Zimm Model (Non-draining)

Zimm model predicts

$D = kT/\xi = kT/(6\pi\ \eta_s\ b\ N^{1/2}) \sim N^{-1/df}$

$\tau = N\ \xi = 6\pi\ \eta_s\ b\ N^{3/2} = 6\pi\ \eta_s\ b\ N^{3/df}$ $\langle r^2 \rangle = 2Dt$

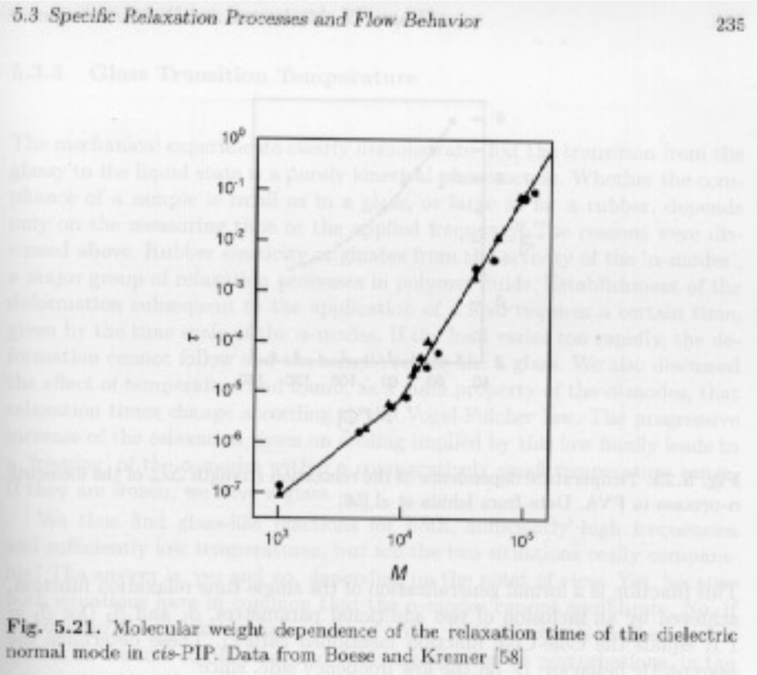
$\eta \sim N^{3/df\ -1} = N^{0.5 \text{ or } 0.8}$ $\eta = \eta_0(1 + [\eta]\phi) \sim \eta_0\left(1 + {}^{\phi}/_{\phi^*}\right) \sim N^{{}^{3}/_{d_f} - 1}$

Rouse Model

Dilute Solution Chain

Dynamics of the chain

Rouse Motion



5.3 Specific Relaxation Processes and Flow Behavior 235

Fig. 5.21. Molecular weight dependence of the relaxation time of the dielectric normal mode in *cis*-PIP. Data from Boese and Kremer [58]

Rouse model predicts relaxation time follows N^2

$D = kT/\xi = kTN/\tau$ follows $D \sim kT/N$

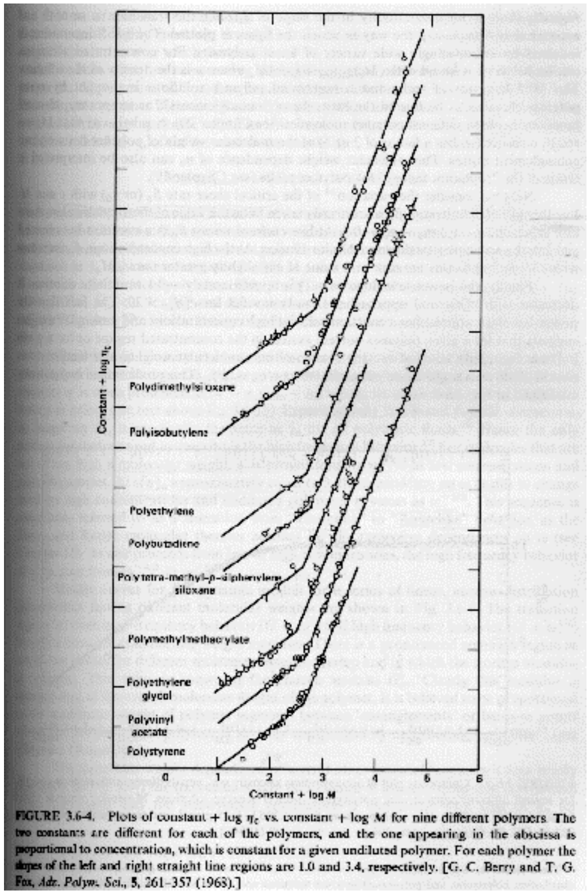


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261–357 (1968).]

Predicts that the viscosity will follow N which is true for low molecular weights in the melt and for fully draining polymers in solution

Rouse Model

$$\zeta \frac{dz_l}{dt} = k_{spr}(z_{l+1} + z_{l-1} - 2z_l)$$

Debye used ma for heat capacity

For L = ∞ You have a wave solution with no modes for δ

$$z_l \sim e^{-\frac{t}{\tau}}\, e^{il\delta}$$

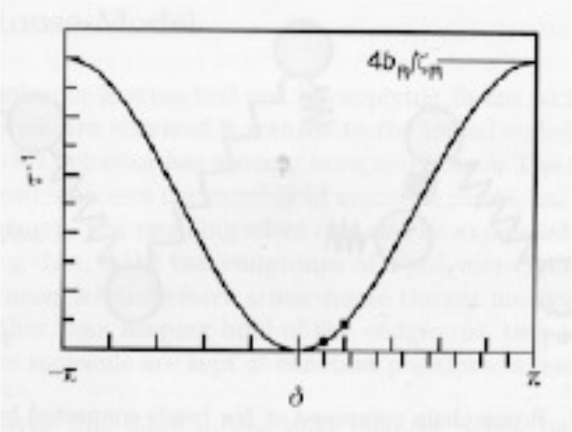
Debye gets $\omega = (k/m)^{1/2}$

τ is the relaxation time ζ/k_{spr}

δ is the phase shift between beads

There are four unknowns and two equations; z, t, τ, δ
So, we can solve for a relationship between τ and δ

$$\tau^{-1} = \frac{4k_{spr}}{\zeta} sin^2\left(\frac{\delta}{2}\right)$$



Cyclic Boundary Conditions:

For $N_R = 10$

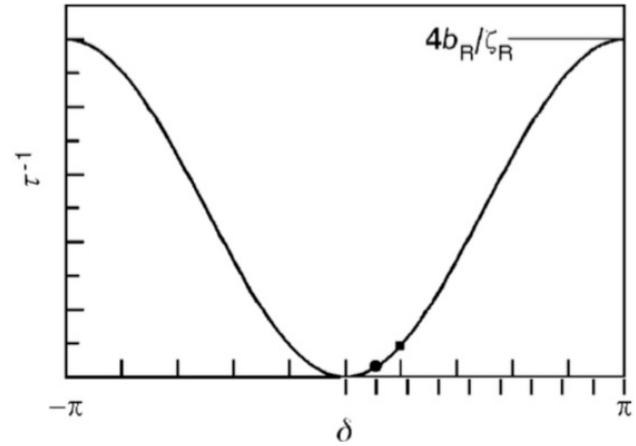


Fig. 8.2. Relaxation rates of Rouse modes as a function of the phase shift δ. *Marks on the inside* of the abscissa show the mode positions for a cyclic chain with $N_R = 10$ beads, the *marks on the outside* give the modes of a linear chain with the same length. The lowest order Rouse modes of the two chains with relaxation rates τ_R^{-1} are especially indicated by a *filled square* and a *filled circle*

$$\tau^{-1} = \frac{b_R}{\zeta_R}\left(2 - 2\cos\delta\right) = \frac{4b_R}{\zeta_R}\sin^2\frac{\delta}{2}$$

$$z_l = z_{l+N_R}$$

$$N_R\delta = m2\pi$$

N_R values of phase shift

$$\delta_m = \frac{2\pi}{N_R}m; \quad m = -\left(\frac{N_R}{2} - 1\right), \ldots, \frac{N_R}{2}$$

For $N_R = 10$

Free End Boundary Conditions:

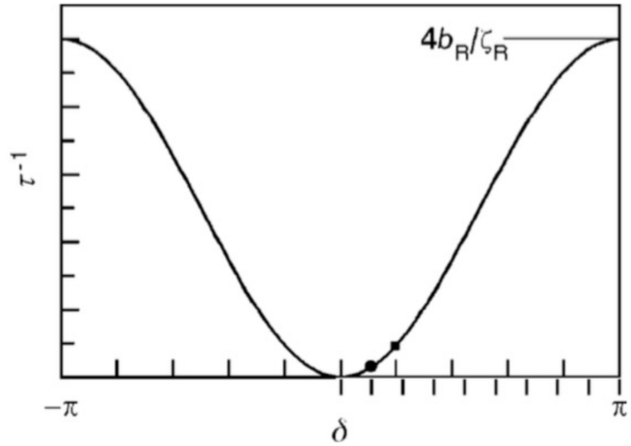


Fig. 8.2. Relaxation rates of Rouse modes as a function of the phase shift δ. *Marks on the inside* of the abscissa show the mode positions for a cyclic chain with $N_R = 10$ beads, the *marks on the outside* give the modes of a linear chain with the same length. The lowest order Rouse modes of the two chains with relaxation rates τ_R^{-1} are especially indicated by a *filled square* and a *filled circle*

$$z_l - z_0 = z_{N_R-1} - z_{N_R-2} = 0$$

$$\frac{dz}{dl}(l=0) = \frac{dz}{dl}(l = N_R - 1) = 0$$

$$(N_R - 1)\delta = m\pi$$

N_R values of phase shift

$$\delta_m = \frac{\pi}{(N_R - 1)} m; \quad m = 0,1,2,\ldots,(N_R - 1)$$

N_R Rouse Modes of order “m”

The amplitude of the Rouse modes is given by:

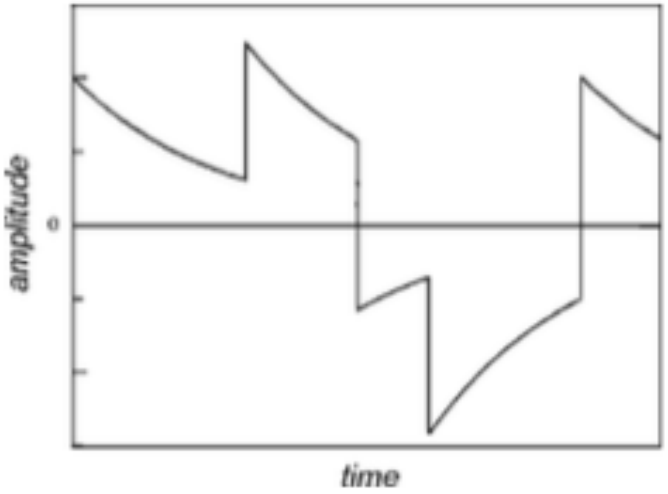
$$\left\langle Z_m^2 \right\rangle = \frac{2}{3\pi^2} \frac{R_0^2}{m^2}$$

The amplitude is independent of temperature because the free energy of a mode is proportional to kT and the modes are distributed by Boltzmann statistics

$$p\left(Z_m\right) = \exp\left(-\frac{\langle F \rangle}{kT} \right)$$

90% of the total mean-square end to end distance of the chain originates from the lowest order Rouse-modes so the chain can be often represented as an elastic dumbbell

Rouse dynamics (like a dumbell response)



Dumbbell

$$\frac{dx}{dt} = -\frac{\left(\frac{dU}{dx}\right)}{\zeta} + g(t) = -\frac{k_{spr}x}{\zeta} + g(t)$$

$$x(t) = \int_{-\infty}^{t} dt'\exp\left(-\frac{t-t'}{\tau}\right)g(t)$$

$$\tau = \frac{\zeta}{k_{spr}}$$

Rouse

$$\tau_R = \frac{\zeta_R}{4b_R \sin^2\frac{\delta}{2}}$$

$$\delta = \frac{\pi}{N_R - 1}m \ , \quad \mathrm{m=0,1,2,...,N_R\text{-}1}$$

$$G'(\omega) \propto (\eta_0 \omega)^{1/2}$$

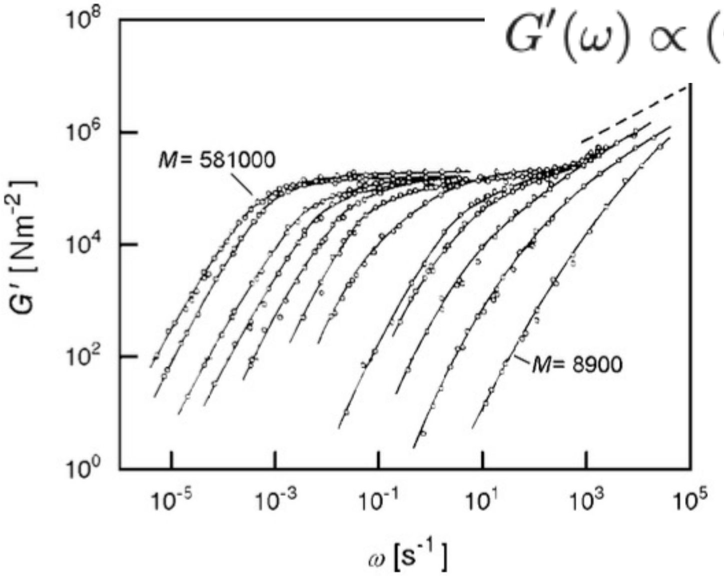


Fig. 6.16. Storage shear moduli measured for a series of fractions of PS with different molar masses in the range $M = 8.9 \times 10^3$ to 5.81×10^5 g mol^{-1}. The *dashed line in the upper right corner* indicates the slope corresponding to the power law Eq. (8.82) derived for the Rouse model of the glass transition. Data from Onogi et al. [74]

Some rules and approaches for complex constitutive parameters

Cox-Merz Rule time measurements are equivalent to frequency measurements. Complex viscosity and steady shear viscosity are equivalent measurements.

Kramers-Kronig Relation

Since there is a response function, μ(t), from which all mechanical responses can be calculated, then the loss and storage moduli are related to each other through the *Cauchy integral, P()*.

$$\alpha'(\omega) - i\alpha''(\omega) = \left\{\int_{-\infty}^{\infty} \mu(t)\cos(\omega t)dt\right\} - i\left\{\int_{-\infty}^{\infty} \mu(t)\sin(\omega t)dt\right\}$$

$$P\left(\int_{-\infty}^{\infty}\frac{\alpha''}{\omega-\omega_0}d\omega\right) = \lim_{\phi\to 0}\left[\int_{-\infty}^{\omega_0-\phi}\frac{\alpha''}{\omega-\omega_0}d\omega + \int_{\omega_0+\phi}^{\infty}\frac{\alpha''}{\omega-\omega_0}d\omega\right]$$

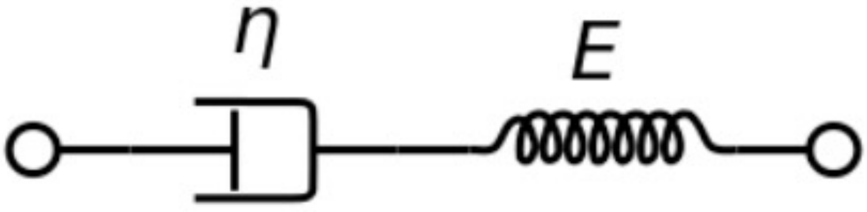
Then the Kramers-Kronig dispersion relations can be written using the Cauchy integral as,

$$\alpha'(\omega) = \frac{1}{\pi} P\left[\int_{-\infty}^{\infty} \frac{\alpha''(\omega)}{\omega - \omega_0} d\omega \right]$$

$$\alpha''(\omega) = \frac{1}{\pi} P\left[\int_{-\infty}^{\infty} \frac{\alpha'(\omega)}{\omega - \omega_0} d\omega \right]$$

Consider the creep compliance, J(t) because it is easier to model.
(Stress relaxation is easier to measure, G(t).)

Maxwell Model or Simple relaxor or Dumbell Model

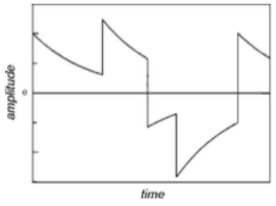


Dumbbell

$$\frac{dx}{dt} = -\frac{\left(\frac{dU}{dx}\right)}{\zeta} + g(t) = -\frac{k_{spr}x}{\zeta} + g(t)$$

$$x(t) = \int_{-\infty}^{t} dt' \exp\left(-\frac{t-t'}{\tau}\right) g(t)$$

$$\tau = \frac{\zeta}{k_{spr}}$$



Debye Single Relaxation time "Relaxor"

$$J(t) = J_0 exp\left(-{}^{t}/_{\tau}\right)$$

For an oscillatory strain

$$J^*(\omega) = \int_0^\infty \Delta J exp\left(-{}^{t}/_{\tau}\right) exp(-i\omega t)dt = \int_0^\infty \Delta J exp\left(-t\left({}^{1}/_{\tau} + i\omega\right)\right) dt = \frac{\Delta J}{{}^{1}/_{\tau} + i\omega}$$

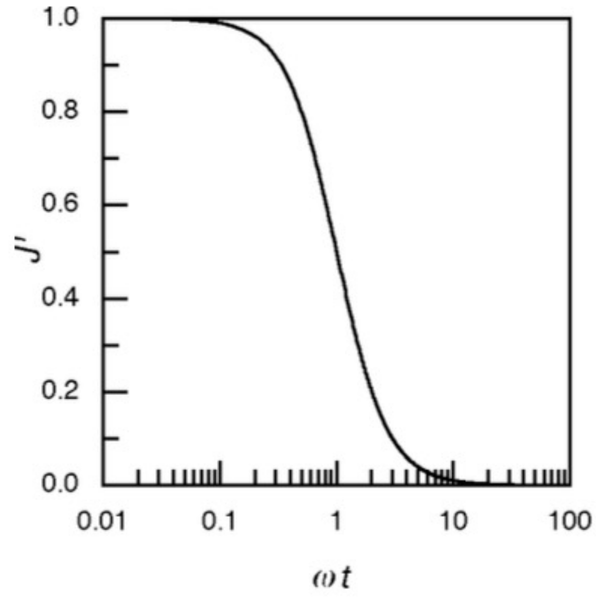
$$J^*(\omega) = \frac{\Delta J}{{}^{1}/_{\tau}+i\omega} = \frac{\Delta J}{{}^{1}/_{\tau}+i\omega}\frac{{}^{1}/_{\tau}-i\omega}{{}^{1}/_{\tau}-i\omega} = \frac{{}^{\Delta J}/_{\tau}}{{}^{1}/_{\tau^2}+\omega^2} - i\,\frac{\omega\Delta J}{{}^{1}/_{\tau^2}+\omega^2} = \frac{\tau\Delta J}{1+\tau^2\omega^2} - i\,\frac{\omega\tau\Delta J}{1+\tau^2\omega^2} = J' - iJ''$$

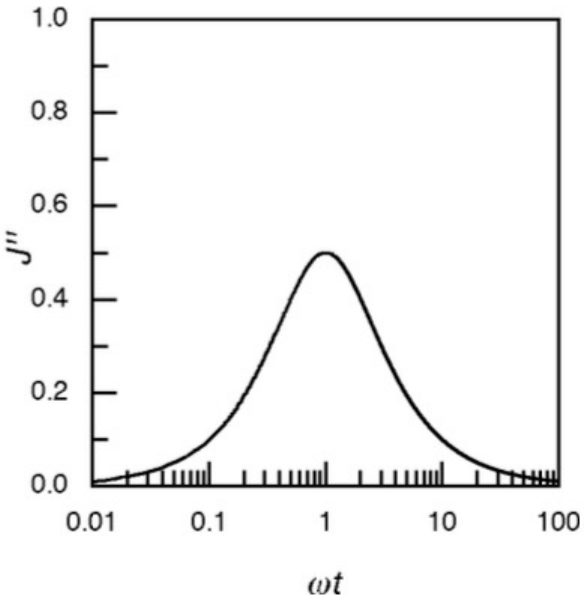
Maxwell Model

$$J^*(\omega) = \frac{\tau\Delta J}{1+\tau^2\omega^2} - i\,\frac{\omega\tau\Delta J}{1+\tau^2\omega^2} = J' - iJ''$$

$$J' = \frac{\tau\Delta J}{1+\tau^2\omega^2}$$

$$J'' = \frac{\omega\tau\Delta J}{1+\tau^2\omega^2} = \frac{\Delta J}{10^{-log(\omega\tau)} + 10^{log(\omega\tau)}}$$





Cole-Cole Plot as an indication of a simple Debye relaxor

$$J^*(\omega) = J_u + \frac{\tau\Delta J}{1+\tau^2\omega^2} - i\,\frac{\omega\tau\Delta J}{1+\tau^2\omega^2} = J_u + J' - iJ''$$

J_u is the unrelaxed compliance

$$\left[J' - \left(J_u + \frac{\Delta J}{2}\right)\right]^2 + \left[J''\right]^2 = \left[J' - \left(J_u + \frac{\Delta J}{2}\right)\right]^2 + \left[J''\right]^2 = \left[\frac{2J' - 2J_u - \Delta J}{2}\right]^2 + \left[J''\right]^2$$

$$= \left[\frac{2\Delta J - \Delta J(1+\omega^2\tau^2)}{2(1+\omega^2\tau^2)}\right]^2 + \left[\frac{\Delta J^2\omega^2\tau^2}{(1+\omega^2\tau^2)^2}\right] = \frac{\Delta J^2(1+\omega^2\tau^2)^2}{4(1+\omega^2\tau^2)^2} = \frac{\Delta J^2}{4}$$

$(x\text{-}a)^2 + (y\text{-}b)^2 = r^2$

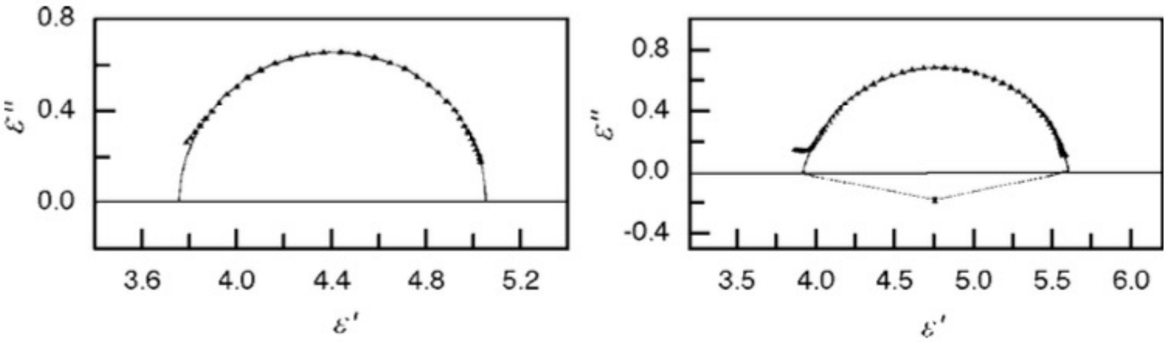


Fig. 6.6. Cole–Cole plots of dielectric data obtained for a dipole carrying a rod-like molecule of low molar mass (*left*) and a polysiloxane with these molecules attached as side-groups (*right*) [67]

Shear compliance, *J**(ω), easy to calculate. Shear modulus, G*(ω), easy to measure.

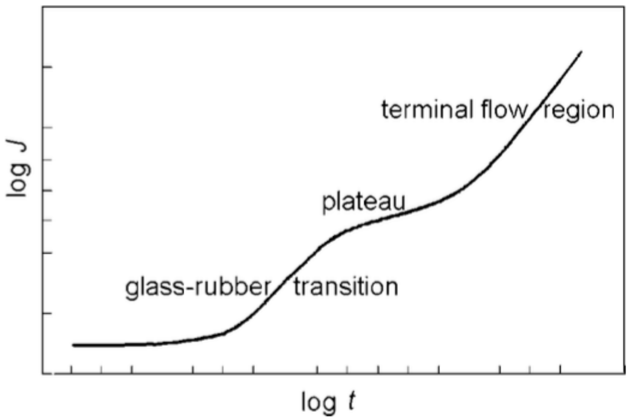
$$J^*(\omega) = J_u + \frac{\Delta J}{1 - i\omega\tau}$$

$$G^*(\omega) = \frac{1}{J^*(\omega)} = \frac{1 - i\omega\tau}{J_u(1 - i\omega\tau) + \Delta J} = \frac{1}{J_u} - \frac{\Delta J}{J_u J_r}\frac{1}{1 - i\omega\hat{\tau}} = G_u + \frac{\Delta G}{1 - i\omega\hat{\tau}}$$

$$J_r = J_u + \Delta J; \hat{\tau} = \frac{\tau J_u}{J_r}; G_r = \frac{1}{J_r}; G_u = \frac{1}{J_u}; \Delta\mathrm{G} = G_u - G_r$$

$$J^*(\omega) = \int_0^\infty \Delta J exp\left(-{}^{t}/_{\tau}\right) exp(-i\omega t) dt = \int_0^\infty \Delta J exp\left(-t\left({}^{1}/_{\tau} + i\omega\right)\right) dt = \frac{\Delta J}{{}^{1}/_{\tau} + i\omega}$$

In the terminal flow regime



At long times, the Maxwell element is just viscous

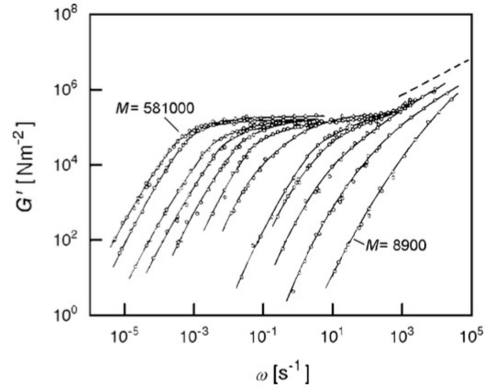
$$\gamma(t) = J(t)\tau_0 \quad \tau(t) = G(t)\gamma_0$$

$$\tau = \eta_0 \frac{d\gamma}{dt} = \tau_0 \eta_0 \frac{dJ(t)}{dt} \qquad \frac{dJ(t)}{dt} = \frac{1}{\eta_0} \qquad slope\ is\ \frac{1}{\eta_0}\ at\ long\ times$$

In the terminal flow regime for the dynamic compliance

$$At\ low\ \omega \sim 1/t \quad J^*(\omega) = J_e^0 + i\frac{1}{\eta_0 \omega}$$

In the terminal flow regime/low frequency regime



In the terminal flow regime for the dynamic compliance

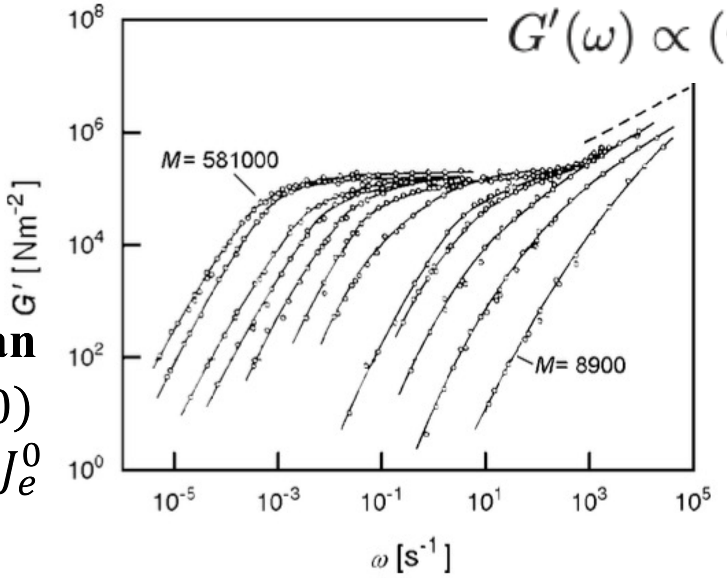
$$\boldsymbol{At\ low\ \omega} \sim 1/t \quad J^*(\omega) = J_e^0 + i\,\frac{1}{\eta_0\omega}$$

$$G^*(\omega \to 0) = \frac{1}{J^*(\omega \to 0)} = \frac{\eta_0\omega}{\eta_0\omega J_e^0 + i} = \frac{(\eta_0\omega)^2 J_e^0 - i\eta_0\omega}{(\eta_0\omega J_e^0)^2 + 1}$$

$$G'(\omega \to 0) = (\eta_0\omega)^2 J_e^0 \qquad G''(\omega \to 0) = \eta_0\omega$$

Rouse

$$G'(\omega) \propto (\eta_0\omega)^{1/2}$$



Newtonian

$$G'(\omega \to 0) = (\eta_0\omega)^2 J_e^0$$

Fig. 6.16. Storage shear moduli measured for a series of fractions of PS with different molar masses in the range $M = 8.9\times10^3$ to 5.81×10^5 g mol^{-1}. The *dashed line in the upper right corner* indicates the slope corresponding to the power law Eq. (8.82) derived for the Rouse model of the glass transition. Data from Onogi et al. [74]

Rouse

$$G'(\omega) \propto (\eta_0\omega)^{1/2}$$

Modulus has units of energy per volume, MPa
Each mode of vibration, p, in the Rouse Model has

$$\tau_p = \tau_0 \left(\frac{N}{p}\right)^2$$

Larger p modes have smaller τ_p so **larger p modes are relaxed** when $t = \tau_p$
When $t = \tau_p$ there are **p unrelaxed modes** composed of segments **with kT** energy
Each of these segments have **N/p monomers** of volume b^3
For a volume fraction of monomers of ϕ, the **number of unrelaxed segments per volume** is $\phi/(b^3N/p)$
So, the storage modulus is $G(\tau_p) \sim kT\,(\phi/(b^3N/p)$
We know that $\tau_p = \tau_0\,(N/p)^2$ so $p \sim (\tau_0/\tau_p)^{1/2}N$ and
$G(\tau_p) \sim kT\,(\phi/(b^3N/p) = (kT/b^3)\phi(\tau_p/\tau_0)^{-1/2}$ and for time $t = \tau_p$

For $\boldsymbol{\tau_0} < t < \boldsymbol{\tau_R}$

$$\mathbf{G}(t) \sim (\mathbf{kT/b^3})\phi(t/\tau_0)^{-1/2}$$

$$\mathbf{G'}(\omega) \sim (\mathbf{kT/b^3})\phi(\omega\tau_0)^{1/2} \sim (\mathbf{kT/b^3})\phi(\omega\eta_0)^{1/2}$$

$$\mathbf{G}(t) \sim (\mathbf{kT/b^3})\phi(t/\tau_0)^{-1/2}\,\mathbf{exp}(-t/\tau_R)$$

For $\boldsymbol{\tau_0} < t$

Rouse

$\mathbf{G}(t) \sim (\mathbf{kT/b^3})\phi(t/\tau_0)^{-1/2}\ \mathbf{exp(-t/\tau_R)}$ For $\tau_0 < t$

$$G'(\omega) = G_{eq} + \omega \int_0^\infty \left[G(t) - G_{eq}\right] sin\,(\omega \mathrm{t})dt$$

$$G''(\omega) = \omega \int_0^\infty \left[G(t) - G_{eq}\right] cos\,(\omega \mathrm{t})dt$$

$$G'(\omega) = \frac{\phi kT}{b^3}\frac{(\omega\tau_R)^2}{\sqrt{[1+(\omega\tau_R)^2]\left[1+\sqrt{[1+(\omega\tau_R)^2]}\right]}}$$

For $\omega < 1/\tau_0$

$$G''(\omega) = \frac{\phi kT}{b^3}\omega\tau_R\sqrt{\frac{\left[1+\sqrt{[1+(\omega\tau_R)^2]}\right]}{[1+(\omega\tau_R)^2]}}$$

Rouse

$$G'(\omega) = \frac{\phi kT}{b^3}\frac{(\omega\tau_R)^2}{\sqrt{[1+(\omega\tau_R)^2]\left[1+\sqrt{[1+(\omega\tau_R)^2]}\right]}}$$

$$G''(\omega) = \frac{\phi kT}{b^3}\omega\tau_R\sqrt{\frac{\left[1+\sqrt{[1+(\omega\tau_R)^2]}\right]}{[1+(\omega\tau_R)^2]}}$$

For $\omega\tau_R << 1$, low frequency Normal Viscoelastic Fluid

$$G'(\omega) = \frac{\phi kT}{b^3}(\omega\tau_R)^2 \qquad G''(\omega) = \frac{\phi kT}{b^3}\omega\tau_R$$

kT per monomer

For $1/\tau_R << \omega << 1/\tau_0$, Rouse Range, Fluid acts like a gel (Winter-Chambon)
(Solution in the limit $\tau_R\omega >> 1$)

$$G'(\omega) = G''(\omega) \sim (\omega)^{1/2}$$

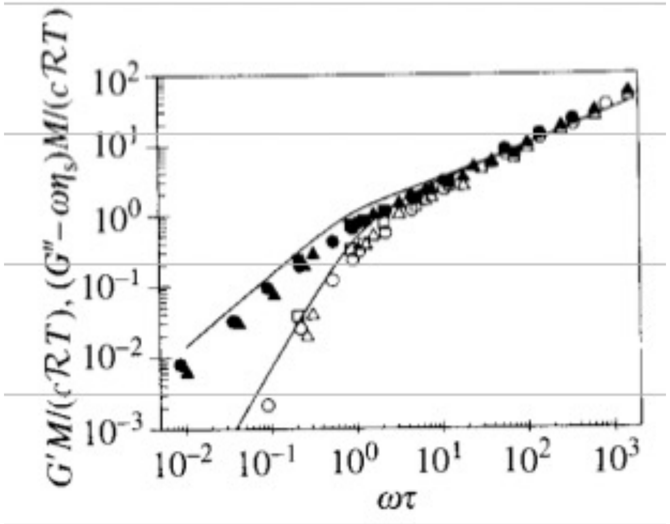


Fig. 8.5
Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\,L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\,L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\,L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

For $1/\tau_0 << \omega$, High Frequency limit

No relaxation modes,

$G'(\omega) = kT\,\phi/b^3$

High-frequency saturation of G'

$G''(\omega) \sim \omega$

This is Solid Behavior

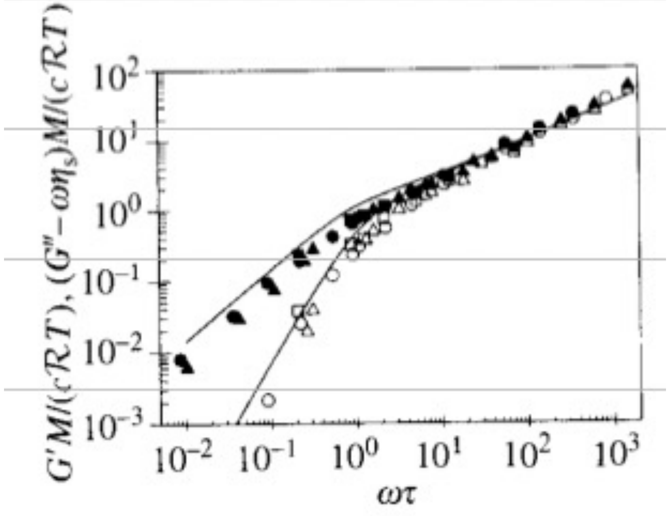


Fig. 8.5

Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\,L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\,L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\,L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

Winter HH, Chambon F, *Analysis of Linear Viscoelasticity of a Crosslinking Polymer at the Gel Point* J. Rheo. **30** 367-382 (1986).

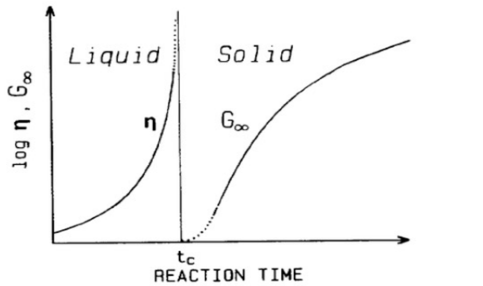


Fig. 1. Schematic of steady shear viscosity and equilibrium modulus of a crosslinking polymer. No such experiments are possible in the close vicinity of transition from liquid to solid.

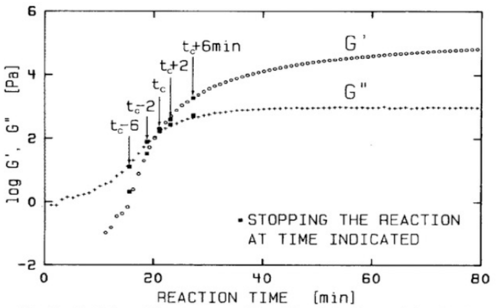


Fig. 2. Evolution of the storage modulus G' and the loss modulus G'' of a crosslinking PDMS in an oscillatory shear experiment at constant frequency ω.

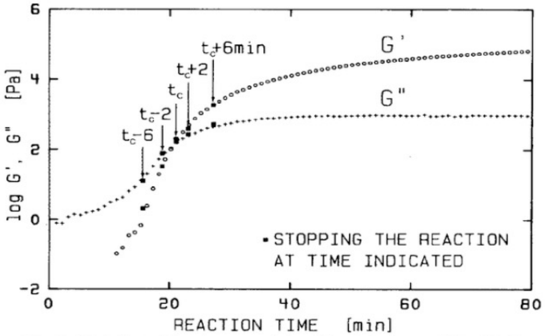


Fig. 2. Evolution of the storage modulus G' and the loss modulus G'' of a crosslinking PDMS in an oscillatory shear experiment at constant frequency ω.

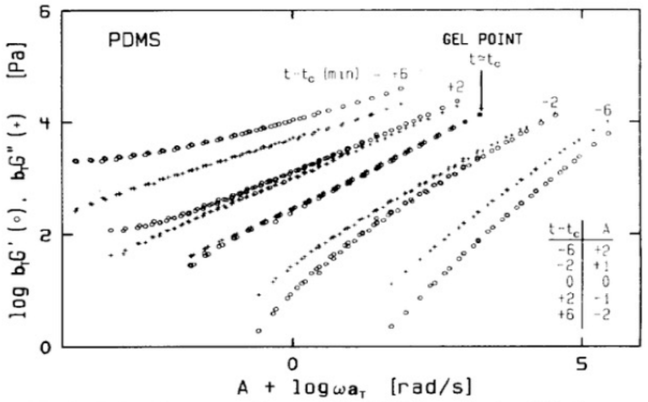


Fig. 3. Reduced storage and loss moduli of PDMS samples for which the reaction has been stopped at intermediate states of conversion. t_c is the instant of intersection (see Figure 2) of G' and G''. The curves were shifted sideways (factor A) to avoid overlap.

The Power-Law is not Restricted in Frequency Range

$G'(T, \omega) = G''(T, \omega) = (\pi/2)^{1/2} S(T)\, \omega^{n}, \quad 0 < \omega < \infty$

$S(T) = (2/\pi)^{1/2} C\, a_T^{\ 1/2} b_T$

Experimentally n = ½ (same as Rouse at moderate ω)

Winter HH, Chambon F, *Analysis of Linear Viscoelasticity of a Crosslinking Polymer at the Gel Point* J. Rheo. **30** 367-382 (1986).

Kramers and Kronig relationship must be followed for this equation

$$\frac{G'(\omega)}{\omega^2} = \frac{2}{\pi}\int_0^\infty \frac{G''(x)/x}{\omega^2 - x^2}\,dx$$

$$1 = \frac{2}{\pi}\int_0^\infty y^{n-1}(1 - y^2)^{-1}\,dy$$

Solve for n (only positive values are physical)

$$n = 1/2,\ -3/2,\ -7/2,\ -11/2\ \ldots$$

$$\eta_0 = \int_0^\infty G(t)\,\mathrm{d}t \qquad\qquad J_\mathrm{e}^0 \eta_0^2 = \int_0^\infty G(t) t\,\mathrm{d}t$$

The ratios of the two integrals that define J_e^0 and η_0, yields a time,

$$\bar{\tau} = \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt} = J_e^0\eta_0$$

This time is called the mean viscoelastic relaxation time. For non-entangled melts (below M_e) this time is proportional to the molecular weight squared. For entangled melts it is proportional to the moleculare weight to the 3.4 power. This is because for entangled melts J_e^0 is constant (plateau) and the time is proportional to the viscosity that increases with a 3.4 power experimentally. Below the entanglement molecular weight both J_e^0 and the zero shear rate viscosity are proportional to M (as will be discussed later).

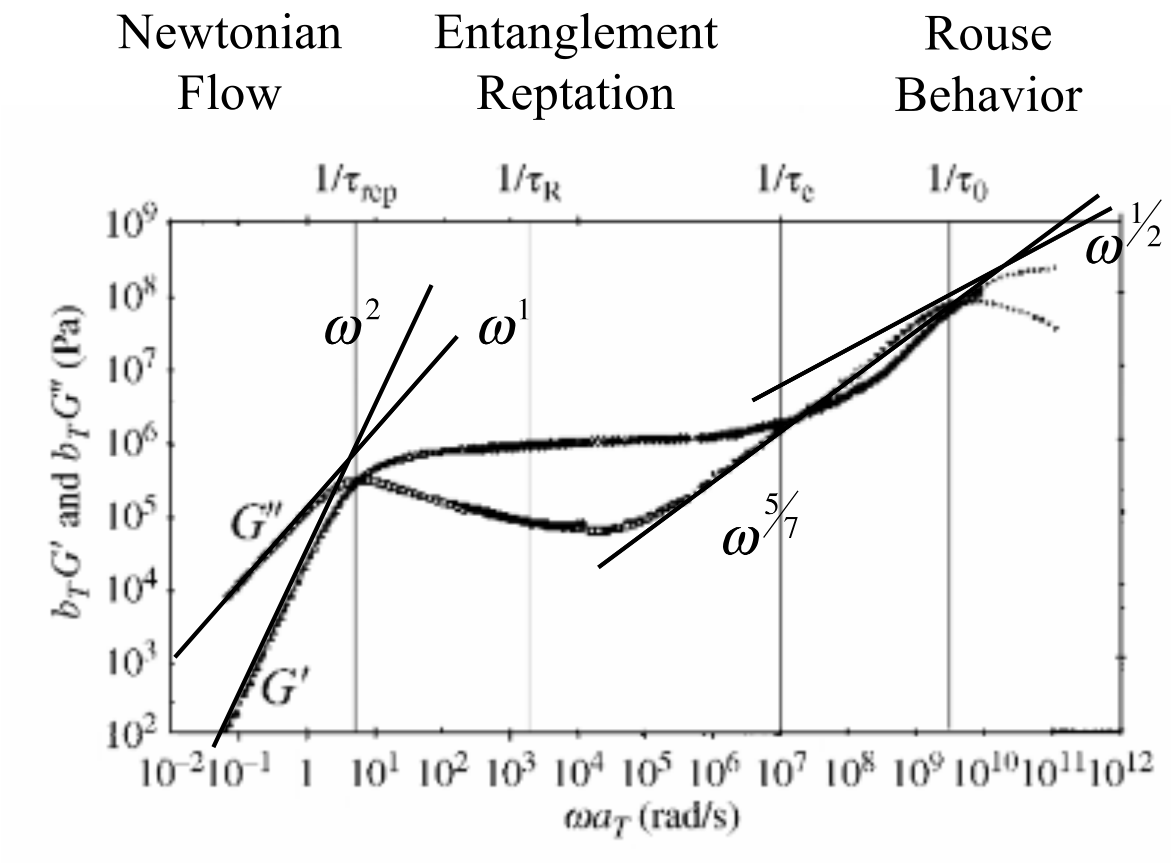
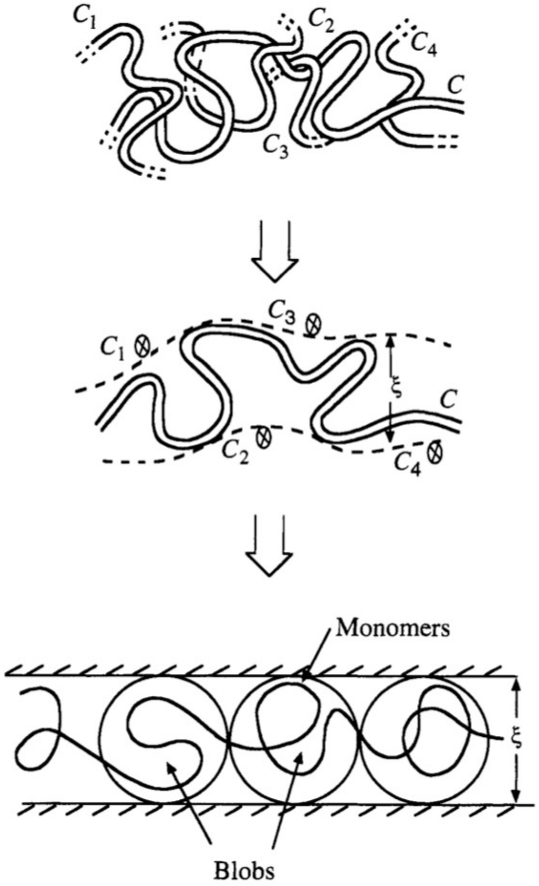


Fig. 9.3
Master curve at 25 °C from oscillatory shear data at six temperatures for a 1,4-polybutadiene sample with $M_w = 130\,000\ \mathrm{g\,mol^{-1}}$. Data from R. H. Colby, L. J. Fetters and W. W. Graessley, *Macromolecules* **20**, 2226 (1987).

Reptation



-One-dimensional diffusion along the tube

-Relaxation time, $\tau_{\text{reptation}}$, is the time for the chain to diffuse a distance L ~ N by Rouse diffusion, $D_0 \sim 1/N$

$$\frac{dP}{dt} = D_0 \frac{d^2 P}{ds^2} \qquad Fick's\ 2'nd\ Law\ in\ 1-d$$

$$P(s,t) = \frac{1}{(4\pi D_0 t)^{1/2}} e^{-s^2/4D_0 t}$$

$$\langle s^2 \rangle = \int_{-\infty}^{\infty} s^2\, P(s,t)\text{ds} = 2D_0 t$$

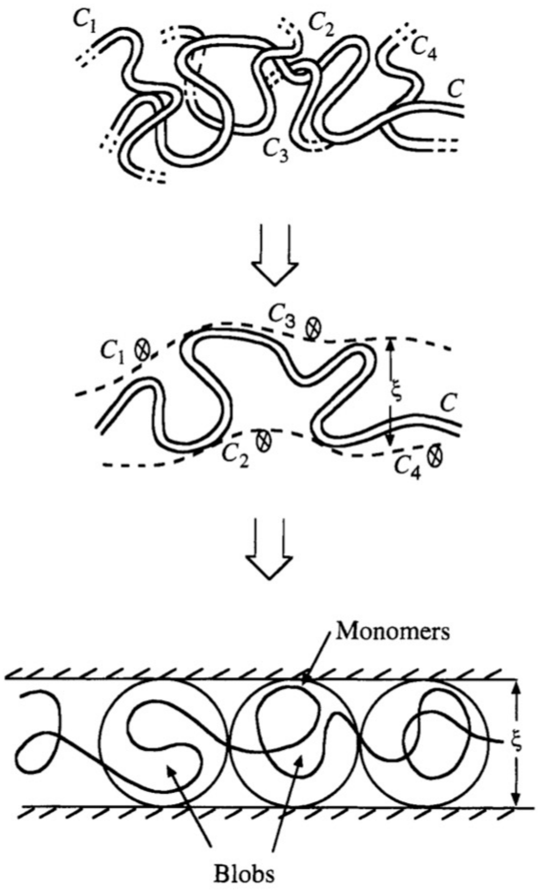
$$\tau_{rep} = \frac{L^2}{2D_0} \sim \frac{N^2}{N^{-1}} \sim N^3$$

Compare: $\tau_{\text{Rouse}} \sim N^2$

$$D_{rep} = \frac{\langle R^2 \rangle}{6\tau_{rep}} \sim \frac{N}{N^3} \sim N^{-2}$$

Compare: $D_{\text{Rouse}} \sim N^{-1}$

Reptation



-Consider a Maxwell model for the fluid

$$\tau_{rep} = \frac{\eta_{rep}}{G_0}$$

Where G_0 is the plateau modulus, $G_0 \sim 3kT/M_e$

$$\eta_{rep} \sim G_0 \tau_{rep} \sim (3kT/Me) N^3$$

Experimental shows $N^{3.4}$ due to tube renewal

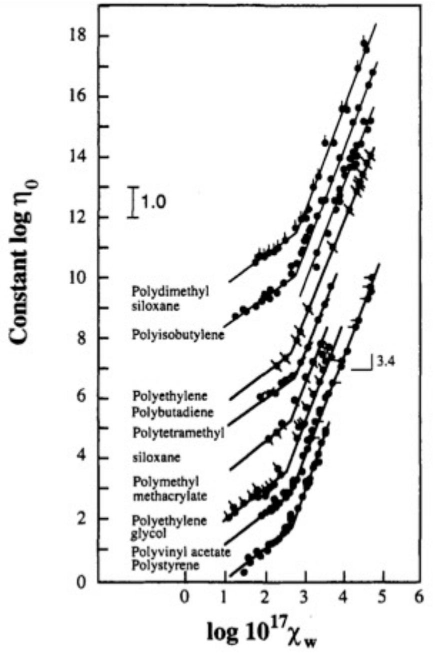


Figure 11.5.4.
Typical viscosity–molecular weight dependence for molten polymers. x_w is proportional to the number of backbone atoms and M_w. From Berry and Fox (1968).

Stress Relaxation Modulus for Reptation

$\tau_e = \tau_0 N_e^2$ Follows Rouse Relaxation

$G(t) \sim G_0(t/\tau_0)^{-1/2}$ For $\tau_0 < t < \tau_e$

Normal Stress and Recoverable Shear Compliance

$$\eta(\gamma') = \sigma_{zx}/\gamma'$$

$$\Psi_1(\gamma') = (\sigma_{xx} - \sigma_{zz})/(\gamma')^2$$

$$\Psi_2(\gamma') = (\sigma_{yy} - \sigma_{zz})/(\gamma')^2$$

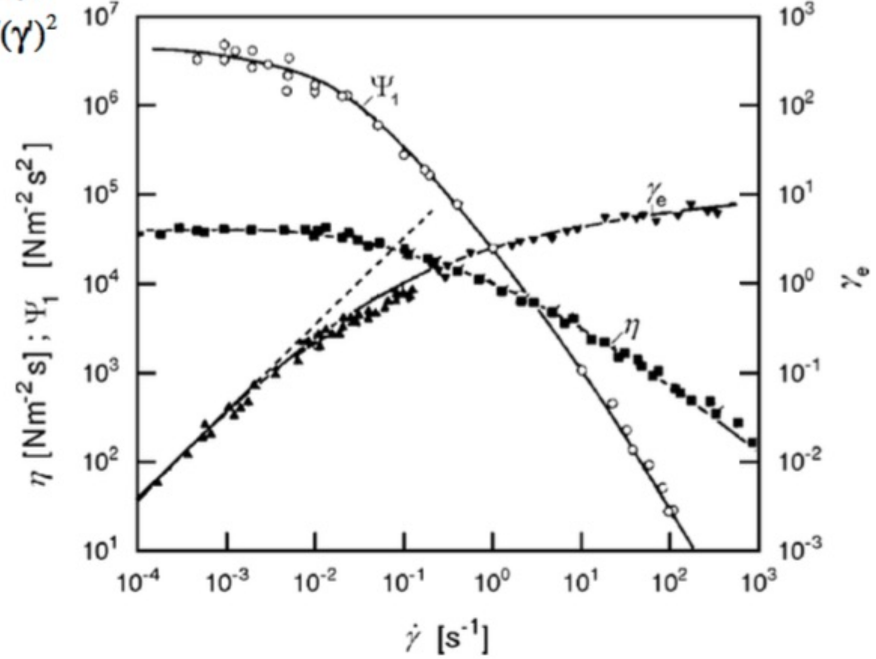


Fig. 9.17. PE under steady state shear flow at 150 °C: Strain rate dependencies of the viscosity η, the primary normal stress coefficient Ψ_1 and the recoverable shear strain γ_e. The *dotted line* represents Eq. (9.157). Results obtained by Laun [116]

Figure 7.15 shows the recoverable shear strain, γ_e, that is proportional to the recoverable shear compliance, $J_e = \gamma_e/\sigma_{zx}$. At low strain rates the recoverable shear strain is just linear in the rate of strain as indicated by the dashed line. The linear behavior occurs in the regime where the viscosity and first normal stress coefficient are constant. In fact, the dashed line follows a linear function of the viscosity and first normal stress coefficient,

$$\gamma_e(\gamma'=>0) = (\Psi_1(\gamma'=>0) \,/\, \{2\ \eta(\gamma'=>0)\})\ \gamma' = (\sigma_{xx} - \sigma_{zz})/(2\ \sigma_{zx})$$

then,

$$J_e^0 = \gamma_e(\gamma'=>0)/\sigma_{zx} = \Psi_{1,0}/(2\ \eta_0^2)$$

At low shear rates there remain only two independent parameters that describe polymeric flow.

Relaxation Spectrum (Ströbl (2007) p. 242-245)

$$J(\omega) = J_\mathrm{u} + \sum_l \frac{\Delta J_l}{1 - \mathrm{i}\omega\tau_l}$$

If there are multiple relaxations like $x(t) = x_0 \exp-(t/\tau)$
Each with an amplitude ΔJ_l and a relaxation time τ_l.

$$J(\omega) = J_\mathrm{u} + \int \frac{1}{1 - \mathrm{i}\omega\tau} \mathrm{L}_J(\log\tau)\,\mathrm{d}\log\tau\ .$$

In integral form. Here we use ln τ as the argument since each relaxation is of exponential form.

$$G(\omega) = G_\mathrm{u} - \int \frac{1}{1 - \mathrm{i}\omega\hat{\tau}} \mathrm{H}_G(\log\hat{\tau})\,\mathrm{d}\log\hat{\tau}$$

The modulus function has a similar form but dramatically different values for τ.

$$G(t) = G_\mathrm{r} + \int \exp\left(-\frac{t}{\hat{\tau}}\right) \mathrm{H}_G(\log\hat{\tau})\,\mathrm{d}\log\hat{\tau}$$

$$\hat{\tau} = \tau\frac{J_\mathrm{u}}{J_\mathrm{r}}$$

Relaxation Spectrum (Ströbl (2007) p. 242-245)

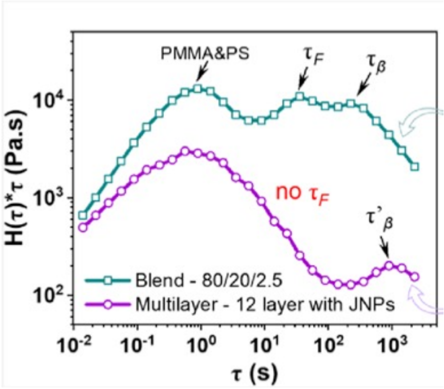
$$G(\omega) = G_\mathrm{u} - \int \frac{1}{1 - \mathrm{i}\omega\hat{\tau}} \mathrm{H}_G(\log\hat{\tau})\,\mathrm{d}\log\hat{\tau}$$

$$\mathrm{d}\ \ln\tau = \mathrm{d}\tau/\tau$$

Then the functional dependence of interest is:

$\tau H_G(\tau)$ vs. τ

That is why we see plots like:



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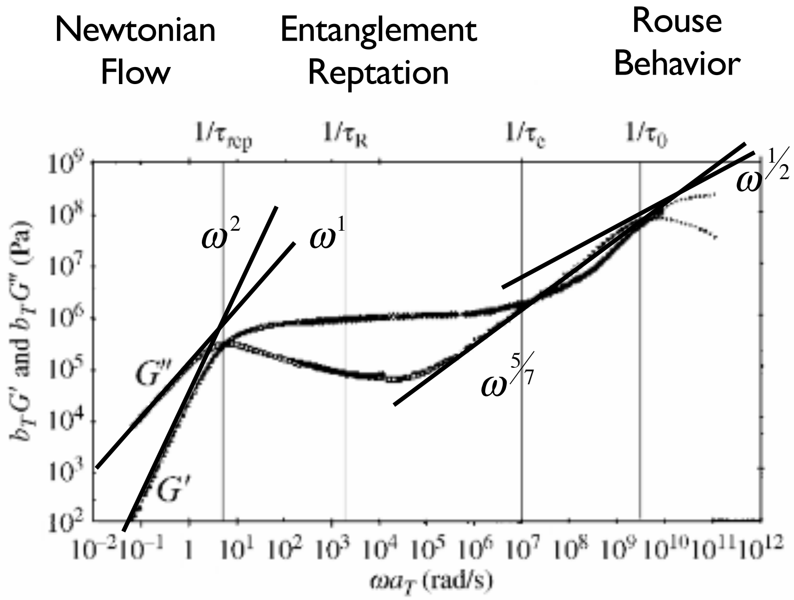

Fig. 9.3
Master curve at 25 °C from oscillatory shear data at six temperatures for a 1,4-polybutadiene sample with $M_w = 130\,000\ \mathrm{g\,mol^{-1}}$. Data from R. H. Colby, L. J. Fetters and W. W. Graessley, *Macromolecules* **20**, 2226 (1987).