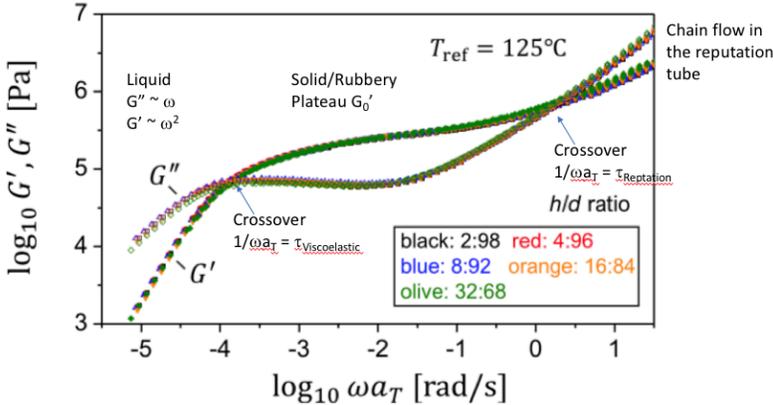


Fig. 2. Linear viscoelastic spectra of the polystyrene samples of different h/d ratios, constructed by using the Time-Temperature Superposition (TTS) Principle. a_T is the shift factor for the TTS procedure. The reference temperature is 125 °C. Solid symbols: $G'(\omega)$. Open symbols: $G''(\omega)$.

d) *Explain the similarity between the equations for G_0' and C_1 .*

Both equations are based on the spring constant (modulus) for a Gaussian polymer chain, $k_{spr} = 3kT/(nl^2)$ where n is the degree of polymerization of the chain, l is the Kuhn step size. When the chain is crosslinked n is the number of units between crosslink sites, this leads to the rubber modulus. When the chain is entangled, n is the number of units between entanglement sites or the entanglement molecular weight which leads to the plateau modulus within a certain time or rate regime, faster than the viscoelastic relaxation time but slower than the relaxation time for chains in the reptation tube.

e) *Comment on how you might distinguish between orientation of asymmetric chains and deformation of chains in the experiments conducted by Wang.*

Wang did several measurements. He looked at the dynamic spectra, he did a static stress-strain measurement and he did oriented and unoriented neutron scattering measurements at different concentrations. Figure 5 would look the same for asymmetric chains that were oriented and for stretched chains, that is unless the degree of stretching were high where the dimension of the chain would go from 2 to 1 for a rod. In this paper he insists and shows evidence that the dimension of the chain remains 2 in the stretched condition, which might indicate that the chains are not perturbed, but he also insists that the chain is substantially deformed. The Mooney-Rivlin plot indicates that the polymer melt is not showing resistance and that the chains are not substantially deformed as discussed above. Wang doesn't indicate the strain rate in his stress strain measurement and doesn't relate it to the dynamic rheometry plot so that you could tell if he is straining in the rubbery plateau region or in the viscous flow region which could make a big difference for desired the chain stretching. The indications seem to support that he doesn't significantly deform the chains and that the observed orientation is due to orientation of asymmetric chains.