Characterization of Branched Chain Polymers

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Effect of Branching on the Chain Dimensions

$R_G^2 = g\,(R_G^2)_{LIN}$; e.g., from static light scattering

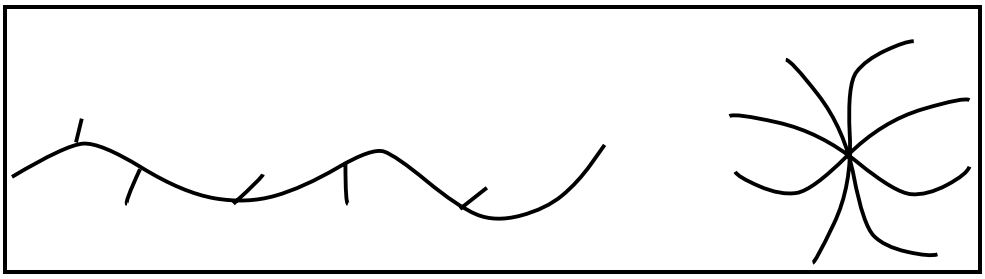
$0 \leq g \leq 1$ (linear: g = 1)

$R_H = h\,(R_H)_{LIN}$; e.g., from dynamic light scattering

($R_H = \Xi/6\pi\eta_{solvent}$)

$0 \leq hg^{-1/2} \leq 1.4$ (several models)

Model structures:



Comb-shaped chain **Star-shaped chain**

Number Branches	n	Number Branches	n
Branch	M_{br}	Branch	M_{br}
Backbone	M_{bb}		

λ = fraction of the mass in the backbone

Comb: $\lambda = M_{bb}/M_{total} = M_{bb}/\{M_{bb} + nM_{br}\}$

Star: $\lambda = 0$

E. F. Casassa and G. C. Berry (1988) in Comprehensive Polymer Science; Ed. G. Allen; Pergamon Press, New York, p. 71-120

g may be calculated for the random-flight model:

star: $g = g_{STAR} = \frac{3n - 2}{n^2}$ ("regular" star)

comb: $g \approx \lambda$ as λ tends to zero

approximation: $g \approx g_{gcb} = \lambda + (1 - \lambda)^{7/3} g_{STAR}$

"random" branching: $g_w = g(n_w, f)$ (Zimm & Stockmayer)

$g_w \approx \lambda_w$ (Macosko)

$\lambda_w = (M_{longest})_w / (M_{total})_w$

For a tri-functional branch node (f = 3)

n_w	g_w	λ_w	$g_{gcb}(n_w)$
0.417	0.917	0.931	0.926
1.000	0.843	0.853	0.864
2.571	0.694	0.692	0.747

5.494	0.541	0.532	0.614
10.364	0.410	0.390	0.475
49.000	0.165	0.122	0.167
165.67	0.069	0.039	0.055

B.H. Zimm and W.H. Stockmayer (1949) J. Chem. Phys. 17:1301

M. Kurata and M. Fukatsu (1964) J. Chem. Phys. 41:2934-44

G.R. Dobson and M. Gordon (1964) J. Chem. Phys. 41: 2389-98

D.R. Miller, E.M. Valles and C.W. Macosko (1979) Polym. Eng. Sci. 19:272-83

Complications:

- **Non-Gaussian effects (under Flory Θ-conditions);**
  - **(i)** $g_{measured}$ **usually exceeds** $g_{random\text{-}flight}$
  - **(ii)** Θ **may depend on the extent of branching**

- **Excluded volume effects:**

$$\alpha^2 = R_G^2 / (R_G^2)_\Theta$$

$$\alpha^2 = 1 + a_1\, s(z); \quad z \propto d_{THERMO} M^{1/2}$$

$$\alpha^2 \approx \left(\{1 + \frac{a_1}{2\nu - 1} z + k \left(\frac{a_1}{2\nu - 1} z \right)^2 \right)^{2\nu - 1}$$

$$\nu \approx 0.589$$

$$k_{LIN} \approx 0.21$$

- **(i)** $(a_1)_{BR} \geq (a_1)_{LIN} = 134/105$

  $(a_1)_{BR} = (a_1)_{LIN} A(\lambda, n, f)$, **known for some models**
- **(ii)** **The effect of branching on** k **is unknown**
- **(iii)** d_{THERMO} **may depend on branching**

Note: $R_G^2 = g\, \alpha^2 [(R_G^2)_{LIN}]_\Theta$

- **The effects of branching on α^2 and the non-Gaussian effects of branching on g tend to compensate**

- **To a useful approximation, in some cases:**

$$R_G^2 = g_{\text{random-flight}}(\alpha^2)_{LIN}[(R_G^2)_{LIN}]_\Theta$$

The Intrinsic Viscosity

- L: contour length $(M_L = M/L)$
- $R_G^2 = g\,\alpha^2[(R_G^2)_{LIN}]_\Theta \propto g\,\alpha^2 L l$
- $R_H \approx h\,\alpha\,[(R_H)_{LIN}]_\Theta \propto h\,\alpha\,(L l)^{1/2}$

$$[\eta] = [\eta]_{FD} K_\eta R_H / L$$

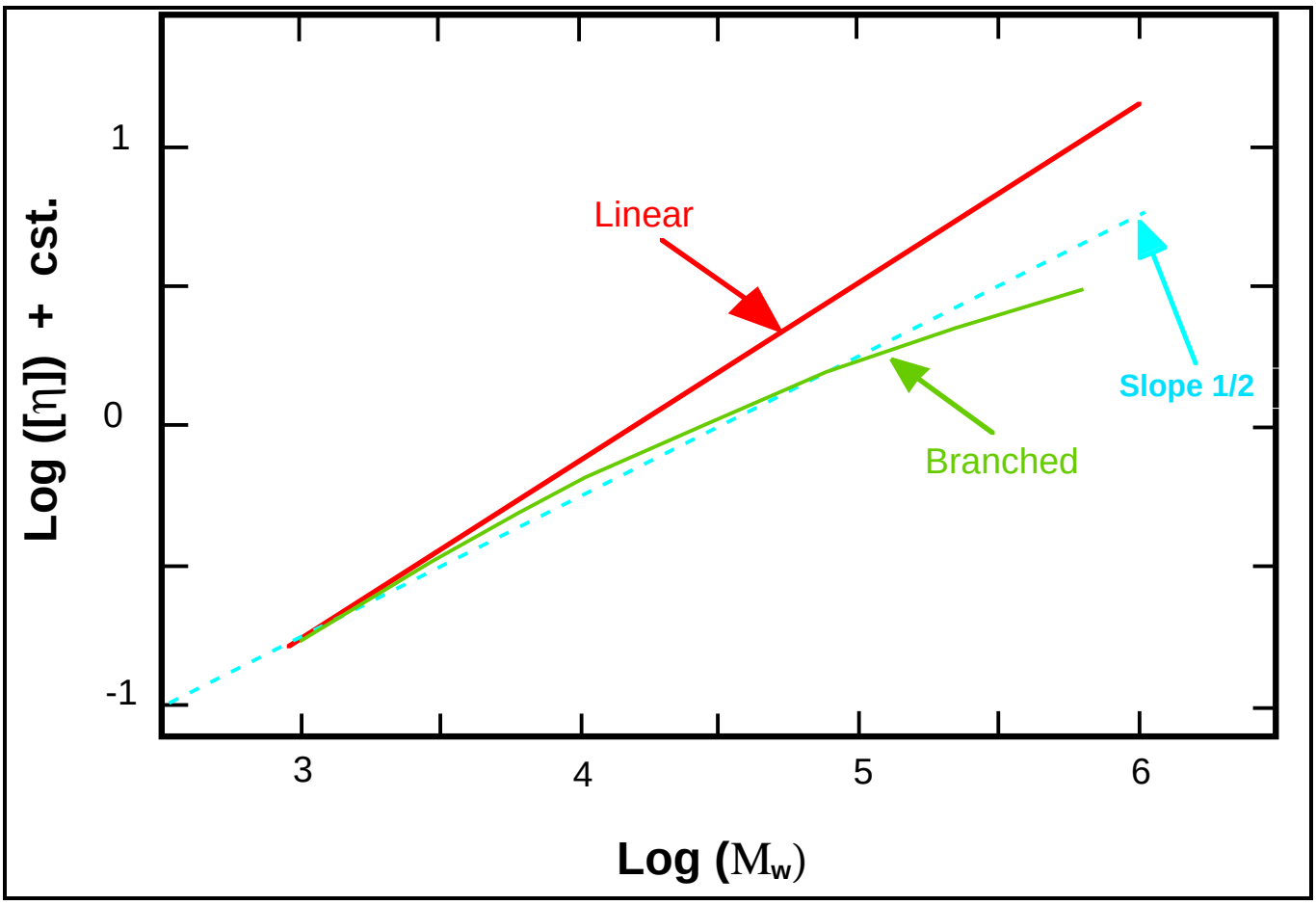
$$[\eta]_{FD} = \pi N_A R_G^2 / M_L$$

$$[\eta] = k(K_\eta)_{LIN}(\alpha_{BR}^3/\alpha_{LIN}^3)g[(R_G^2)_{LIN}]_\Theta h[(R_H)_{LIN}]_\Theta \alpha_{LIN}^3/M$$

$$= kgh(\alpha_{BR}^3/\alpha_{LIN}^3)[\eta]_{LIN} = g'[\eta]_{LIN}$$

G. C. Berry (1988) J. Polym. Sci.; Pt. B: Polym. Phys. 26: 1137-42

Typical behavior with g decreasing with increasing M



Characterization Parameters

- To characterize branching from data on dilute solutions, some model information is required:

  ◊ g as a function of appropriate model parameters

  ◊ g' as a function of g and any other necessary parameters

Approximations:

$$h \approx g^{\beta}$$

$$k \approx g^{\mu}$$

$$[\eta] = g'[\eta]_{LIN}$$

$$g' = g^{m} = g^{\mu}\, g\, g^{\beta}$$

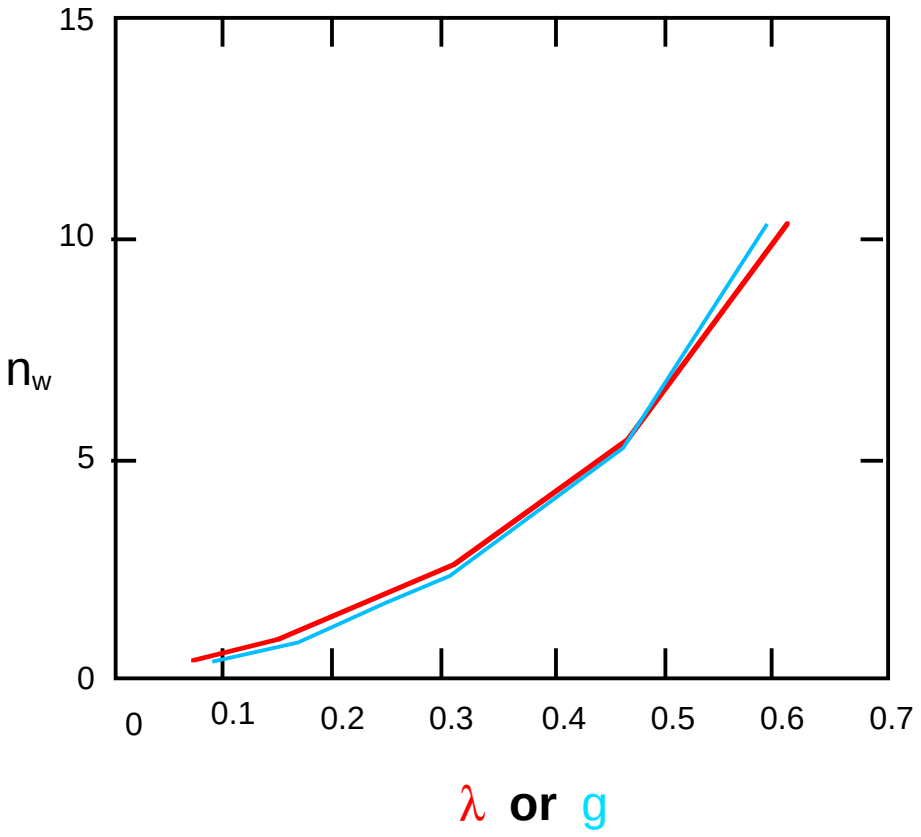
		μ	β	m
Zimm/Thurmond	**Approximation**	**0**	**1/2**	**3/2**
Zimm/Kilb	**Calculation (Stars)**	**-1**	**1/2**	**1/2**
Osaki	**Calculation (Combs)**	**-1 to 0**	**1/2**	**1/2 to 3/2**
Berry	**Correlation**	$\mu(g,\lambda)$	**1/2**	$m(\lambda)$

$$m(\lambda) \approx 0.44 + \lambda^{10/3}$$

Typically, for randomly branched chains, m ≈ 1, or

$$[\eta] \approx g\,[\eta]_{LIN}$$

An approximate interpretation of g or λ_w for a randomly branched polymer:



Size Exclusion Chromatography

Basic Postulate of "Universal Calibration":

$$V_e = \nu(M[\eta])$$

- For linear chains, SEC analysis can be done with c_e vs V_e, and the function $\nu(M[\eta])$ if the postulate is valid

- To assess branching using SEC, additional data are needed:

  ◊ c_e and M_e vs V_e, and the function $\nu(M[\eta])$, or

  ◊ c_e and $[\eta]_e$ vs V_e, and the function $\nu(M[\eta])$, or

  ◊ c_e, M_e and $[\eta]_e$ vs V_e

- To increase the ability to assess branching using SEC, additional data would be useful:

  ◊ $R^2_{G,e}$ vs V_e

  ◊ $R_{H,e}$ vs V_e

- Given the basic postulate ($V_e = \nu(M[\eta])$), the average over the elution volume is one at constant $M[\eta]$ (with neglect of axial diffusion).

Examples:

C. Jackson, Y.-J. Chen and J. W. Mays (1996) J. Appl. Polym. Sci. 59:179-88 N. Sakurai, T. Mori, K. Imaeda (1995) Y. Gotoh and A. Itsubo, PMSE Prep. 72: 359-60

The Viscosity of Concentrated Solutions and Bulk Polymer

Dimensionless reduced viscosity

$$\tilde{\eta} = \eta/\eta_{LOC}^{(c)} = 1 + (c/\rho)^{\beta}\tilde{X}\,\mathcal{E}(\tilde{X}/\tilde{X}_c)$$

$\eta_{LOC}^{(c)}$ is a "Local viscosity", tending to the solvent viscosity $\eta_{solvent}$ at infinite dilution and to the "viscosity" η_{repeat} of a repeat unit for undiluted polymer:

Following Arrhenius (1887):

$$\eta_{LOC}^{(c)} \approx \eta_{solvent}^{1-\mu(\varphi)}\eta_{repeat}^{\mu(\varphi)}; \qquad \mu \approx \varphi$$

In general, for either $\eta_{solvent}$ or η_{repeat}:

$$\eta_{\mu} \propto \exp\left(\frac{W_{\mu}}{T}\right) + \exp\left(\frac{\mathcal{K}}{T - (T_g)_{\mu} + \Delta}\right)$$

with $\mathcal{K}$ and Δ both (essentially) universal constants.

- The dependence on chain structure

$$\tilde{X} = c[\eta]_{FD} = \pi N_A (R_G^2)_\Theta c/M_L$$

$\tilde{X}_c$ = constant ≈ 115; empirical for many systems

◊ Linear Chains:

$$\Phi(y) \approx y^{2.4}$$

◊ Branched Chains with $\tilde{X}_{BR} < \tilde{X}_c$:

Same behavior, with $R_{G,\Theta}^2 = g[(R_G^2)_{LIN}]_\Theta$

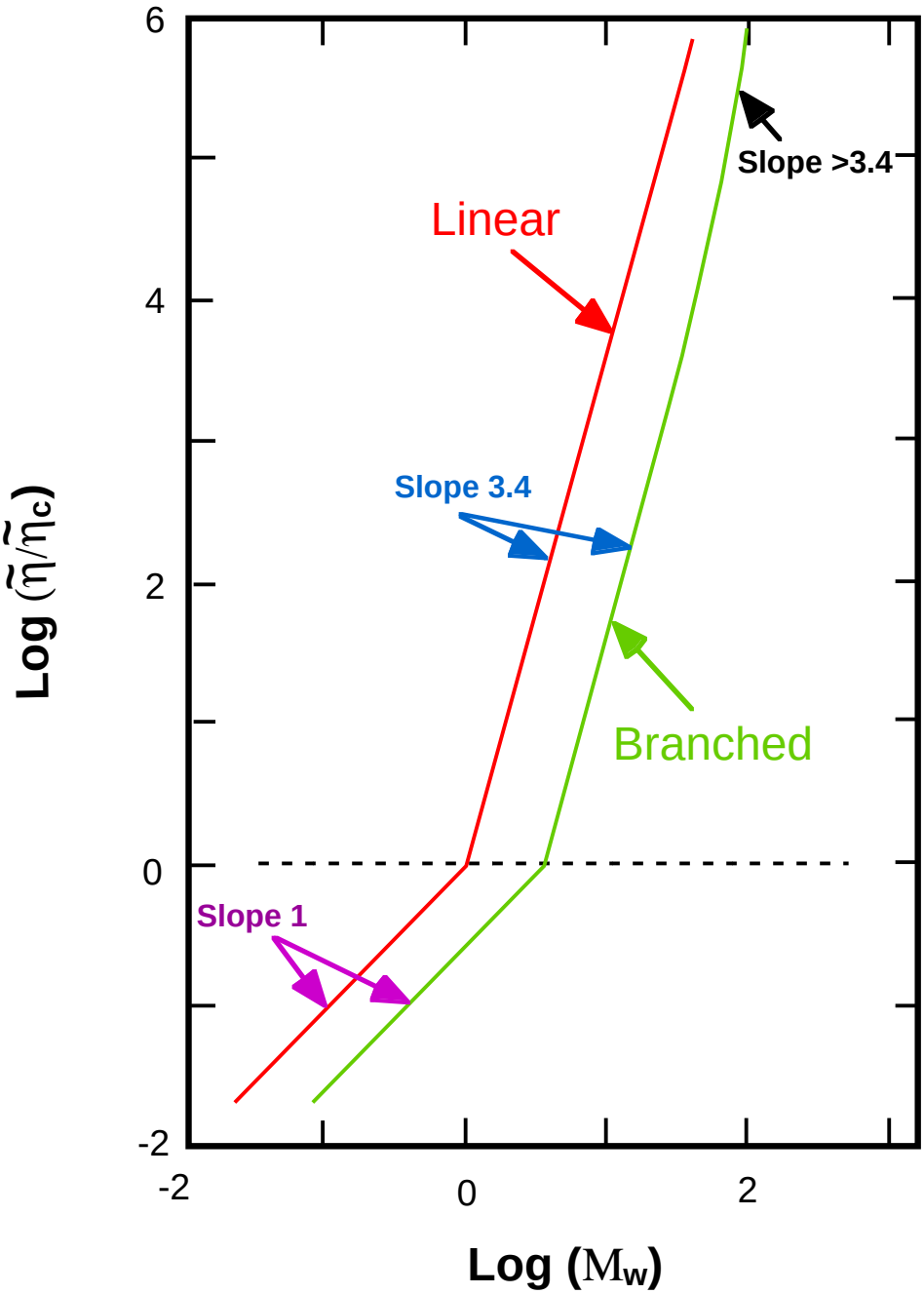
This results in $\tilde{\eta}_{BR} < \tilde{\eta}_{LIN}$

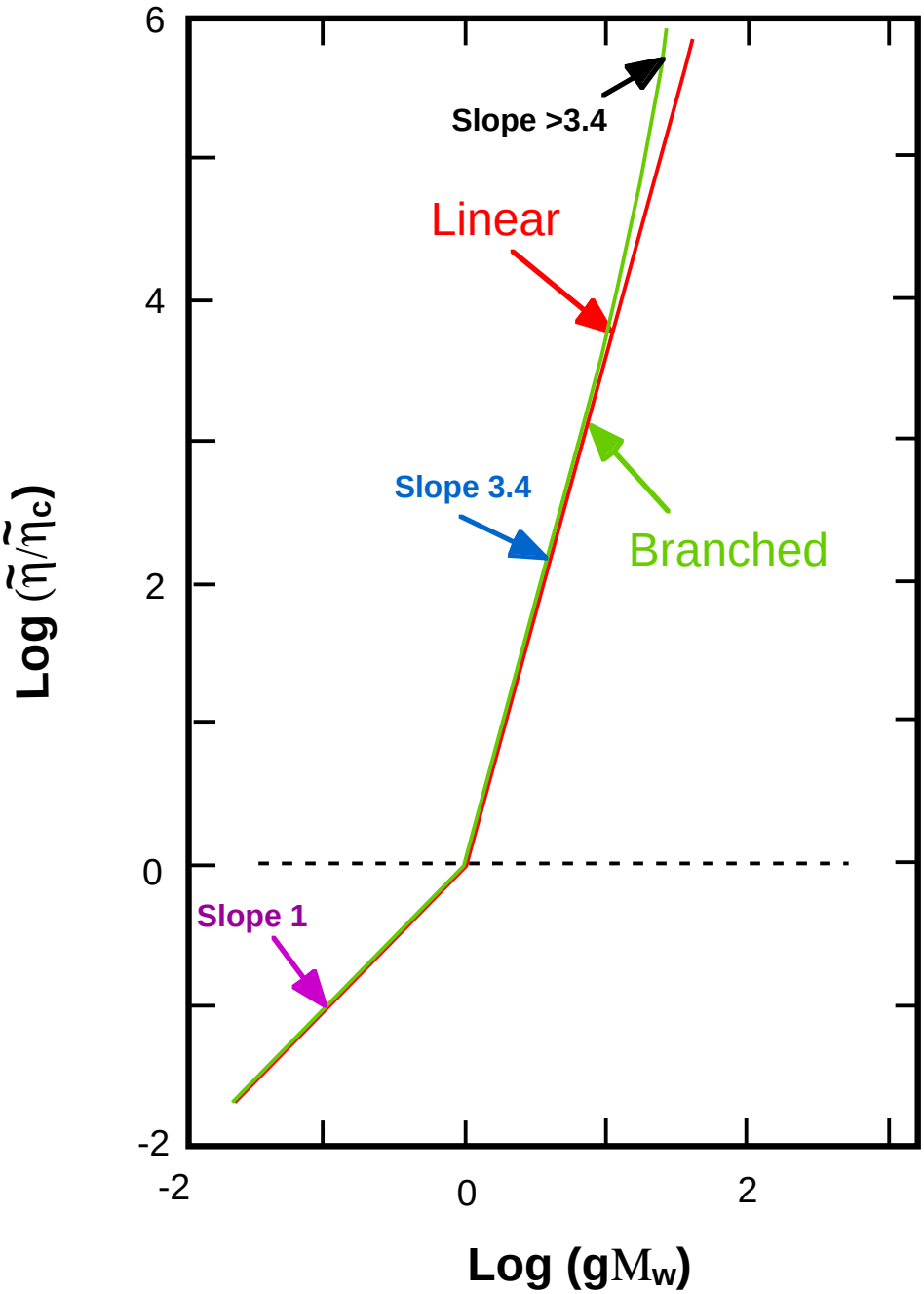
◊ Branched Chains with $\tilde{X}_{BR} > \tilde{X}_c$:

An enhancement function may be needed, depending on the nature of the branching. For comb branched chains, this effect is strong, and can cause $\tilde{\eta}_{BR} > \tilde{\eta}_{LIN}$

G. C. Berry and T. G Fox (1968) Adv. Polym. Sci. 5: 261-357

G. C. Berry (1996) J. Rheol. 40:1129-54


6
4
2
0
-2
-2
0
2
Log ($\tilde{\eta}/\tilde{\eta}_c$)
Log (M_w)
Linear
Slope >3.4
Slope 3.4
Branched
Slope 1



G. C. Berry and T. G Fox (1968) Adv. Polym. Sci. 5: 261-357

D. R. Miller, E. M. Valles and C. W. Macosko (1979) Polym. Sci. Eng. 19:272-83

Approximate Representation of Enhancement Effect

$$\tilde{\eta} = \eta/\eta_{LOC}^{(c)} \approx \tilde{X}\mathcal{E}(\tilde{X}/\tilde{X}_c)\mathcal{F}(\sigma\tilde{X}/\tilde{X}_c)$$

The function $\mathcal{F}(\sigma\tilde{X}/\tilde{X}_c) \geq 1$ is intended to account for the enhancement effect, with σ the ratio of the molecular weight of a branch to the total molecular weight, e.g., for a comb branch molecule with n branches, $\sigma = (1 - \lambda)/n$.

An empircial relation suggested for $\mathcal{F}(\sigma\tilde{X}/\tilde{X}_c)$:

$$\mathcal{F}(\sigma\tilde{X}/\tilde{X}_c) \approx \exp\{b[(\sigma\tilde{X}/\tilde{X}_c) - 1)$$

$$(\sigma\tilde{X}/\tilde{X}_c) \geq 1; \quad b \approx [2.16 + 0.848\lambda](1 - g)$$

$$(\sigma\tilde{X}/\tilde{X}_c) < 1; \quad b \approx 0$$

Reptation models provide a qualitative description for the behavior, but not as yet a quantitative one.

G. C. Berry and T. G Fox (1968) Adv. Polym. Sci. 5: 261-357
W. W. Grassley and V. R. Raju (1984) J. Poly. Sci.: Polym. Symp. 71: 77-93

THERMORHEOLOGICAL SIMPLICITY

- Not required for linear viscoelastic behavior at a particular temperature

- If a useful approximation, then in the "terminal response range" (t > ca. $\tau_c/100$) for a linear viscoelastic fluid:

$$J(t/\tau_c) \approx J_R\{\psi(t/\tau_c) + t/\tau_c\}$$

$$J'(\omega\tau_c) \approx J_R\{j'(\omega\tau_c)\}$$

$$J''(\omega\tau_c) \approx J_R\{\omega\tau_c + j''(\omega\tau_c)\}$$

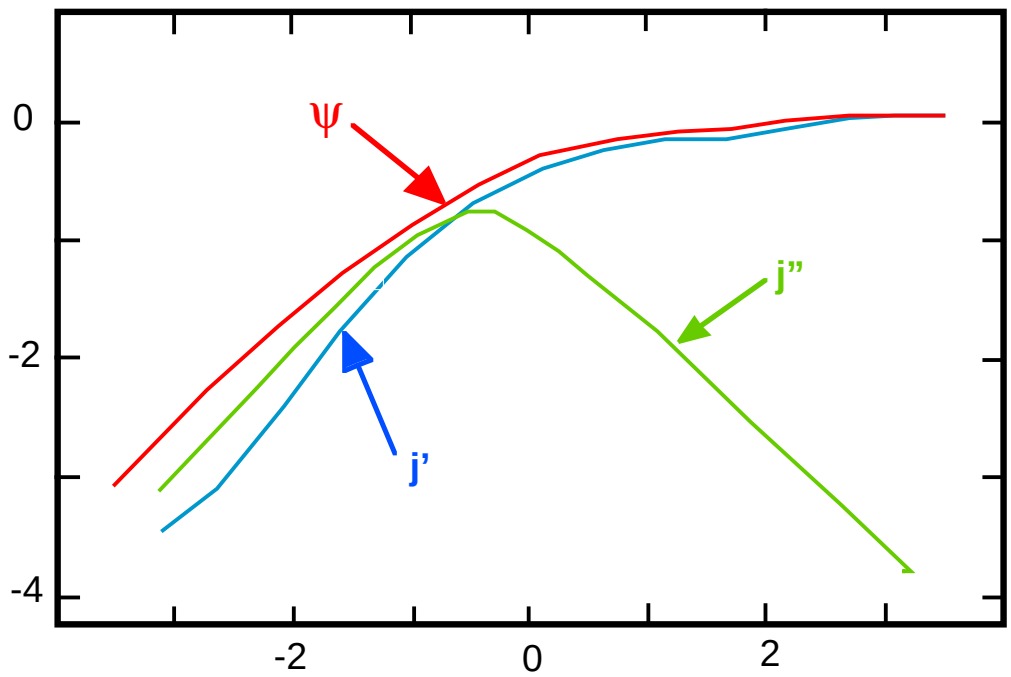
$$G' = J'/\{J'^2 + J''^2\}^{1/2}$$

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

$$\tau_c = J_R \eta_o$$

J_R is the steady-state recoverable compliance

Representative Behavior



Log (t/τ_c) or –Log ($\omega\tau_c$)

These functions are very sensetive to the distribution of retardation (or relaxation) times, e.g., as influenced by molecular weight or shape distribution.

$$\psi(t/\tau_c) \approx [\{j'(\omega\tau_c)^2 + j''(\omega\tau_c)^2\}^{1/2}]_{\omega t = 1}$$

$$\tau_c = J_R \eta_o$$

J. D. Ferry (1980) Viscoelastic Properties of Polymers, 3rd Ed.; Wiley, NY

H. Markovitz (1975) J. Polym. Sci.: Symp. 50:431-56

G. C. Berry and D. J. Plazek (1986) in Glass: Science and Technnology, Vol. 3, Viscosity and Relaxation; eds: D. R. Uhlmann and N. J. Kreidl; Academic Press, New York; p.319-62

Nonlinear Steady-state Flow

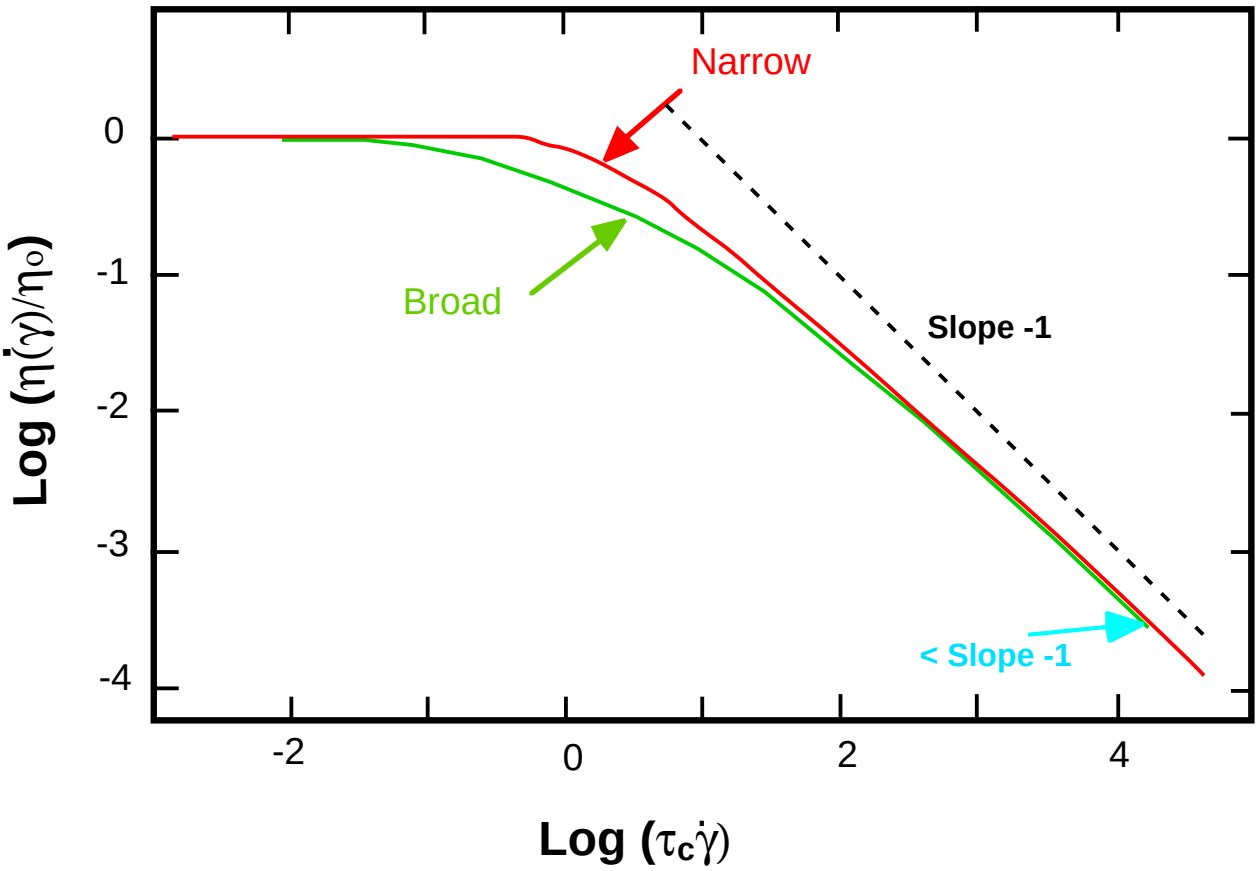
$$\eta(\dot{\gamma}) \approx \eta_o P(\tau_c \dot{\gamma})$$

$$\tau_c = J_R \eta_o$$

- ◊ $\eta(\dot{\gamma})$ is the steady-state viscosity at shear rate $\dot{\gamma}$
- ◊ η_o is the linear steady-state viscosity
- ◊ J_R is the linear recoverable compliance
- ◊ In general, for polymers in the entanglement regime, $P(\cdot)$ depends only on the nature of the distribution of relaxation times, and not otherwise on the material properties.

◊ For a thermorheologically simple material, P(·) is not expected to depend on temperature (though η_o and hence τ_c) will depend on strongly on T, and J_R will ususally depend weakly on T.

Representative Behavior



This function is very sensitive to the distribution of retardation (or relaxation) times, e.g., as influenced by molecular weight or shape distribution.

$$E(\dot{\gamma}) = \frac{\partial \ln \eta(\dot{\gamma})}{\partial(1/T)} = \frac{\partial \ln \eta_o \mathbf{P}(\tau_c \dot{\gamma})}{\partial(1/T)}$$

$$= E_o + E_P$$

$$E_o = \frac{\partial \ln \eta_o}{\partial(1/T)}$$

$$E_P = \frac{\partial \ln \mathbf{P}(\tau_c \dot{\gamma})}{\partial(1/T)} = \left\{ E_o + \frac{\partial \ln J_R}{\partial(1/T)} \right\} \beta(\tau_c \dot{\gamma})$$

$$\beta(\tau_c \dot{\gamma}) = \frac{\partial \ln \mathbf{P}(\tau_c \dot{\gamma})}{\partial \ln \tau_c \dot{\gamma}}$$

$$E(\dot{\gamma}) = E_o\{1 + \beta(\tau_c \dot{\gamma})\} + \frac{\partial \ln J_R}{\partial(1/T)} \beta(\tau_c \dot{\gamma})$$

With increasing $\tau_c \dot{\gamma}$, $\beta(\tau_c \dot{\gamma})$ tends to $\approx$ -0.85

The apparent activation energy for linear viscous flow

$$E_o = \frac{\partial \ln \eta_o}{\partial (1/T)} \approx \frac{\partial \ln \eta_{LOC}^{(c)} \tilde{X} \mathcal{E}(\tilde{X}/\tilde{X}_c) \mathcal{F}(\sigma \tilde{X}/\tilde{X}_c)}{\partial (1/T)}$$

$$\approx E_{LOC} + E_{\tilde{X}} + E_{\mathcal{E}} + E_{\mathcal{F}}$$

$$E_{LOC} = \frac{\partial \ln \eta_{LOC}^{(c)}}{\partial (1/T)} \approx W + \frac{\partial \ln [\kappa/(T - T_g + \Delta)]}{\partial (1/T)}$$

$$E_{\tilde{X}} = \frac{\partial \ln \tilde{X}}{\partial (1/T)} \approx \frac{\partial \ln R_G^2}{\partial (1/T)}$$

$$E_{\mathcal{E}} = \frac{\partial \ln \mathcal{E}(\tilde{X}/\tilde{X}_c)}{\partial (1/T)} \approx \{E_{\tilde{X}} - E_{\tilde{X}_c}\} \frac{\partial \ln \mathcal{E}(\tilde{X}/\tilde{X}_c)}{\partial \ln \tilde{X}/\tilde{X}_c}$$

$$E_{\mathcal{F}} = \frac{\partial \ln \mathcal{F}(\sigma \tilde{X}/\tilde{X}_c)}{\partial (1/T)} \approx \{E_{\tilde{X}} - E_{\tilde{X}_c}\} \frac{\partial \ln \mathcal{F}(\sigma \tilde{X}/\tilde{X}_c)}{\partial \ln \sigma \tilde{X}/\tilde{X}_c}$$

Of these contributions, those that might be affected by branching might include: $E_{\tilde{X}}$, $E_{\tilde{X}_c}$ and $\frac{\partial \ln \mathcal{F}(\sigma \tilde{X}/\tilde{X}_c)}{\partial \ln \sigma \tilde{X}/\tilde{X}_c}$

Examples from the literature:

Polymer	$\frac{\partial \ln R_G^2}{\partial \ln T}$	Structure	Viscosity Enhanc. Effect?	Activation Energy Enhanc.Effect?	Ref.
Ethylene	–0.40	random		yes	1
Styrene	+0.02	4, 6 arm star	yes	no (not accurate)	2
Butadiene (0.4 cis 1,4; 0.08 1,2)	+0.12	4 arm star	yes	no	3
Hydrogenated Budatiene (0.4 cis 1,4; 0.08 1,2)	–0.40	3, 4 arm star	yes	Increase up to 2× with increasing M_{arm}	4
Hydrogenated Budatiene (0.4 cis 1,4; 0.08 1,2)	–0.40	3, 4 arm star	yes	$E_O \approx E_{O,LIN} + 0.28\ \tilde{X} / \tilde{X}_c$	5
Butadiene (var. 1,2)	*	3, 4, 8 arm star	yes	yes	5
Hydrog. Budatiene (var. 1,2)	*	3, 4, 8, 18 arm star	yes	yes	5
Isoprene	+0.09	3 arm star	yes	yes	5
Hydrog. Isoprene	+0.09	3 arm star	yes	yes	6
Ethylene	–0.40	random	yes	no	7
Isoprene	+0.09	3 arm star	yes	yes	8

* From –0.40 to +1.0 with 1,2 from 0.08 to 1

1. **see: Berry, G.C. and Fox, T.G (1968) Adv. Poly. Sci. 5: 261 (see § 2.2.3)**
2. **Grassley, W.W. and Roovers, J. (1979) Macromolecules 12: 959**
3. **Rochefort, W.E., Smith, G.G., Rachapudy, H., Raju, V.R. and Graessley,W.W. (1979) J. Polym. Sci.: Polym. Phys. Ed. 17: 1197**
4. **Raju, V.R., Rachapudy, H. and Graessley, W.W. (1979) J. Polym. Sci.: Polym. Phys. Ed. 17: 1223**
5. **Graessley, W.W. and Raju, V.R. (1984) J. Polym. Sci., Polym. Symp. 71: 77**
6. **Carella, J.M., Gotro, J.T. and Graessley, W.W. (1986) Macromolecules 19: 659**
7. **Wasserman, S.H. and Graessley, W.W. (1996) Polym. Eng. Sci. 36: 852**
8. **Bero, C.A. and Roland, C.M. (1996) Macromolecules 29:1562**

Grassely had suggested that $E_o - E_{O,LIN}$ might depend on $\partial \ln R_G^2 / \partial \ln T$, but these data do not support that conjecture.

Bartels, C.R., Crist Jr., B., Fetters, L.J. and Graessley, W.W. (1986) Macromolecules 19, 785
Graessley, W.W. (1982) Macromolecules 15, 1164