Final Polymer Physics (Dynamics) Fall 2000 12/5/00

1) In polymers the viscosity is often measured using a cone and plate viscometer where the zero shear rate viscosity, η_0 and coefficient of the first normal stress difference, Ψ_1^0, are the primary parameters of interest. We discussed η_0 in class and it was one of two principle parameters that describe viscoelastic relaxation, the other being the recoverable shear compliance, J_e^0.

a) State what the zero shear rate viscosity, η_0, is by answering the following questions:

-How is the viscosity related to the shear stress and the shear strain rate?

-How is η_0 extrapolated from experimental values of η?

-How does η_0 empirically behave with molecular weight?

-How do the regimes of η_0's behavior in molecular weight correspond with the two models for polymer relaxation we discussed in class?

-What is the temperature dependence of η_0?

-How is η_0 related to the relaxation time?

b) State what the recoverable shear compliance, J_e^0, is by answering the following questions.

-Define the compliance in a creep experiment in terms of the two measured parameters.

-Consider an experiment where a fixed stress is applied until a terminal equilibrium creep occurred, followed by release of the stress and a recovery from creep. In this context what is J_e^0?

-For a cone and plate rheometer how would you measure the recoverable shear compliance?

c) Give two integral expressions that relate the time dependent modulus, G(t), to J_e^0 and η_0.

d) The first normal stress difference relates the shear strain rate, $d\gamma/dt$, to the force that tends to push the cone and plate apart in a cone and plate rheometer (the normal stress also pushes on the walls of an extruder or capillary). *Normal Stress* = $\Psi_1 (d\gamma/dt)^2$. The normal stress is expected to decay after removal of the shear stress. In the context of part "b" and your description of the measurement of J_e^0:

-Explain qualitatively how the parameter Ψ_1^0 might be related to J_e^0.

e) Quantitatively the following relation is true: $\Psi_1^0/(2\eta_0) = J_e^0\,\eta_0 = \langle\tau\rangle$

-What is $\langle\tau\rangle$ called?

-What integral function relates the time dependent modulus, G(t), to the zero shear rate coefficient of the first normal stress difference, Ψ_1^0?

-What is the molecular weight dependence of Ψ_1^0 (in the terminal regime)?

2) Bueche (J. Chem. Phys. 20, 1959 (1952) and in "Physical Properties of Polymers" Interscience NY (1962)) calculated a power-law dependence of zero-shear rate viscosity on molecular weight of 3.5 based on a model that used the idea of one chain dragging another in shear flow. This idea has been called "entanglement coupling" and is in contrast to the tube model of Doi and Edwards where there is no dynamic feature associated with the "tube", i.e. the tube is fixed for τ_d time-scales.
The entanglement coupling model of Bueche is unable to describe the M^{-2} dependency of the diffusion coefficient while it comes very close to predicting the bulk dynamic properties, i.e. η_0 scaling with $M^{3.4}$. The opposite is true of the tube model (reptation) of Doi and Edwards.

a) What are the predictions for the molecular weight dependence of D and η_0 from the reptation model?
-What are the values from experiment?

b) In our discussion of the fluctuation-dissipation thereom we made an association between bulk constitutive parameters such as η_0 and dynamic molecular features such as the diffusion coefficient, D.
-Under what conditions can this association be made?
-Are these conditions potentially broken when one considers entanglement coupled flow in a polymer melt?
-Are these conditions met when considering the diffusion coefficient for a reptating chain?

c) Use your answer to part "a" to **explain** why the Bueche model comes very close to the experimental viscosity behavior, but fails for the diffusion coefficient, while the reptation model works for the diffusion coefficient and fails for the viscosity.

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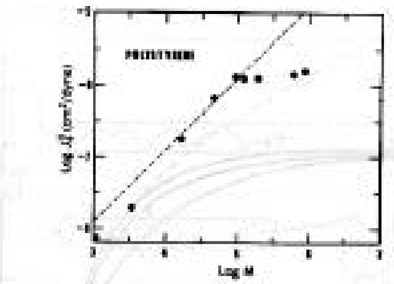

FIG. 10-14. Logarithmic plot of J_e^0 against molecular weight for polystyrenes of narrow molecular weight distribution. (Plazek and O'Rourke.[42])

From Ferry "Viscoel. Prop. of Poly."

d) Give 4 reasons why quasi-elastic neutron scattering is ideal for verification of the tube model.

e) Sketch S(q, t)/S(q, 0) versus time for various q-values (similar to the plot in the notes) and **explain** how this plot supports the tube model of reptation theory.

3) In J. D. Ferry's book "Viscoelastic Properties of Polymers", Chapter 18 deals with viscoelastic behavior in bulk deformation such as when a material is subject to a sudden change in temperature. Figure 18-6 from Ferry (below) shows such relaxations in T-jump (bottom) and T-drop (top) measurements done by Kovacs. The samples in both curves show the volumetric response to a jump (bottom) or drop (top) in temperature as a function of time after a thermal shock well above the glass transition temperature.

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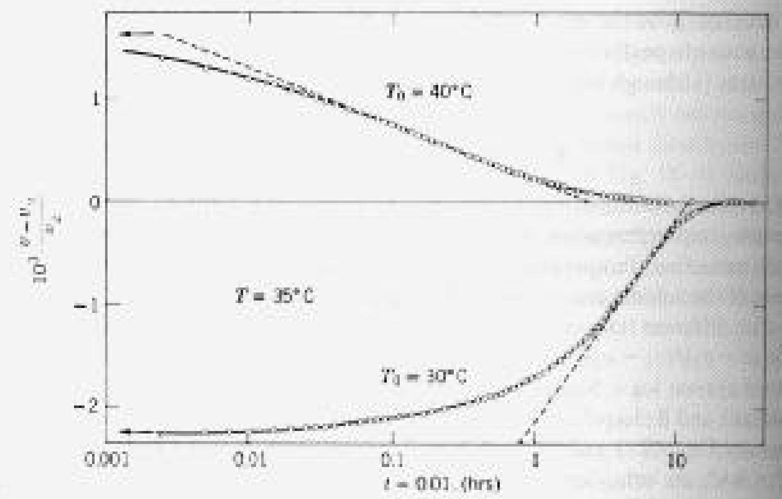


FIG. 18-6. Asymmetric isothermal volume changes of poly(vinyl acetate) at 35° following sudden ΔT of −5° and +5° respectively, plotted as $(v - v_\infty)/v_\infty$ against t − 0.01 in hours with logarithmic scale. (Kovacs.[17])

a) -Propose an equation to describe the T-drop data, v(t), top curve, that includes 3 summed terms.

b) -Propose a parallel equation to describe the T-jump data, bottom curve.

c) -Explain each of the three summed terms in these two equations.

d) For the T-jump experiment what are

-the perturbation;

-the response and

-try to estimate a plot of the primary response function, μ(t), for such a system.

e) If the T-jump is considered instantaneous,

-What simple mechanical measurement are each of these volumetric measurements similar to?

-How are these measurements different from the simple mechanical measurements, and

-What effect would this difference have on the validity of the function you have proposed in parts a and b?

Answers Question 1:

a) $\eta\,(d\gamma/dt) = \tau/(d\gamma/dt)$, where τ is the shear stress and γ is the shear strain. η_0 is obtained by extrapolation to zero shear rate in a plot of log η versus $\log(d\gamma/dt)$. η_0 shows two regimes, at low molecular weight η_0 is proportional to M and at high molecular weight it is proportional to $M^{3.4}$. The low molecular weight regime is related to the Rouse model and the high molecular weight to the reptation model. η_0 follows a Vogel relationship with temperature (exponential). η_0 is proportional to the relaxation time.

b) The time dependent compliance in a creep experiment and is defined as $J(t) = \gamma(t)/\sigma_0$. In the context of an experiment where a fixed stress is applied until a terminal equilibrium creep occurred, followed by release of the stress and a recovery from creep, J_e^0 is the strain recovered divided by the stress released. For a cone and plate rheometer the recoverable shear compliance is the distance of motion opposite the direction of flow when the rheometer torque is turned off. That is it is the recoil shear strain divided by the shear stress when the torque is removed.

c)

$$\eta_0 = \int_0^\infty G(t)\,dt \qquad\qquad J_e^0\eta_0^2 = \int_0^\infty tG(t)\,dt$$

d) The recoverable creep compliance is related to a restoration of an isotropic molecular state. This results in the fluid recoiling after flow. Similarly, the decay of the first normal stress difference is related similarly to a restoration of the isotropic state. Both are based on molecular scale orientation of the chain units.

e) $<\tau>$ is the mean viscoelastic relaxation time. Since,

$$J_e^0\eta_0^2 = \int_0^\infty tG(t)\,dt$$

it can be easily seen that,

$$\Psi_1^0 = 2\int_0^\infty tG(t)\,dt$$

Since η_0 and J_e^0 are proportional to M in the terminal regime, and since $\Psi_1^0/(2\eta_0) = J_e^0\,\eta_0$, then Ψ_1^0 is proportional to M^3. The normal stress difference increases dramatically with molecular weight.

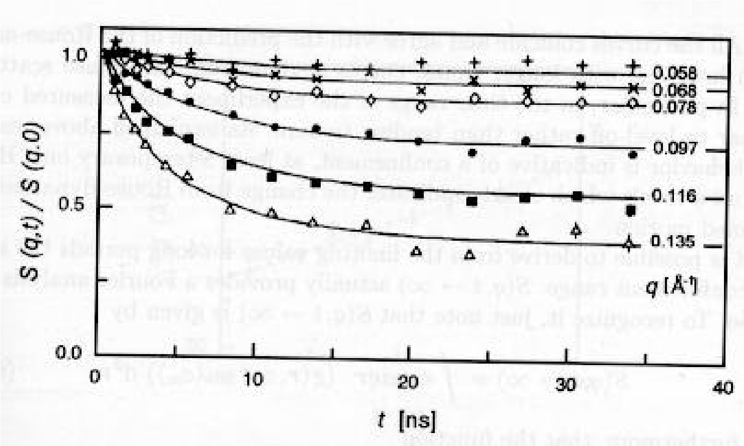
Answers Question 2:

a) Reptation predicts D scaling with M^2 and η_0 scaling with M^3. Experimentally D scales with M^2 and η_0 with $M^{3.4}$ at high molecular weights.

b), c) The link between bulk and molecular behavior is made for small perturbations on the system. It is possible that bulk shear flow is too large a deformation for this association to hold. That is, a static tube may be entirely appropriate for the diffusion coefficient measurement but inappropriate for shear flow where the tube can be potentially dragged along with the chain to some extent as implied by the Bueche theory.

d) 1) The dynamics of a single chain can be observed by deuterium tagging.
2) The size scale observed matches the size of the chain and it's internal dynamic structure.
3) The time resolution by spin polarization, matches the time scale of polymer relaxations.
4) The technique measures the correlation function (time and spatially dependent) and this is one of the basic features predicted by theory.

e)



Low-q corresponds with large sizes (the whole chain). At these q's the chain deviates from free behavior (S(q, t)/S(q, 0) => 0). At high-q the chain approaches 0 or free Rouse-like behavior. There is a fairly discrete transition from Rouse-like to non-Rouse-like constrained behavior (tube constraint). All of the curves show relaxation at longer times.

Answers Question 3:

a) and b) In the T-drop measurement the material volumetrically contracts. Kovacs in the 1960's compares this measurement to an experiment where the sample is subjected to a pressure increase. The latter was described by Kovacs using a Voigt model and an equation of the type:

$$v(t) = v_i + (v_2 - v_i)(1 - \exp(-t/\tau))$$

where v_2 can be larger or smaller than vi depending on if the measurement reflects volumetric contraction or expansion. The expression does not have a flow term or a modulus term. Later expressions included such terms.

c) If you proposed a function of the type shown in class:

$$v(t) = \beta(\Delta T) + (K/\eta)\, t + (1 - \exp(-t/\tau)) \text{ for expansion}$$

and with the latter term $\exp(-t/\tau)$ for contraction,

then the three terms reflect Hookean, Newtonian and Anelastic behavior in the material.

d) The perturbation is a temperature jump that leads to motion of the polymer chains and a larger occupied volume per chain (increase in the free volume). The response is a change in free volume or a change in the volume. The primary response function is complex, reflecting Hookean, Newtonian and Anelastic components, i.e. a pulse (delta function), a constant value and a pulse followed by a decay.

e) The T-drop is similar to a stress relaxation experiment. The T-jump is also, basically a stress relaxation but with a compressive stress.
The measurements have one major difference, that Kovacs was quick to point out in the late 1960's: *with a change in temperature, there is a corresponding change in the "free volume" of the material. A change in the free volume directly changes the relaxation time, t, in all of the equations above, as well as changing the modulus and viscosity.* This means that the T-jump experiment can not, strictly, be described using the simple mechanical analogy equations and very complicated, integral equations have been proposed by Kovacs. In the end, the simple equations may be sufficient for most applications. The measurements and theories of Kovacs on this subject is a rich area in the literature and is worth looking at.