## Experimental Data (Chapter 6)

*Steady shear flow*

- •Linear Polymers
- •Limits on measurability
- •Material effects - MW, MWD, branching, mixtures, copolymers
- •Temperature and pressure

---

***later . ..***

*Unsteady shear flow (SAOS, step strain, start up, cessation)*
*Steady elongation*
*Unsteady elongation*

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Steady shear viscosity and first normal stress coefficient

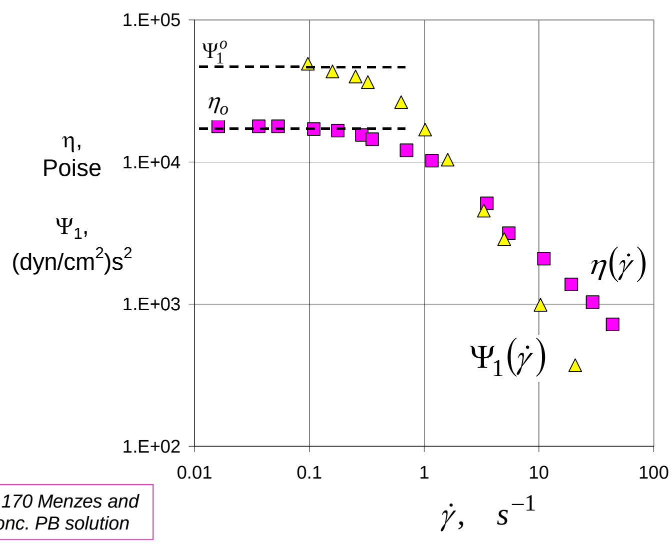


*Figure 6.1, p. 170 Menzes and Graessley conc. PB solution*

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## Steady shear viscosity and first normal stress coefficient

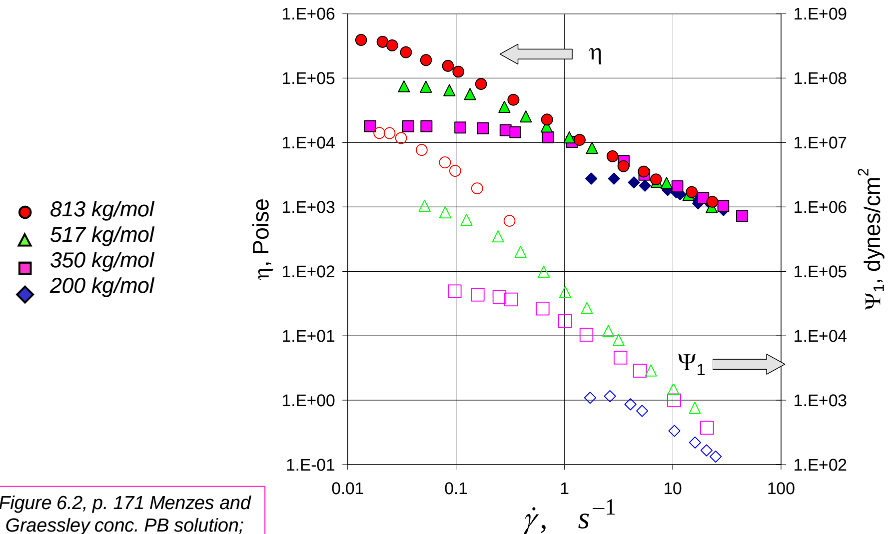


*Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; c=0.0676 g/cm³*

63



## Steady shear viscosity and first normal stress coefficient

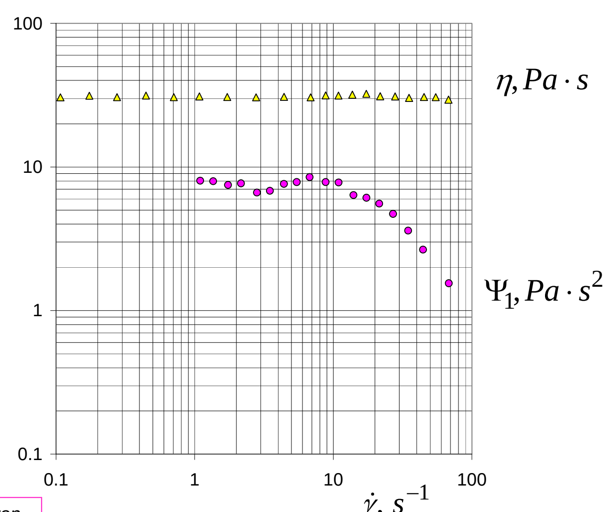


*Figure 6.5, p. 173 Binnington and Boger; PIB soln*

64

Steady shear viscosity and first and ***second*** normal stress coefficient

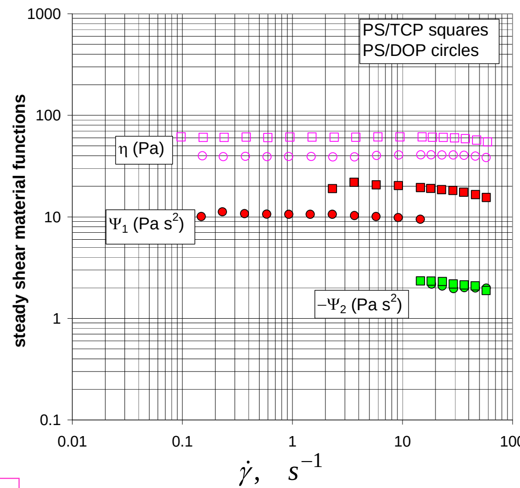


*Figure 6.6, p. 174*
*Magda et al.; PS solns*

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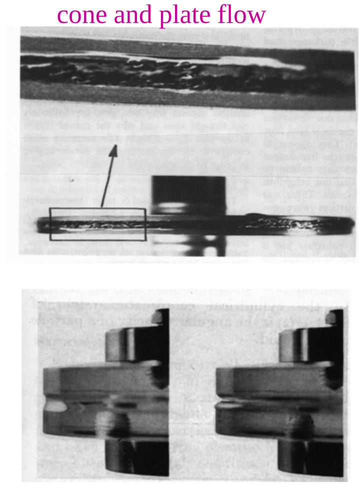
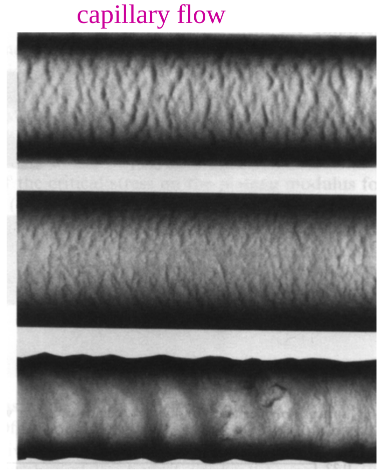
## Limits on Measurements: Flow instabilities in rheology

cone and plate flow



capillary flow



*Figures 6.7 and 6.8, p. 175 Hutton; PDMS*

*Figure 6.9, p. 176 Pomar et al. LLDPE*

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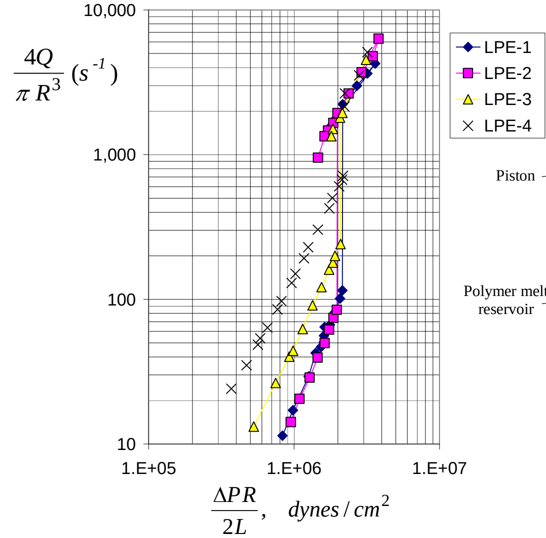
## Spurt instability




$\frac{4Q}{\pi R^3}$ $(s^{-1})$

$\frac{\Delta P R}{2L}$, $dynes/cm^2$

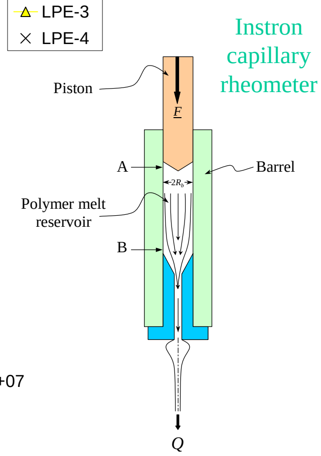



*Figure 6.10, p. 177*
*Blyler and Hart; PE*

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## Steady shear viscosity and first normal stress coefficient - *Molecular weight effects*

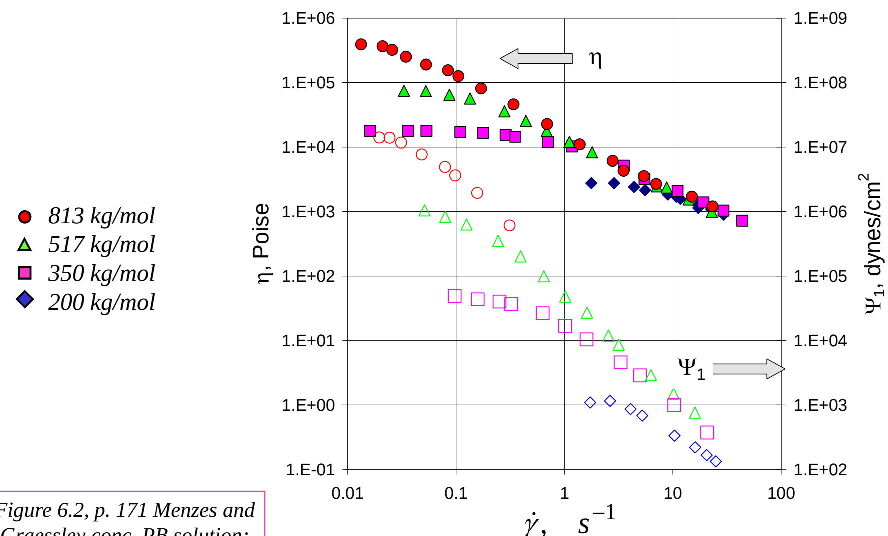


*Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; various MW*

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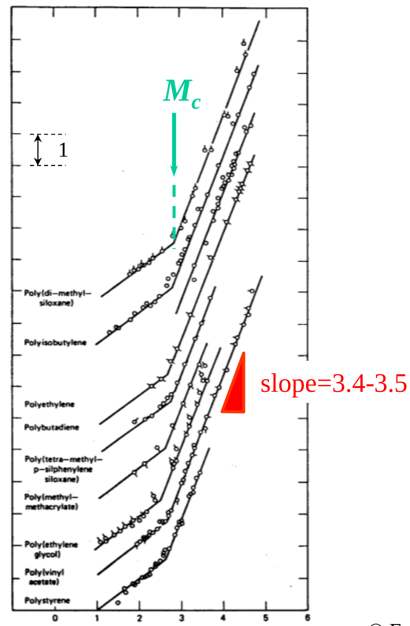
**Variation of viscosity with molecular weight**




$\log \eta_0$ + constant

log M + constant

*Figure 6.12, p. 178 Berry and Fox, 1968; various polymers*

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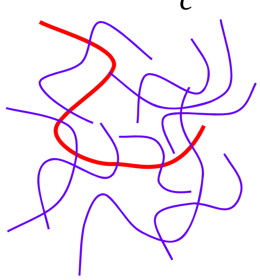
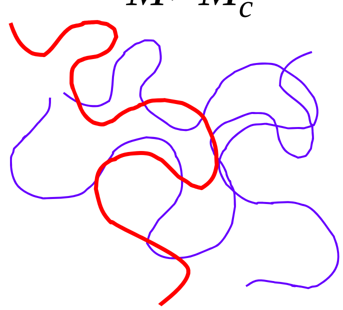
*Entanglements strongly affect polymer relaxation*

$M<M_c$



Unentangled
relaxation is rapid

$M>M_c$



Entangled
relaxation is retarded

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## *Effect of Distribution of Molecular Weight*

A - $M_w/M_n$=*1.09*

B - $M_w/M_n$= *2.0*

C - *branched*

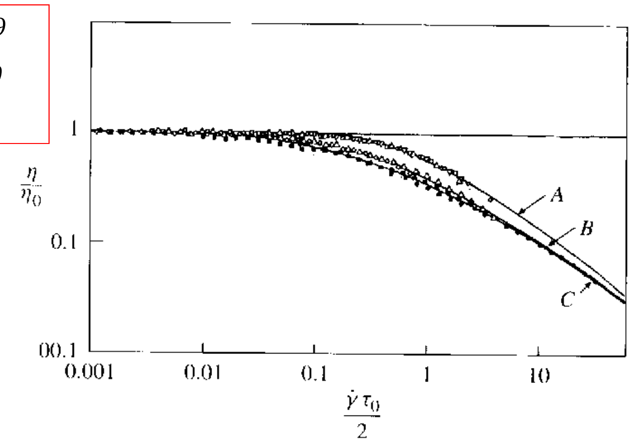


*Figure 6.14, p. 179 Berry and Fox; PVA solns in DEP*

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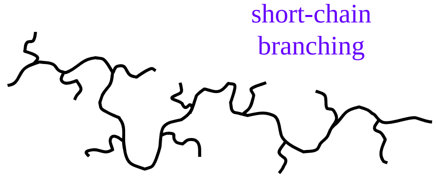
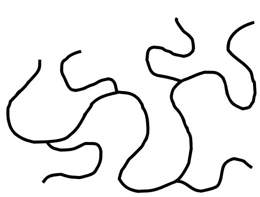
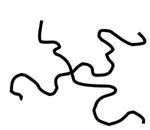
## Types of polymer architecture

short-chain branching

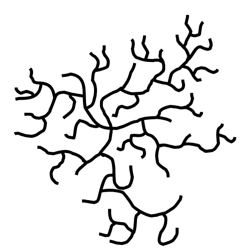




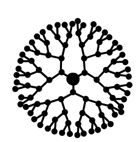
long-chain branching



star



hyperbranching



dendrimer

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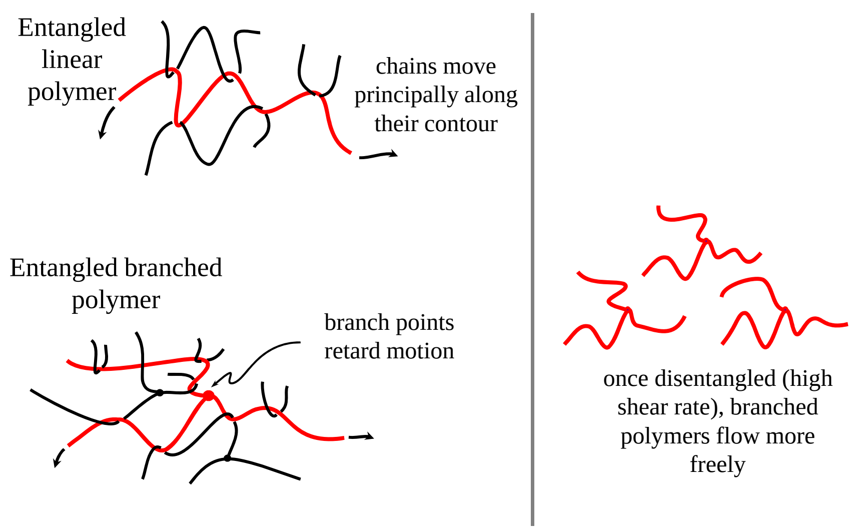
## *Motion of Branched Polymers*

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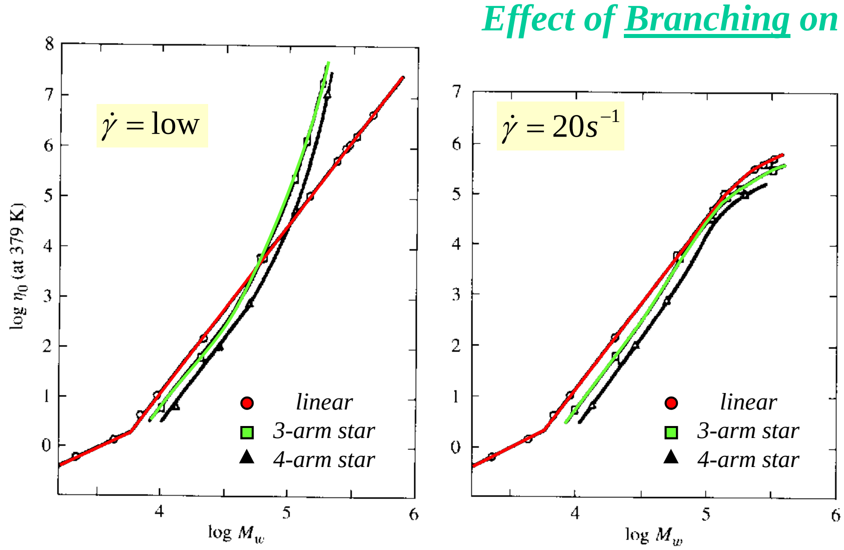
## *Effect of Branching on $\eta$*




*Figures 6.17, 6.18, pp. 181,3 Kraus & Gruver; PB*

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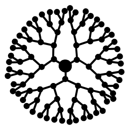
## Steady shear rheology of PAMAM dendrimers



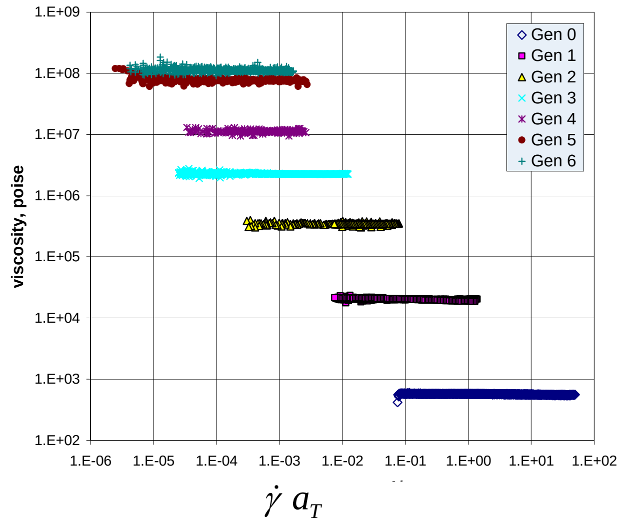



*Figure 6.20 p. 183; from Uppuluri*

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## Steady Shear Summary:

1. General traits
2. Effect of MW on linear polymers
3. Effect of architecture
4. Measurement issues

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## *Mixtures of Polymers with other materials - Filler Effect*

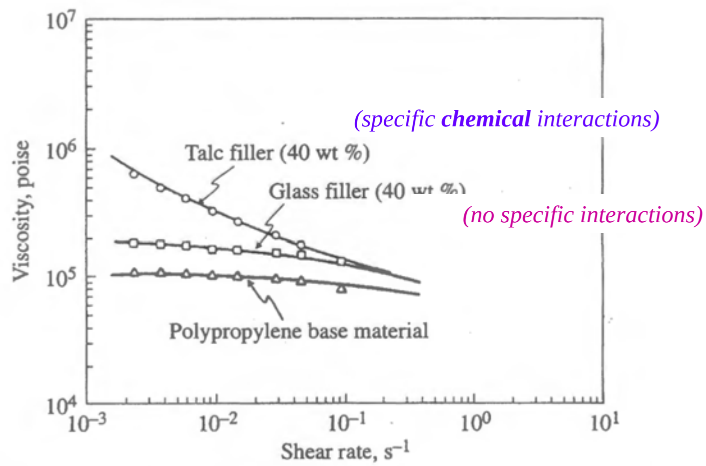


*Figure 6.22, p. 184 Chapman and Lee; PP and filled PP*

For more on filled systems, see Larson, *The Structure and Rheology of Complex Fluids*, Oxford, 1999.

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## *Mixtures of Polymers with other materials - Filler Effect*

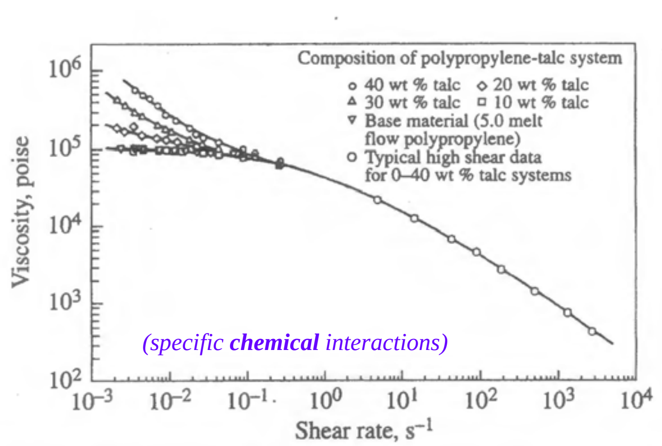


*Figure 6.21, p. 184 Chapman and Lee; filled PP*

For more on filled systems, see Larson, *The Structure and Rheology of Complex Fluids*, Oxford, 1999.

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## Steady shear viscosity - shear thickening

For discussion of causes of shear thickening, see Wagner and Brady, *Phys. Today*, October 2009

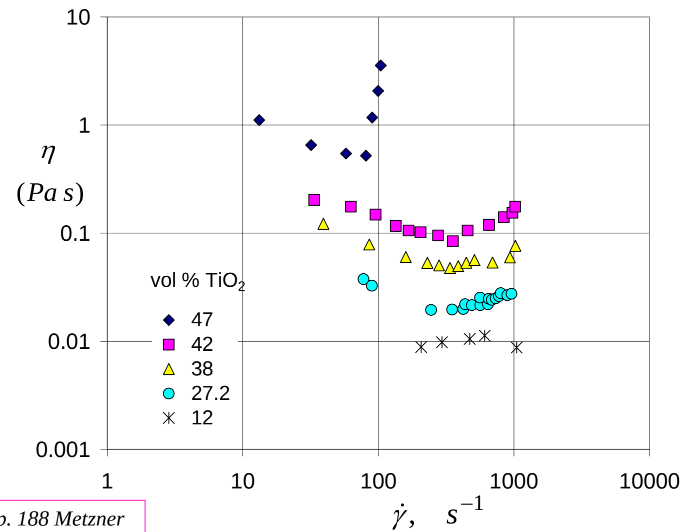


*Figure 6.27, p. 188 Metzner and Whitlock; $TiO_2$/water suspensions*

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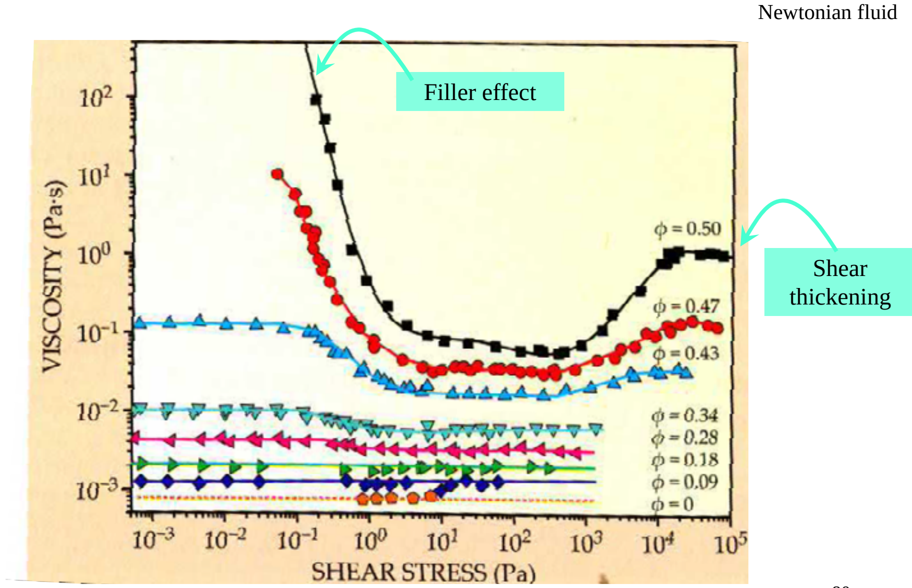
## Steady shear viscosity - shear thickening

Wagner and Brady, *Phys. Today*, Oct 2009

Latex spheres in Newtonian fluid

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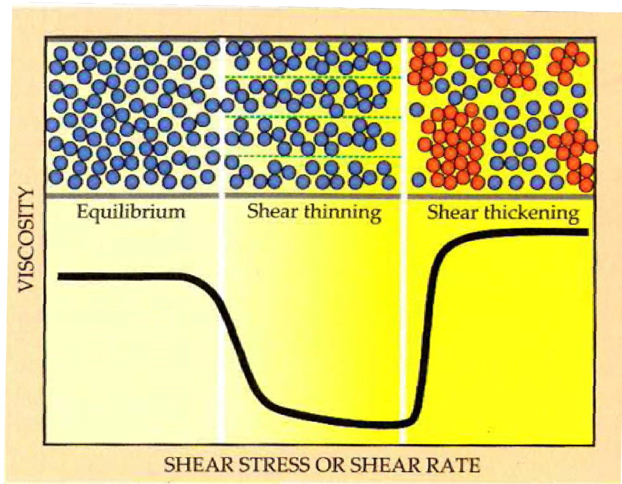
## Steady shear viscosity - shear thickening

Wagner and Brady, *Phys. Today*, Oct 2009

Particles bump into each other

Layers of particles slide past each other

Clusters of particles bump into each other




*Hydrodynamic interaction* causes shear thickening:

The pressure distribution in the Newtonian suspending fluid exerts forces on the particles and causes them to form structures in flow.

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## Steady shear viscosity - temperature dependence

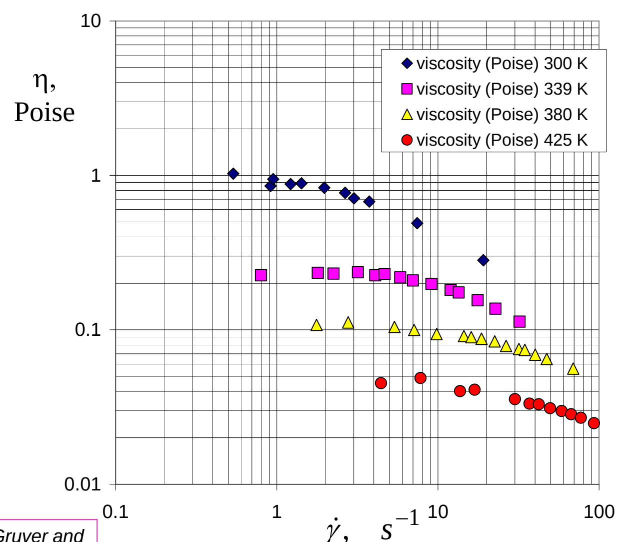


*Figure 6.28, p. 189 Gruver and Kraus; PB melt*

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## Steady shear viscosity - pressure dependence

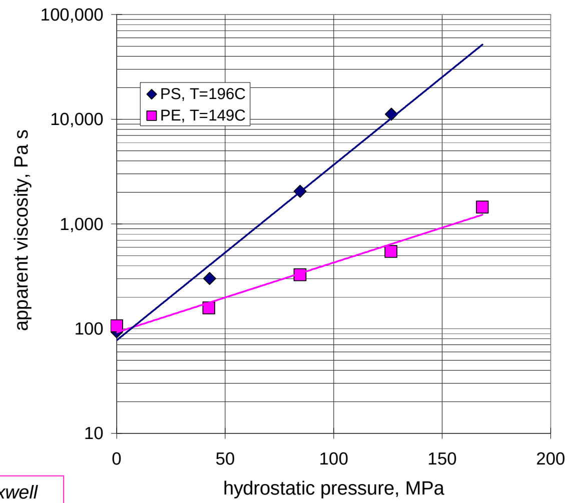


*Figure 6.29, p. 189 Maxwell and Jung; PS and PE*

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## Steady Shear Summary:

1. General traits
2. Effect of MW (linear polymers)
3. Effect of architecture
4. Measurement issues
5. Effect of chemical composition
6. Effect of temperature
7. Effect of pressure

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## Experimental Data (continues)

***Next:***

*Unsteady shear flows (small and large strain)*
*Steady elongation*
*Unsteady elongation*

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Small-Amplitude Oscillatory Shear - Storage and Loss Moduli

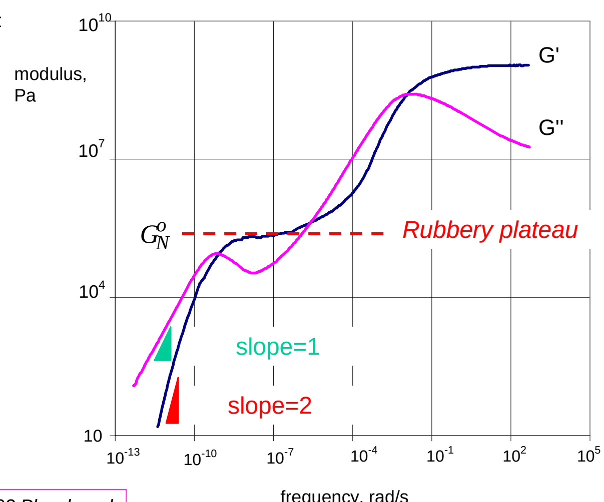


*Figure 6.30, p. 192 Plazek and O'Rourke; PS*

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## Small-Amplitude Oscillatory Shear - Storage and Loss Moduli

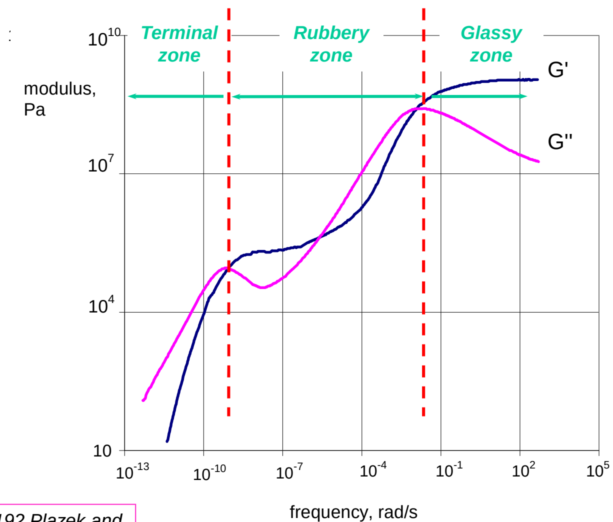


*Figure 6.30, p. 192 Plazek and O'Rourke; PS*

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## Step Shear Strain - Relaxation Modulus

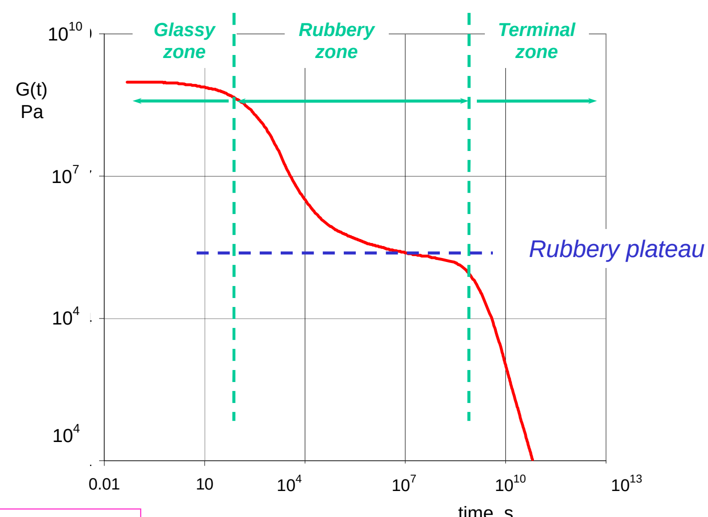


*Figure 6.31, p. 192 Plazek and O'Rourke; PS*

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Ferry's Summary of Viscoelastic properties of several classes of polymers

Storage modulus

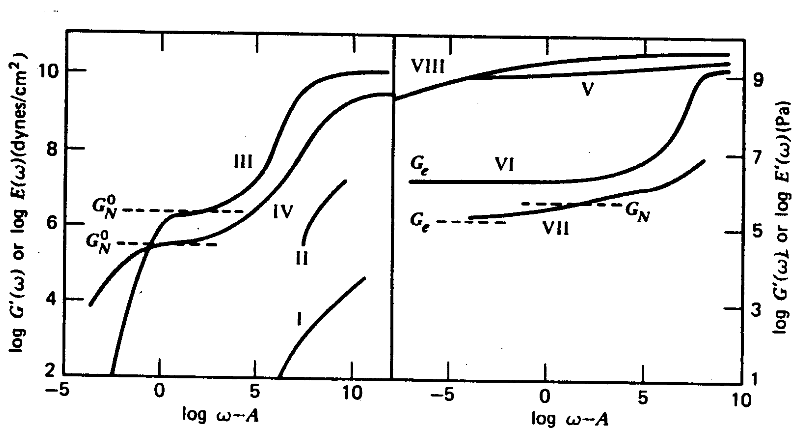


*Figure2-3 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980*

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Key to Ferry's plots

I. **Dilute polymer solutions: atactic polystyrene**, 0.015 g/ml in Aroclor 1248, a chlorinated diphenyl with viscosity 2.47 poise at 25°C. $M_w$=86,000, $M_w/M_n$ near 1.

II. **Amorphous polymer of low molecular weight**: poly(vinyl acetate), M=10,500, fractionated.

III. **Amorphous polymer of high molecular weight**: atactic polystyrene, narrow MW distribution, $M_w$=600,000.

IV. **Amorphous polymer of high molecular weight with long side groups**: fractionated poly(n-octyl methacrylate), $M_w$=3.62 x $10^6$.

V. **Amorphous polymer of high molecular weight below its glass transition temperature**: poly(methyl methacrylate).

VI. **Lightly cross-linked amorphous polymer**: lightly vulcanized Hevea rubber.

VII. **Very lightly cross-linked amorphous polymer**: styrene butadiene random copolymer, 23.5% styrene by weight.

VII. **Highly crystalline polymer**: linear polyethylene.

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## Ferry's Summary of Viscoelastic properties of several classes of polymers

Loss modulus

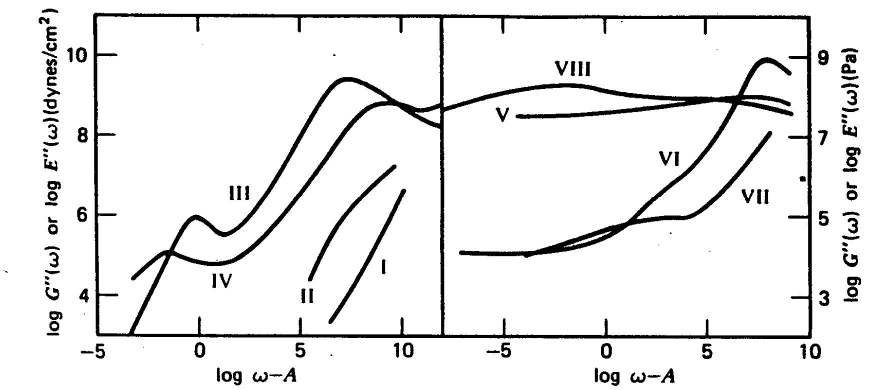


Figure2-4 from Ferry, <u>Viscoelastic Properties of Polymers</u>, Wiley, 1980

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## Ferry's Summary of Viscoelastic properties of several classes of polymers

Relaxation modulus

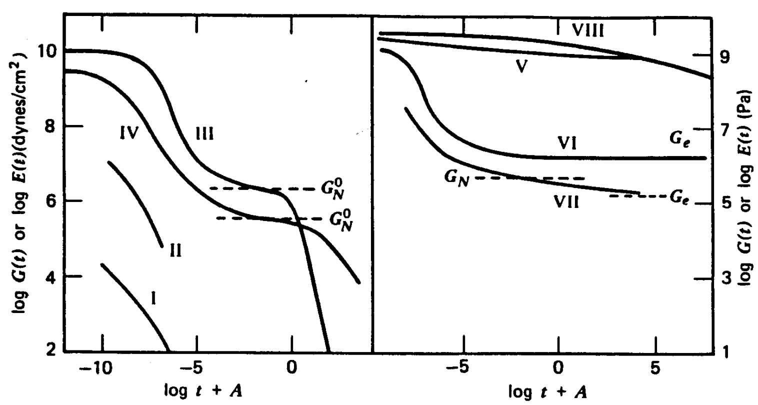


Figure2-2 from Ferry, <u>Viscoelastic Properties of Polymers</u>, Wiley, 1980

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Ferry's Summary of Viscoelastic properties of several classes of polymers

Loss tangent

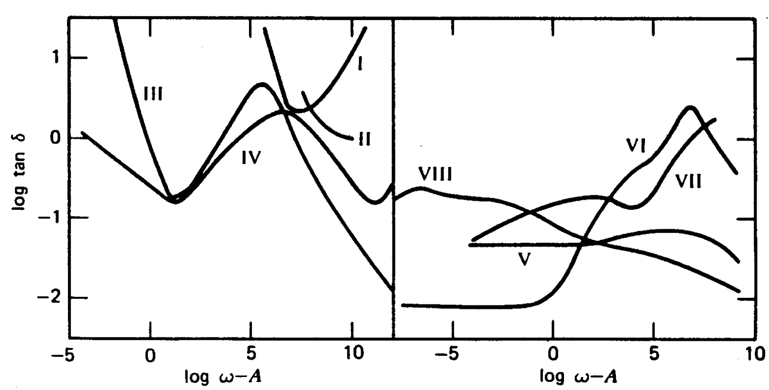


*Figure2-8 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980*

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**Cox-Merz Rule**

$$\eta(\dot{\gamma}) = \left|\eta^*(\omega)\right|_{\dot{\gamma}=\omega}$$

*An empirical way to infer steady shear data from SAOS data.*

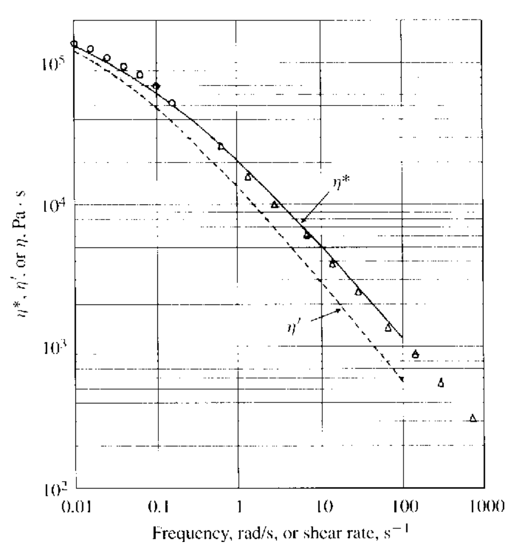


*Figure 6.32, p. 193 Venkataraman et al.; LDPE*

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Small-Amplitude Oscillatory Shear - *G'*
molecular weight dependence

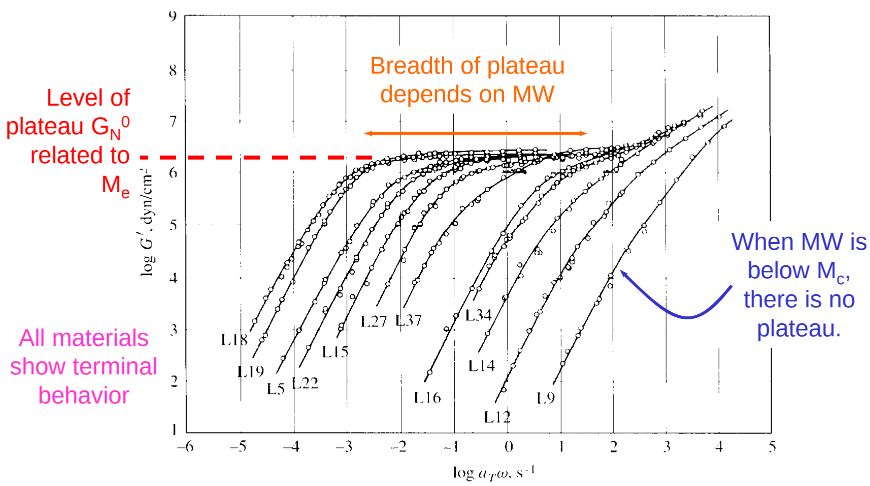


*Figure 6.34, p. 195 Onogi et al; narrow MWD PS*

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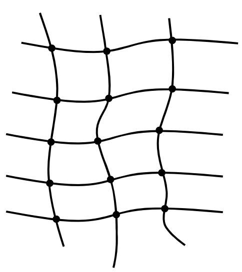
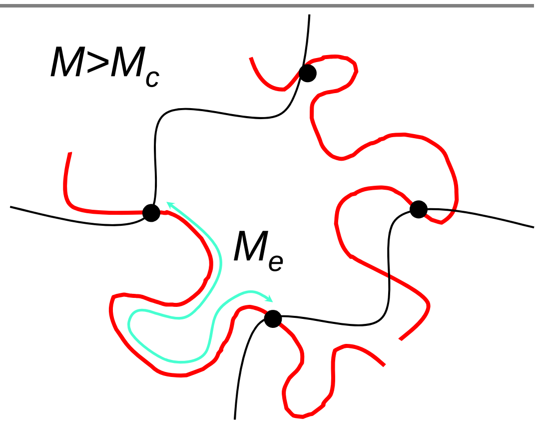
*Entanglements form a temporary network*



crosslinked elastic network – constant modulus G at all $\omega$




Entangled polymers – over a range of w when unable to disentangle, exhibit a constant modulus $G_N^0$

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## Small-Amplitude Oscillatory Shear - *G'*
## molecular weight dependence

Level of plateau $G_N^0$ is related to $M_e$

(molecular theory for temporary networks)

$$M_c \cong 2M_e$$

$$G_N^0 = \frac{4}{5}\nu\, k_B T$$

$\nu$ = density of effective cross links

$\nu$ = cross links/volume

$$M_e = \frac{\left(\frac{mass}{volume}\right)\left(\frac{crosslinks}{mole}\right)}{\left(\frac{crosslinks}{volume}\right)} = \frac{\rho N_A}{\nu}$$

$$G_N^0 = \frac{4}{5}\frac{\rho N_A k_B T}{M_e}$$

Larger the MW between entanglements, the softer the network

*See Larson, The Structure and Rheology of Complex Fluids, Oxford, 1999*

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## Small-Amplitude Oscillatory Shear - *G"*
## molecular weight dependence

All materials show terminal behavior

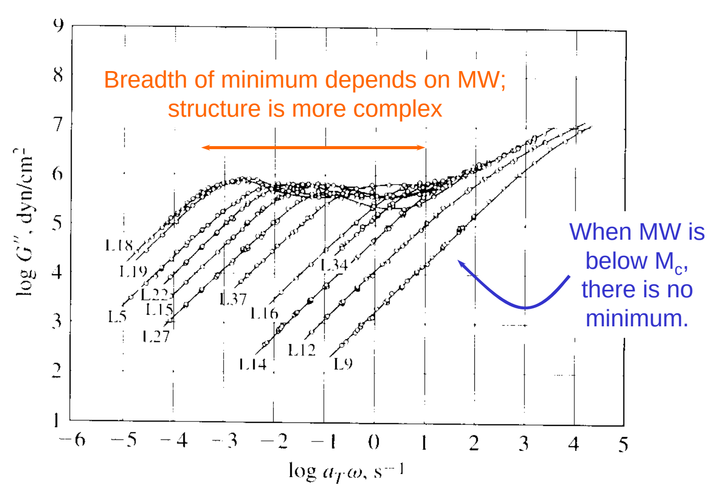


*Figure 6.36, p. 196 Onogi et al; narrow MWD PS*

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Small-Strain Unsteady Shear Summary:

1. General traits
2. Effect of MW (linear polymers)
3. Effect of architecture
4. Relationship to steady flow material functions
5. Measurement issues
6. Effect of chemical composition




Small-Amplitude Oscillatory Shear - *G′ as a function of temperature for copolymers*

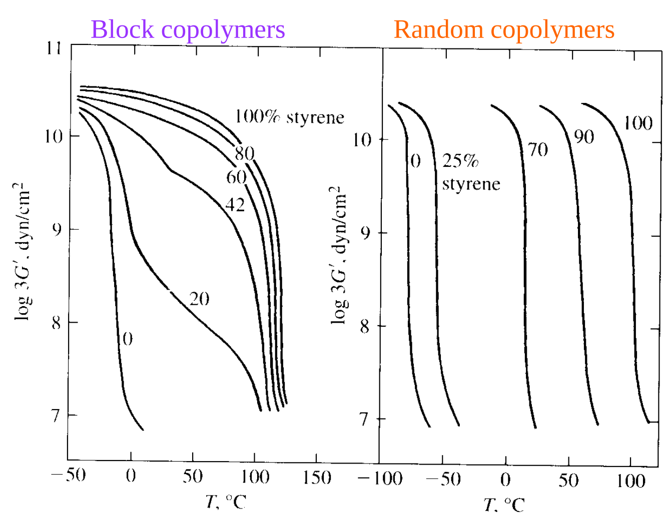


*Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random*

## Small-Amplitude Oscillatory Shear - temperature dependence

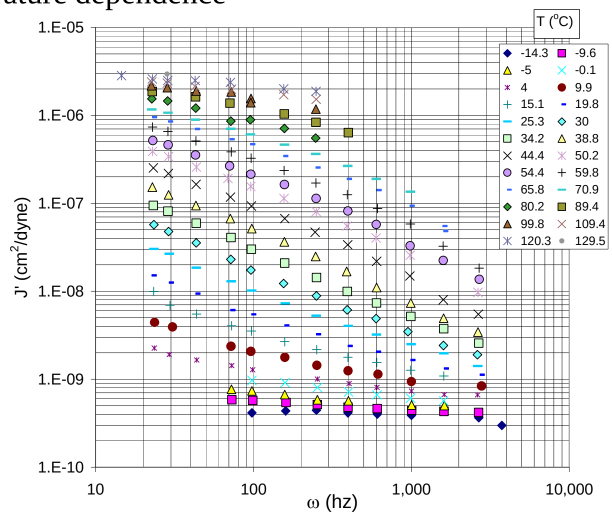


*Figure 6.43, p. 202 Dannhauser et al.; P-OctylMethacrylate*

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## *Time-Temperature Superposition*

Material functions depend on $g_i$, $\lambda_i$

relaxation times

relaxation moduli

$$G' = G'(\omega, \lambda_i, g_i)$$

$$G'' = G''(\omega, \lambda_i, g_i)$$

$g_i$, $\lambda_i$ are in turn functions of temperature and material properties

*Theoretical result*: in the linear-viscoelastic regime, material functions are a function of $\omega\lambda_i$ rather than of $\omega$ and $\lambda_i$ individually.

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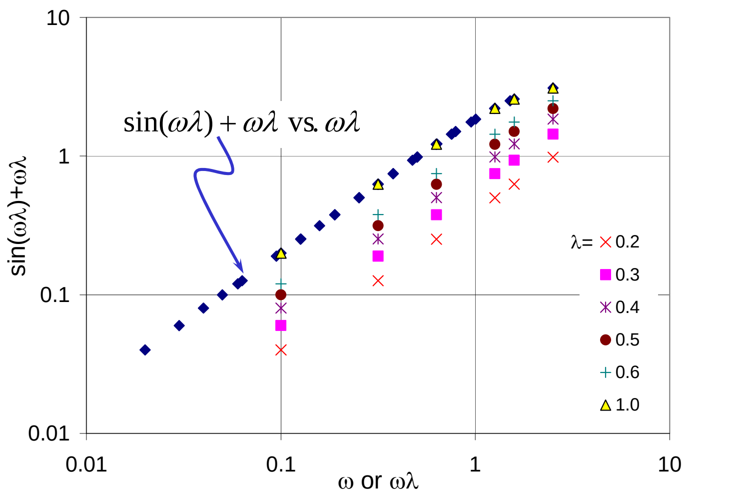
## Example: plot a simple function

$$f(\omega,\lambda) = \sin(\omega\lambda) + \omega\lambda$$

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In general,

$$G' = G'(\omega\lambda_1(T),\ \omega\lambda_2(T),\ \omega\lambda_3(T),\ \ldots\quad)$$

Suppose that the temperature-dependence of $\lambda_i$ could be factored out. Let $a_{Ti}(T)$ be the temperature-dependence of $\lambda_i$.

$$\lambda_i(T) = a_{Ti}(T)\tilde{\lambda}_i$$

**not a function of temperature**

Then we could group the temperature-dependence function with the frequency.

$$G' = G'(a_{T1}\omega\tilde{\lambda}_1,\ a_{T2}\omega\tilde{\lambda}_2,\ a_{T3}\omega\tilde{\lambda}_3,\ \ldots\quad)$$

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## Time-Temperature Superposition

•Relaxation times decrease strongly as temperature increases

•Moduli associated with relaxations are proportional to absolute temperature; depend on density

*Empirical observation*: for many materials, all the relaxation times and moduli have the same functional dependence on temperature

(for the $i^{th}$ relaxation mode)

$$\lambda_i(T) = \tilde{\lambda}_i a_T(T)$$

temperature dependence of all relaxation times

$$g_i(T) = \tilde{g}_i T\rho(T)$$

temperature dependence of all moduli

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*Second theoretical result*: the $g_i$ enter into the functions for $G'$, $G''$ such that $T\rho$ can be factored out of the function

$$\frac{G'}{T\rho} = \tilde{f}(a_T\omega, \tilde{\lambda}_i)$$

$$\frac{G''}{T\rho} = \tilde{h}(a_T\omega, \tilde{\lambda}_i)$$

Therefore if we plot reduced variables, we can suppress all of the temperature dependence of the moduli.

$$G_r' \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G'(T_{ref})$$

$$G_r'' \equiv \frac{G''(T)T_{ref}\rho_{ref}}{T\rho} = h(a_T\omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G''(T_{ref})$$

Plots of $G_r'$, $G_r''$ versus $a_T\omega$ will therefore be independent of temperature.

*(will still depend on the material through the $\tilde{\lambda}_i$)*

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## Small-Amplitude Oscillatory Shear - temperature dependence

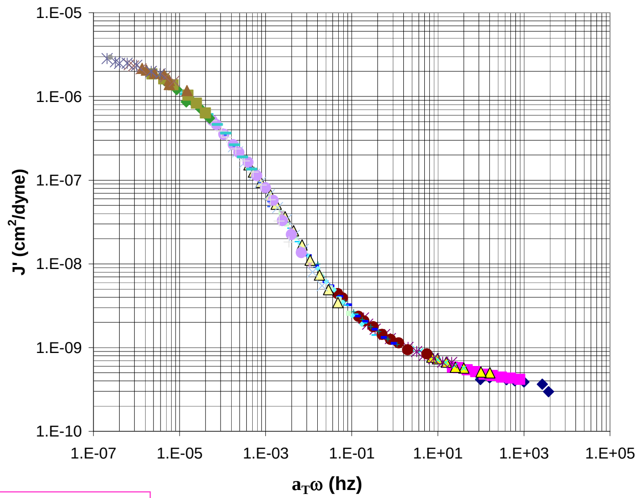


*Figure 6.44, p. 202 Dannhauser et al.; P-OctylMethacrylate*

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## Small-Amplitude Oscillatory Shear - temperature dependence

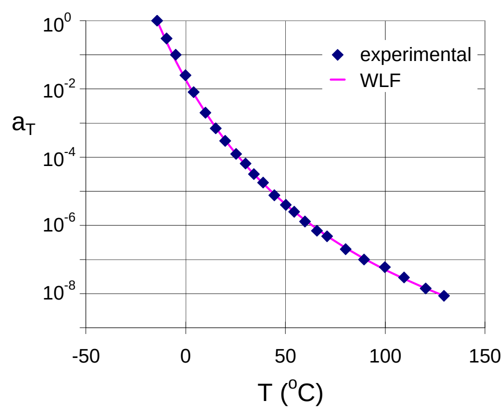


*Figure 6.45, p. 203 Dannhauser et al.; P-OctylMethacrylate*

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## *Shift Factors*

Arrhenius equation

$$a_T = \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

found to be valid for $T > T_g + 100^oC$

Williams-Landel-Ferry (WLF) equation

$$\log a_T = \frac{-c_1^0\left(T - T_{ref}\right)}{c_2^0 + \left(T - T_{ref}\right)}$$

found to be valid *w/in* $100^oC$ of $T_g$

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## *Shifting other Material Functions*

*Other linear viscoelastic material functions:*

$$\eta' \equiv \frac{G''(T)}{\omega}$$

$$\eta'' \equiv \frac{G'(T)}{\omega}$$

$$\tan\delta = \frac{G''}{G'}$$

$$J' = \frac{1/G'}{1+\tan^2\delta}$$

$$J'' = \frac{1/G''}{1+\left(\tan^2\delta\right)^{-1}}$$

$$G_r' \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G'(T_{ref})$$

$$G_r'' \equiv \frac{G''(T)T_{ref}\rho_{ref}}{T\rho} = h(a_T\omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G''(T_{ref})$$

Independent of temperature

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## *Shifting other Material Functions*

*linear viscoelastic*

$$\eta_r' \equiv \frac{G''(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$\eta_r'' \equiv \frac{G'(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta'' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$J_r' \equiv \frac{J'(T)T\rho}{T_{ref}\rho_{ref}}$$

$$J_r'' \equiv \frac{J''(T)T\rho}{T_{ref}\rho_{ref}}$$

*steady shear*

$$\eta_r(a_T\dot{\gamma}) = \frac{\eta(T)T_{ref}\rho_{ref}}{a_T T\rho}$$

$$\tan\delta = \frac{G''}{G'}$$

= independent of temperature when plotted versus reduced frequency)





## Steady shear viscosity - Temperature dependence

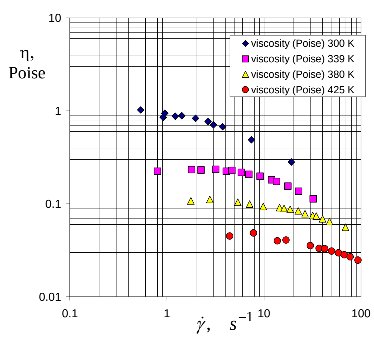
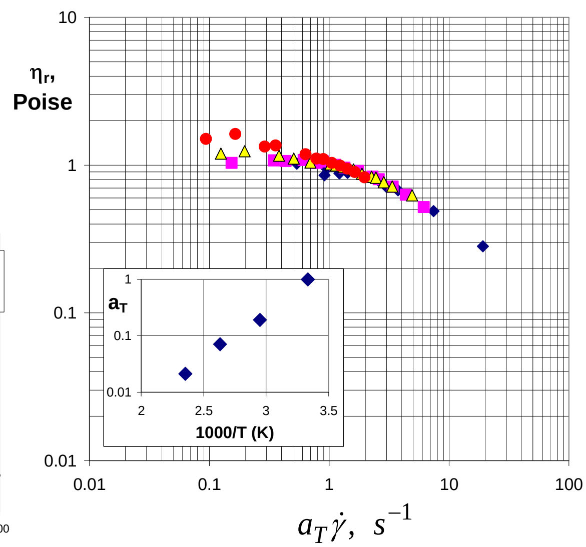
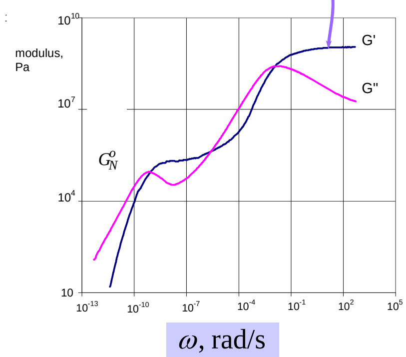



*Figure 6.46, p. 204 Gruver and Kraus; PB melt*



Another consequence of $\lambda_i(T) = \tilde{\lambda}_i a_T(T)$ is the similarity between $\log G'(\omega)$ and $\log G'(T)$.



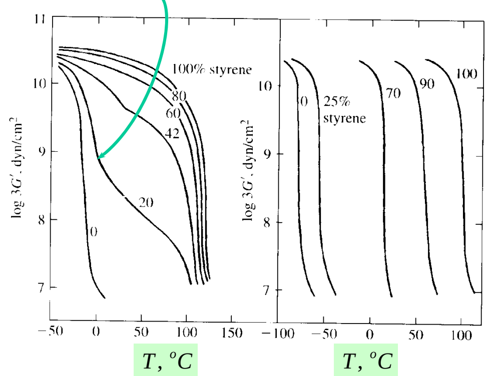




Figure 6.30, p. 192 Plazek and O'Rourke; PS

Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random





Take data for $G'$, $G''$ at a fixed $\omega$ for a variety of $T$.

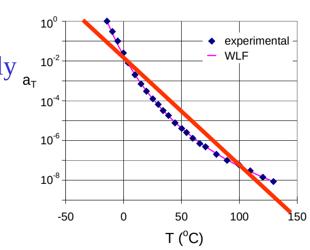
$$G'_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)$$

but, what is $a_T(T)$?

**We do not know.**

$$G''_r \equiv \frac{G''(T)T_{ref}\rho_{ref}}{T\rho} = h(a_T\omega, \tilde{\lambda}_i)$$

But since $\log a_T$ is approximately a linear function of $T$,




curves of $\log G'$ versus $T$ (not $\log T$) at constant $\omega$ resemble slightly skewed plots of $\log G'$ versus $\log a_T\omega$. (mirror image)

Application of SAOS

Using *G'(T)* in research on pressure-sensitive adhesives

○ 0 wt%
△ 30 wt%
□ 50 wt%
▽ 70 wt% tackifier

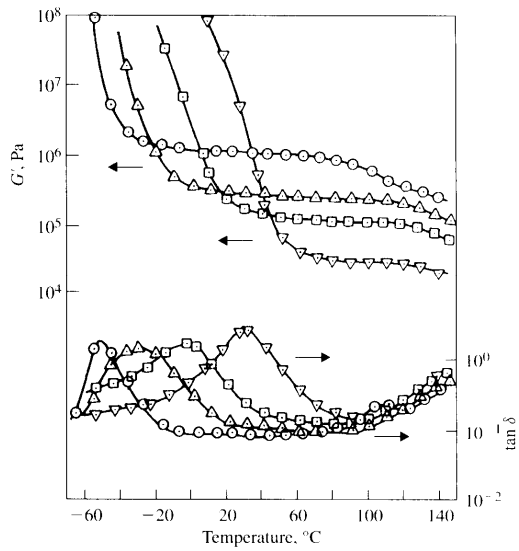



*Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier*

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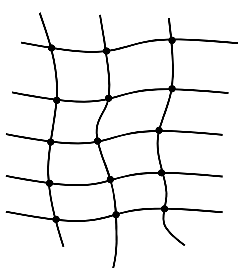
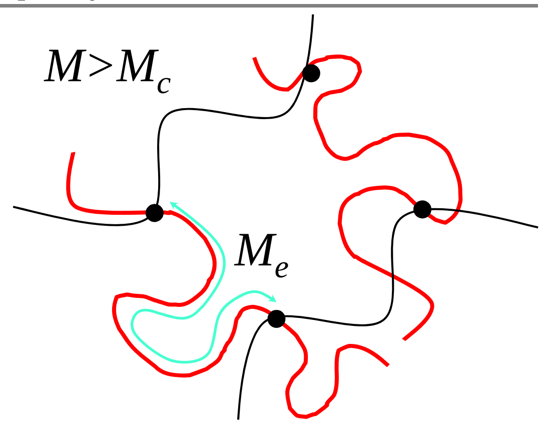
*Entanglements form a temporary network*



crosslinked elastic network – constant modulus G at all ω




Entangled polymers – over a range of ω when unable to disentangle, exhibit a constant modulus $G_N^0$

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## Small-Amplitude Oscillatory Shear - $G'$
## molecular weight dependence

Level of plateau $G_N^0$ is related to $M_e$

(molecular theory for temporary networks)

$$G_N^0 = \frac{4}{5}\frac{\rho N_A k_B T}{M_e}$$

Larger the MW between entanglements, the softer the network

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## Using $G'(T)$ in research on pressure-sensitive adhesives

Height of plateau modulus and temperature of glass transition are key performance factors for PSAs.

**Tack** – if not tacky, will not produce bond

**Shear holding** – if too fluid, will slide under shear

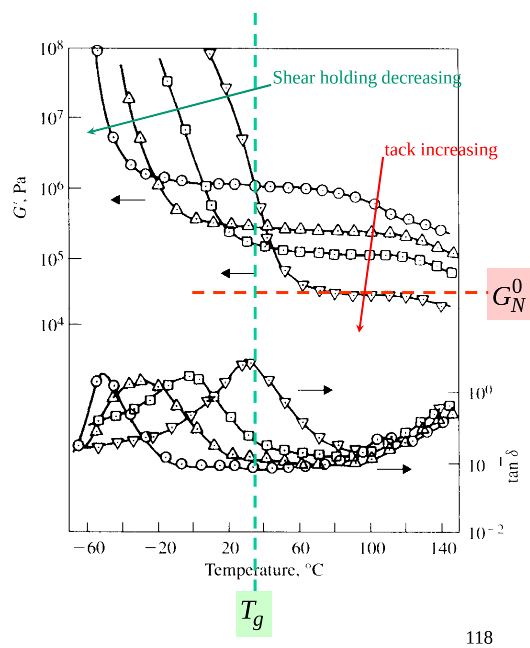


*Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier*

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Small-Strain Unsteady Shear Summary:

1. General traits
2. Effect of MW (linear polymers)
3. Effect of architecture
4. Relationship to steady flow material functions
5. Measurement issues
6. Effect of chemical composition
7. Effect of temperature

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## Experimental Data (continued)

*Unsteady shear flow*

✓ •Small strain - SAOS, step strain

*linear polymers, material effects, temperature effects*

➡ •Large strain - start-up, cessation, creep, large-amplitude step strain

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***lastly . ..***

*Steady elongation*

*Unsteady elongation*

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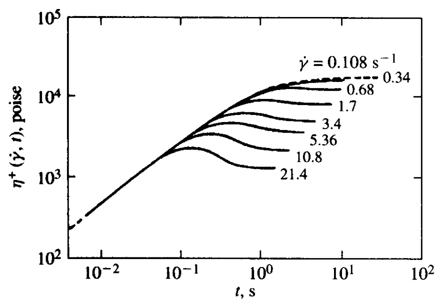
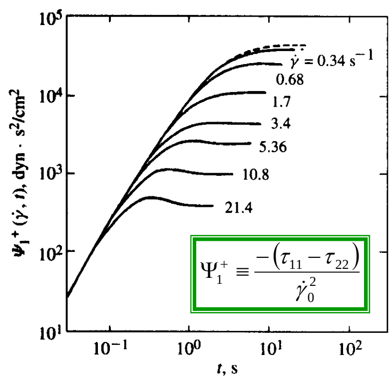
## Startup of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$




$$\eta^+ \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$




$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

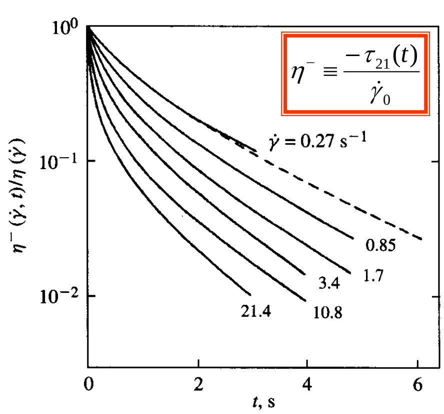
*Figures 6.49, 6.50, p. 208 Menezes and Graessley, PB soln*



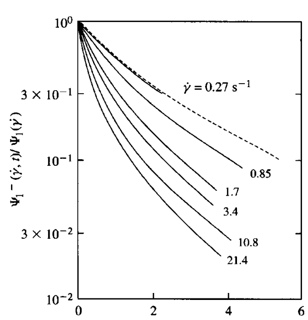


## Cessation of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$




$$\eta^- \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$




$$\Psi_1^- \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

*Figures 6.51, 6.52, p. 209 Menezes and Graessley, PB soln*

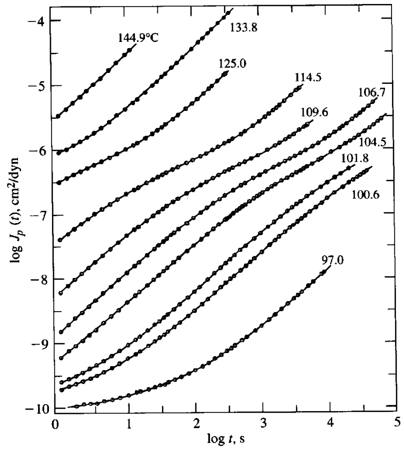
## Shear Creep

$$\underline{v} \equiv \begin{pmatrix} \dot{\gamma}_{21}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

$$\tau_{21}(t) = \begin{cases} 0 & t < 0 \\ \tau_0 & t \geq 0 \end{cases}$$

$$J_p = \frac{J(T) T \rho}{T_{ref} \rho_{ref}}$$

*Data have been corrected for vertical shift.*




$$J(t, \tau_0) \equiv \frac{\gamma_{21}(0,t)}{-\tau_0}$$

*Figure 6.53, p. 210*
*Plazek; PS melt*

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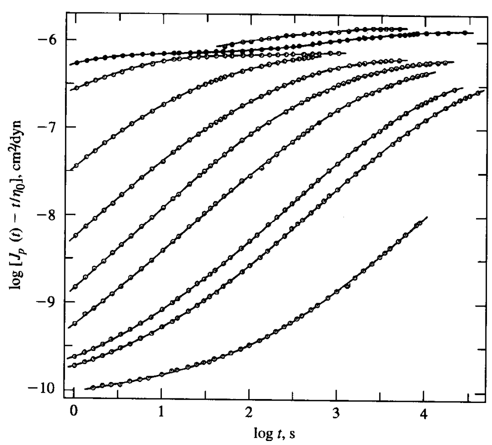
## Shear Creep - Recoverable Compli

$$J(t) = R(t) + \frac{t}{\eta_0}$$

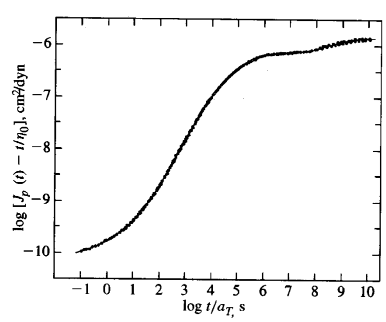



recoverable strain

$$\gamma(t) = \gamma_r(t) + t\dot{\gamma}_\infty$$

total strain

non-recoverable strain




*Figures 6.54, 6.55, p. 211*
*Plazek; PS melt*

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## Step shear strain - *strain dependence*

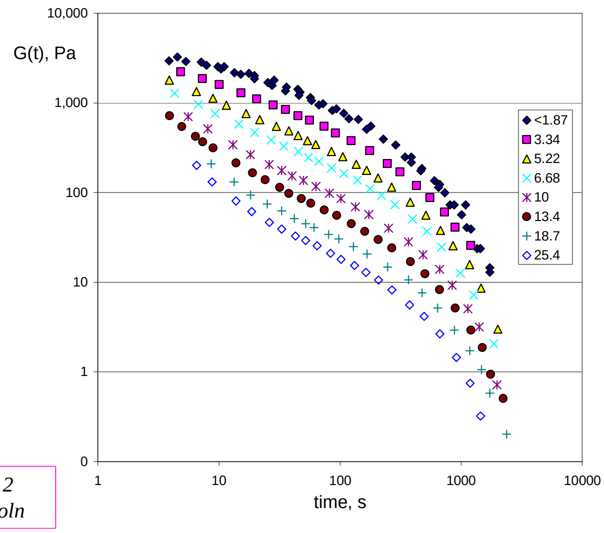


*Figure 6.57, p. 212*
*Einaga et al.; PS soln*

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## Shear Damping Function

*Observation*: step-strain moduli curves have similar shapes and appear to be shifted down with strain.

Damping function

$$G(t,\gamma_0) = G(t)h(\gamma_0)$$

$$\log G(t,\gamma_0) = \log G(t) + \log h(\gamma_0)$$

The damping function gives the strain-dependence of the step-strain relaxation modulus.

When $G(t,\gamma_0) = G(t)h(\gamma_0)$ the behavior is called time-strain separable.

This behavior is predicted by some advanced constitutive equations.

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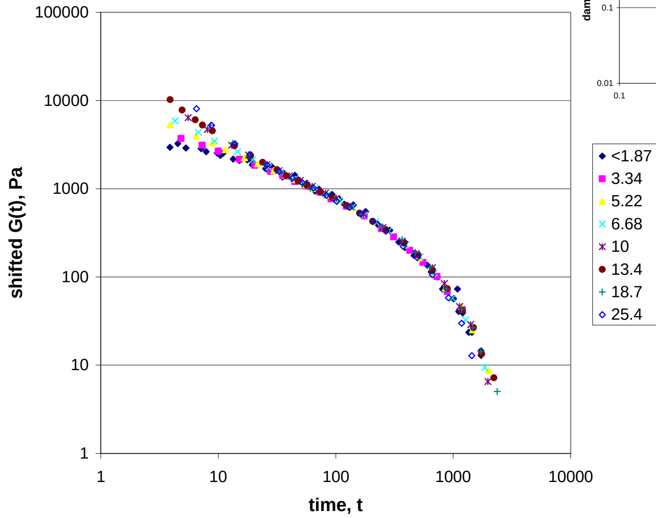
## Step shear strain - **Damping Function**



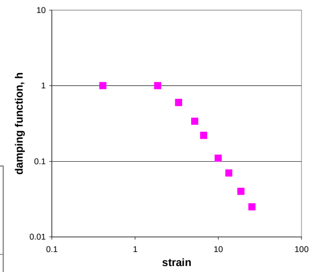




*Figure 6.58, p. 213*
*Einaga et al.; PS soln*

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## Large-Strain Unsteady Shear Summary:

1. General traits
2. Measurement issues

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## Experimental Data (continued)

*Unsteady shear flow*

- •Small strain - SAOS, step strain

  *linear polymers, material effects, temperature effects*

- •Large strain - start-up, cessation, creep, large-amplitude step strain

***lastly . ..***

*Steady elongation*

*Unsteady elongation*





## Steady State Elongation Viscosity

Both tension thinning and thickening are observed.

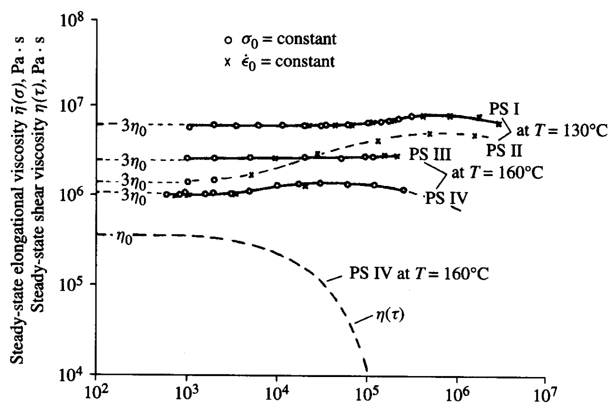
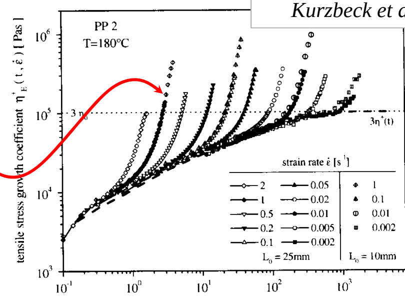



*Figure 6.60, p. 215*
*Munstedt.; PS melt*

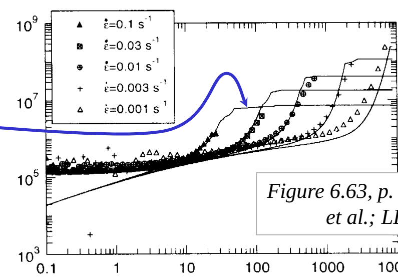
Trouton ratio: $Tr \equiv \dfrac{\bar{\eta}}{\eta_0}$

## Start-up of Steady Elongation

*Figure 6.64, p. 218 Kurzbeck et al.; PP*




Strain-hardening



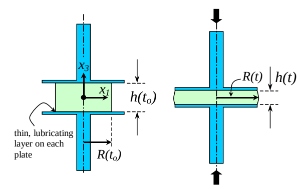

Fit to an advanced constitutive equation (12 mode pom-pom model)

*Figure 6.63, p. 217 Inkson et al.; LDPE*

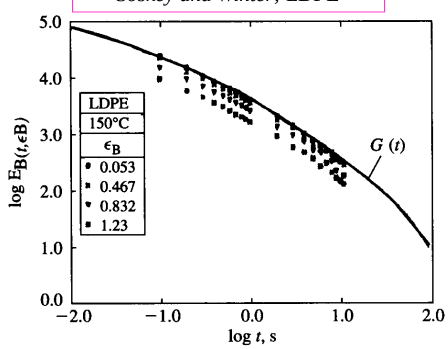




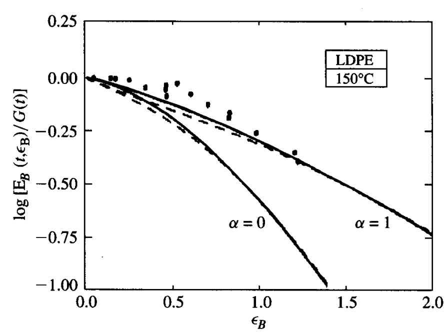
## Elongation Step-Strain




*Figures 6.68, 6.69, pp. 220-1 Soskey and Winter; LDPE*




Relaxation function for step biaxial elongation




Damping function for step biaxial elongation

Elongational Flow Summary:

1. General traits
2. Measurement issues




## More on Material Behavior

### Polymer Behavior

Larson, Ron, *The Structure and Rheology of Complex Fluids* (Oxford, 1999)
Ferry, John, *Viscoelastic Properties of Polymers* (Wiley, 1980)

### Suspension Behavior

Mewis, Jan and Norm Wagner, *Colloidal Suspension* (Cambridge, 2012)

### Journals

*Journal of Rheology*
*Rheologica Acta*
*Macromolecules*