Non-Newtonian Rheology of Entangled Polymer Solutions & Melts:

Linear and Star-Branched Polymers

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GOAL: Develop quantitative understanding of shear thinning behavior by:

(i) assuming "power law" dependence

(ii) utilizing basic understanding of polymer dynamics in the low shear region,

(iii) stipulating about high shear flow relaxation mechanism, in the absence of entanglements.

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VARIABLES

$\dot{\gamma}$ = Shear Rate

$\boldsymbol{\eta}(\dot{\gamma})$ = Viscosity $= \boldsymbol{\sigma} / \dot{\gamma} \approx \boldsymbol{K} \dot{\gamma}^{\boldsymbol{p-1}}$

$\boldsymbol{\Psi_1}(\dot{\gamma})$ = 1st Normal Stress Coeff. = $\boldsymbol{N_1}/\dot{\gamma}^2 \approx \boldsymbol{L} \dot{\gamma}^{\boldsymbol{q-1}} = 2\eta^2(\dot{\gamma})J(\dot{\gamma})$

Recoverable Compliance = $J(\dot{\gamma})$

GOAL: Find the ***K***, ***L*** coefficients & ***p*** and ***q*** exponents ($0 \le p \le 1$, $0 \le q \le 2$)

PARAMETERS:

M = Polymer Mol. Weight …or…. M_a = Arm MW of a Star

M_e = Entanglement MW = $M_C/2$ = MW of Visc. Incr. ~ $\varphi^{(1+\varepsilon)}$

T = Temperature

c = polymer Concentration ……………, $\varphi = c/\rho$ = Polym. Volume Fraction

m = monomer molecular weight ………, b = effective bond length,

$\langle R^2 \rangle$ = End to end distance = $(M/m)\, b^2$, Molecular rigidity ~ $C_\infty = (b/l)^2$,

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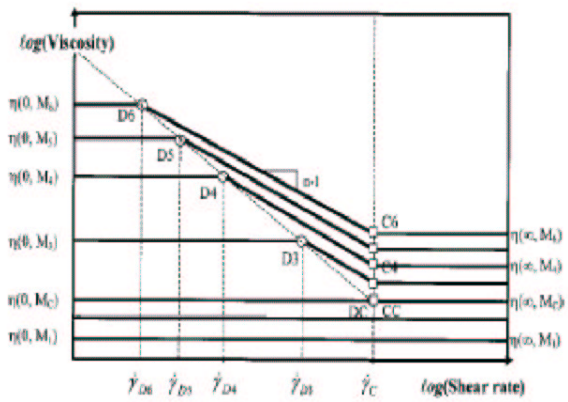

Figure 1. Viscosity vs shear rate corresponding to various linear polymer molecular weights, M_i, above and below the entanglement threshold, M_C: $M_1 \leq ... \leq M_C \leq M_3 \leq ... \leq M_6$. Horizontal lines signify Newtonian behavior while thicker, inclined lines correspond to the non-Newtonian regime, which spans $\dot{\gamma}_{Di} \leq \dot{\gamma} \leq \dot{\gamma}_C$. First normal stress difference coefficient depiction (Ψ_1) would have followed similar lines, but with a non-Newtonian decay slope of $m - 2$, instead of $n - 1$.

where $\Gamma \equiv \dot{\gamma}\lambda/\gamma_0$. The DE value for γ_0 is roughly equal to $\sqrt{5}$. On the other hand, the fact that at low shear rates

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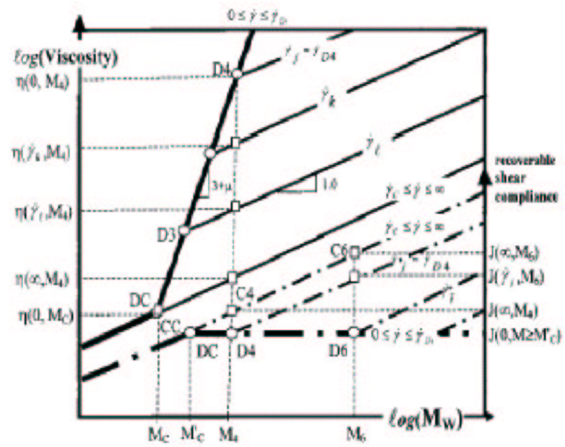

Figure 2. Viscosity (continuous lines in upper part of figure) and recoverable compliance (dashed lines in lower part) vs molecular weight, M_i, at various shear rates, in the shear thinning range and beyond ($0 \leq \dot{\gamma}_{Di} \leq \dot{\gamma}_i \leq ... \leq \dot{\gamma}_l \leq \dot{\gamma}_C \leq \infty$). $\dot{\gamma}_{Di}$ signifies the onset of non-Newtonian behavior and here, $\dot{\gamma}_i = \dot{\gamma}_{D6}$, $\dot{\gamma}_j = \dot{\gamma}_{D4}$, and $\dot{\gamma}_l = \dot{\gamma}_{D3}$. Thicker lines and circular points signify Newtonian behavior while thinner lines and square points correspond to non-Newtonian values. The rest of the symbols stand as in Figure 1, whose information is equivalent to that of Figure 2 but presented in an alternative fashion.

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Molecular Origin of Non-Linar Viscoelasticity = reversible reduction of network connectivity due to entanglement dissolution as flow intensity increases.

ASSUMPTIONS :

1.a) In entangled systems, shear thinning is due to entanglement stripping.

1.b) It can be modeled by a "power law" with respect to $\dot{\gamma}$.

Limits defining the non-Newtonian regime:

2.a) Onset of non-Newtonian behavior at $\dot{\gamma}_0 \approx 1/\lambda_0$ = longest relax. time:

$$\lambda_0(M > M_C) = \frac{\langle R^2 \rangle}{36D} = \eta_0 J_0 = \left(\frac{\zeta b^2}{24kT}\right)\left(\frac{M_C}{m}\right)^2\left(\frac{M}{M_C}\right)^{3+\mu} \qquad \text{(Eq.1)}$$

2.b) Shear thinning cessation at $\dot{\gamma}_\infty \approx 1/\lambda_{Rouse}(M_C) = 1/\lambda_0(M_C)$, i.e. the *M*-invariant frequency of swiftest entanglement renewal process .

3.a) Below $\dot{\gamma}_0$, entangled chain dynamics applies (Eq.1) .

3.b) Beyond $\dot{\gamma}_\infty$, resumption of Rouse-Newtonian behavior, even if $M > M_C$:

$$\eta_{Rouse}(M) = \frac{2cRT}{M}\lambda_{Rouse} = \left(\frac{cN_A\zeta b^2}{12m}\right)\left(\frac{M}{m}\right)$$

4) Non-Newtonian Constitutive Expressions derived by <u>interpolating between D&C</u>

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Predict **Shear and Normal Stress Thinning Behavior ….**

Start by knowing the two shear rate limits that define the non-Newtonian regime, $\dot{\gamma}_0$ and $\dot{\gamma}_\infty$, as well as the Newtonian values on either side of the shear thinning region, η_0 and η_∞.

1) Construct a general power law expression that passes through the very point of abandonment of the Newtonian region, i.e., the point $[\dot{\gamma}_0, \eta_0]$:

$$\frac{\eta(\dot{\gamma}, M)}{\eta(0, M)} \approx \left(\frac{\dot{\gamma}_0}{\dot{\gamma}}\right)^{1-p} \approx \left(\frac{1}{\eta_0 J_0 \dot{\gamma}}\right)^{1-p}$$

2) Substitute for η_0 and J_0 the corresponding M/M_C dependent expressions and obtain:

$$K = \frac{\eta_0^p}{J_0^{1-p}} = \left(\frac{cRT}{m}\right)\left(\frac{\zeta b^2}{12kT}\right)^p \left(\frac{M}{m}\right)^{(3+\mu)p} \left(\frac{m}{M_C}\right)^{2(1-p)}$$

3) Assume Newtonian flow and Rouse like dynamics beyond $\dot{\gamma}_\infty = 1/\lambda_{Rouse}(M_C)$

$\eta(\infty \geq \dot{\gamma} \geq \dot{\gamma}_\infty, M) = \eta(\dot{\gamma}_\infty, M) \equiv \eta(\infty, M) = \eta_R(M)$. Then,

4) Eq for η should also "pass" through (and end at) the $[\dot{\gamma}_\infty, \eta_R]$ point:

$$\frac{\eta(\infty, M)}{\eta(0, M)} \approx \left(\frac{\dot{\gamma}_0}{\dot{\gamma}_\infty}\right)^{1-p} \Rightarrow \frac{\eta_R}{\eta_0} = \left(\frac{\eta_e J_e}{\eta_0 J_0}\right)^{1-p}$$

5) Substitute for the Newtonian Viscosity and Compliance and Solve for…

$$\boldsymbol{p} \equiv \frac{d \ln \sigma}{d \ln \dot{\gamma}} = \frac{1}{3+\mu} \approx \frac{d \ln M}{d \ln \eta_0} \approx \frac{1}{3.5}$$

6) Do the same for Normal Stresses and (for $M > M'_C$) get:

$$\boldsymbol{q} \equiv \frac{d \ln N_1}{d \ln \dot{\gamma}} = \frac{3}{3+\mu} \approx \frac{3}{3.5}$$

$$L = \frac{2\eta_0^q}{J_0^{1-q}} = \left(\frac{2cRT}{m}\right)\left(\frac{\zeta b^2}{12kT}\right)^q \left(\frac{M}{m}\right)^3 \left(\frac{m}{M_C}\right)^{2(2-q)}$$

Steady Shear Rheology for Linear Polymers Compactly Stated

$$\sigma \text{ or } \frac{N_1}{2} \approx \frac{(\eta_0 \dot{\gamma})^r}{J_0^{1-r}} = \frac{\rho RT}{m} \left(\dot{\gamma} \mu_T \frac{\zeta_g b^2}{12kT} \right)^r \frac{N^{(3+\mu)r}}{N_{C1}^{1+(1+\mu)r}} \varphi^{(2+\varepsilon)+(1+\varepsilon)(1+\mu)r}$$

r = the *shear* or normal stress exponent of ***p*** or ***q***, not excluding the corresponding zero-shear values (r_0) of *1* and *2*.

$N = M/m$

$N_{C1} = M_C(\varphi=1)/m$

$\varepsilon = d\ln M_C / d\ln \varphi - 1$

$\mu = d\ln \eta_0 / d\ln M - 3$

REMARKS

- In well entangled linear polymers, $p = q/3 \approx 2/7$ and, consequently, consistent with experience, $\eta \sim \dot{\gamma}^{-0.714}$, $\Psi_1 \sim \dot{\gamma}^{-1.143}$, $(\Rightarrow J \sim M_C \sim \dot{\gamma}^{0.286})$
- Complies with the observed *rate-temperature* and *rate-concentration* superposition principles,
- It correctly predicts that $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ demonstrate a much weaker molecular weight dependence under shear thinning.

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Parametric Dependence on T, φ and Chain Rigidity

EXAMPLE:

For $p = q/3 = 1/3.5$ and
$\mu = 2\varepsilon = 0.5$ and

$M_C/m \sim C_\infty^{0.5(1-\varepsilon)}/\varphi^{1+\varepsilon}$ and $\ln(\eta_{Sg}) \sim 1/C_\infty^{3/2}$ **:**

$$\eta(\dot{\gamma}) \sim (\eta_{Sg} a_T)^{0.286} \frac{T^{0.714} \varphi^{2.79} N}{C_\infty^{1.61} \dot{\gamma}^{0.714}}$$

$$\Psi_1(\dot{\gamma}) \sim (\eta_{Sg} a_T)^{0.857} \frac{T^{0.143} \varphi^{3.86} N^3}{C_\infty^{1.07} \dot{\gamma}^{1.143}}$$

At any given shear rate, and provided that all other parameters (c, $N=M/m$, $T - T_g$) are kept equal,

the stress coefficient of a polymer with a higher rigidity is lower in value than that of a more flexible species.

The opposite should hold for the **self-diffusion** coefficient:

$$D \sim \frac{C_\infty^{0.0625}}{\eta_{Sg} a_T N^{2.5} \varphi^{1.875}}$$

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Non-Newtonian Rheology of Star-Branched Polymers

By methods similar to the above *(Tsenoglou, submitted 2002)*

$$\sigma \text{ or } \frac{N_1}{2} = \frac{(\eta_0 \dot{\gamma})^r}{J_0^{1-r}}$$

$\boldsymbol{r}$ = the *shear* or normal stress exponent of $\boldsymbol{p}$ or $\boldsymbol{q}$, not excluding the corresponding zero-shear values (r_0) of *1* and *2*.

$$q = 2p = \frac{4 \ln A}{\alpha(A-1) + 1.5 \ln A}$$

where $\boldsymbol{A} \equiv M_a/M_e$ = # entanglements per arm, (and $\alpha \approx 1/2$)

IMPLICATIONS

- Shear thinning severity depends on # entanglements per arm, A.
- $N_1(\dot{\gamma}) = 2J_0\sigma^2(\dot{\gamma})$ and, therefore,
- $J(\dot{\gamma}) = J(0)$ = shear rate independent compliance
- Expected failure of the *rate-concentration superposition* i.e. of a universal $\eta(\dot{\gamma}, \varphi)/\eta(0, \varphi)$ vs $\dot{\gamma}/\dot{\gamma}_0(\varphi)$ curve

Temperature (T) and Polymer Concentration (φ) Dependence of Star Rheology:

$$\sigma \text{ or } N_1 \sim (\zeta_g \times a_T \times a_C \times \dot{\gamma})^r \times \varphi^{1-0.5r(1+\varepsilon)} \exp[\alpha r(A_1 \varphi^{1+\varepsilon} - 1)]$$

EXAMPLE

Consider a Polybutadiene star of $A_1 \equiv M_a/M_e(\varphi=1) = 25$, *Raju et al.*[1981]

Melt: $\sigma \sim \sqrt{N_1} \sim \dot{\gamma}^{0.375}$.

Diluted in Flexon 391 ($\varphi = 0.403$, $a_C \approx \varphi^0$, $\varepsilon \approx 0$), $A(\varphi) = 10$.

Solution: $\sigma \sim \sqrt{N_1} \sim \dot{\gamma}^{0.57}$

In the zero shear limit: $\sigma \sim \sqrt{N_1} \sim \dot{\gamma}^1$, irrespective of dilution.

Entanglement Depletion & Star Self-Diffusivity.

$M_e(\dot{\gamma}_0) = M_e(0)$ and $M_e(\dot{\gamma}_\infty) = M_a$, therefore, in the $\dot{\gamma}_0 \le \dot{\gamma} \le \dot{\gamma}_\infty$ interval:

$$\frac{M_e(0)}{M_e(\dot{\gamma})} \equiv h'(\dot{\gamma}) = \frac{G_N(\dot{\gamma})}{G_N(0)} \approx 1 - \left(1 - \frac{M_e(0)}{M_a}\right) \frac{\ln(\eta_0 J_0 \dot{\gamma})}{\ln(\eta_0 J_0 / \eta_e J_e)}$$

where $G_N(\dot{\gamma}) = cR_G T / M_e(\dot{\gamma})$ = plateau modulus.

Complete conformational renewal of a star through "path fluctuations" requires λ_2 sec.
This causes a move on behalf of the polymer by a mere a = $(M_e/m)^{1/2} b$ distance. $\Rightarrow$

***Star* self-diffusivity** = $D_{Star} = a^2/(6\lambda_2) = a^2/(6J\eta)$ $\Rightarrow$

$$D_{Star} = \frac{\rho R_G T b^2 M_e(\dot{\gamma},1)}{2.4\,\varphi^{\varepsilon} \eta(\dot{\gamma}) m\, f g_2 M_a} \qquad \text{while}$$

***Linear* self-diffusivity =** $D_{Linear} = \langle R^2 \rangle / (36\lambda_2)$ $\Rightarrow$

$$D_L \sim \varphi^{2+\varepsilon} M_L / [M_e(0,1) \eta_L\, \dot{\gamma}^{1/3.4}]$$